

Additive Manufacture of Three Dimensional Metal-polymer Nanocomposites through Two- photon Fabrication

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Abstract

Two-photon fabrication is an attractive additive manufacturing (AM) technique that allows the production of 3D objects with high resolution down to 100 nm¹. It has been applied to fabricate nano-photonics, microelectromechanical systems (MEMS), microelectronics, microfluidic devices and biochips². In this thesis, complex 2D and 3D gold-, silver- and copper-polymer nanocomposites were additive manufactured for the first time through two-photon polymerisation (TPP) and two-photon reduction (TPR) in a single step. The research aims to investigate the printability of using simultaneous photopolymerisation and photoreduction to produce 3D metal-polymer nanocomposites that could be potentially applied to microelectronics, metamaterials and SERS (surface-enhanced Raman spectroscopy). A series of formulations were developed and prepared to assess the printability. The relationship between materials composition or processing parameter and final structures were characterised and investigated. The potential applications of fabricated structures were evaluated and discussed.

3D gold-polymer nanostructures were fabricated through the two-photon based manufacturing method. Two kinds of triacrylate based monomers of similar structure were compared and chosen to fabricate gold-polymer nanocomposites. Irgacure 369 was used as a photoinitiator. When gold salt was added, additional photoinitiator was required to provide more free radicals for photoreduction because there was a competition between TPP and TPR. The adding of two-photon sensitive dye, tris(2,2'-

bipyridyl) dichlororuthenium (II) hexahydrate, can stabilise the fabrication process, allowing for the fabrication of 3D gold-polymer nanocomposite structures.

Silver-polymer nanocomposites were developed through simultaneous photopolymerisation and photoreduction for the first time. A series of materials were assessed to produce silver-polymer nanocomposites. A phase-transfer protocol that transferred silver ions from the water phase to toluene phase enabled good mixing of PETA (pentaerythritol triacrylate) as a monomer, Irgacure 369 as a photoinitiator and coumarin 30 as a photosensitive dye. 2D and 3D complex silver-polymer nanostructures were fabricated by TPL (Two-photon lithography). By adding coumarin 30 photosensitive dye, better light interaction, higher resolution of line width and more uniform size and distribution of silver NPs (nanoparticles) were observed. The average size of silver particles well distributed in the fabricated structures was 5.8 ± 1.5 nm.

An initial investigation on the fabrication of copper-containing nanostructures through two-photon fabrication was conducted. 3D copper-polymer nanocomposites were successfully obtained.

The phase transfer method used in this research could be applied in the synthesis of a variety of metal-polymer functional materials through simultaneous photopolymerisation. The successful additive manufacture of complex 2D (two-dimensional) and 3D (three-dimensional) metal-polymer nanocomposite structures provides potential to be used in photonics, metamaterials, plasmonics, electronics, catalysis and bio-sensing.

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List of Abbreviations

2D	Two-dimensional
3D	Three-dimensional
3MLCT	Triplet Metal-to-ligand Charge-transfer
AM	Additive Manufacturing
ASTM	American Society of Testing and Materials
BSE	Backscattered Electron
CAD	Computer Aided Design
CCD	Charge-Couple Device
CVD	Chemical Vapour Deposition
DC	Degree of Conversion
DDA	Dodecylamine
DETC	7-(Diethylamino)-3-(2-thienylcarbonyl)-2H-1-benzopyran-2-one
DLP	Digital Light Processing
DMLS	Direct Metal Laser Sintering
DF-STEM	Dark Field Scanning Transmission Electron Microscopy
EDX/EDX	Energy-dispersive X-ray Spectroscopy
EBM	Electron Beam Machining
EP	Electroless Plating
FDM	Fused Deposition Modeling
FEG	Field Emission Gun
FFF	Fused Filament Fabrication
FIB	Focused Ion Beam

HOMO	Highest Occupied Molecular Orbital
ITO	Indium-tin Oxide
Irgacure 369	2-benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone
IR	Infrared
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
ICT	Intramolecular Charge Transfer
LBMD	Laser-Based Metal Deposition
LUMO	Lowest Unoccupied Molecular Orbital
MSDS	Material Safety Data Sheet
MEMS	Microelectromechanical System
MPA	Multi-Photon Absorption
NA	Numerical Aperture
NIR	Near Infrared
NPs	Nanoparticles
OPP	One-Photon Polymerisation
PETA	Pentaerythritol Triacrylate
PEGDA	Ppoly (ethylene glycol) Diacrylate
PGMEA	Propylene Glycol Monomethyl Ether Acetate
PMMA	poly (methylmethacrylate)
PSS	polystyrene Sulfonate
PVA	polyvinyl Alcohol
PVK	polyvinylcarbazole
SE	Secondary Electrons

SEM	Scanning Electron Microscopy
SERS	Surface-enhanced Raman Scattering
STED-like	Stimulated Emission and Depletion-like
SPR	Surface Plasmon Resonance
STL	Surface Tessellation
SLA	Stereolithography
SLS	Selective Laser Sintering
SIMS	Secondary Ion Mass Spectrometry
T _g	Glass Transition Temperature
TE	Transfer Efficiency
TEM	Transmission Electron Microscopy
TMPTA	Trimethylopropane Triacrylate
TPA	Two-photon Absorption
TPL	Two-photon Lithography
TPP	Two-photon Polymerisation
TPR	Two-photon reduction
UV-vis	Ultraviolet-visible
UHV	Ultra-high Vacuum
WLC	White-light Continuum
WD	Working Distance
XPS	X-ray Photoelectron Spectroscopy

1 Introduction

1.1 Background

AM (Additive manufacturing) is attractive due to its design freedoms, particularly with relation to increased levels of complexity³. There is a growing requirement for 3D micro/nano-fabrication techniques in many applications, such as nanophotonics, MEMS (microelectromechanical systems), microelectronics, microfluidics². These new needs in fabrication technology motivate to explore an extension of AM at nanoscales. However, traditional techniques for the fabrication of microstructures are limited to 2D fabrication, resolution, fabrication time and processing cost^{2, 4-6}. TPL (Two-photon lithography) allows for 3D fabrication of structures with feature sizes less than 100 nm and writing speeds of several centimetres per second^{1, 7-8}. A laser beam that is focused into a photosensitive material and localized within the focal volume leads to material reactions. By moving the laser beam in 3D trajectories, 3D structures can be fabricated.

Materials including monomers/oligomers and metal materials can be employed in TPL for fabricating polymer and metal structures. The fabrication of 3D polymer structures by TPP (two-photon polymerisation) was firstly presented by Maruo in 1997, resulting in features at subwavelength scales⁷. Apart from polymers, metallic gold and silver microstructures built by TPL through metal salt reductions have been reported⁹⁻¹⁰. However, these processes suffer from high surface roughness, difficulties

in particle size control, lack of ability to fabricate complex 2D and 3D structures, time-consuming and complicated processing steps.

A significant step forward, however, is a combination of photopolymerisation and photoreduction in a single step to produce metal-containing nanocomposites. 2D gold-containing nanostructures have been reported by Shukla et al.¹¹⁻¹² and 3D filigree-like conductive elements that are ‘glued’ together with an oligomer resin have been presented by Blasco et al.¹³. The studies provide the potential to create 3D functional metal-polymer nanocomposite structures through simultaneous photopolymerisation and photoreduction.

Au NPs (gold nanoparticles) and Ag NPs (silver nanoparticles) are attractive due to their high chemical and physical stability, high electric conductivity and the optical properties related to LSPR (localised surface plasmon resonance) that can be used in metamaterials and SERS (surface-enhanced Raman scattering) materials¹⁴⁻¹⁷. Cu NPs (Copper nanoparticles) is also a candidate in metamaterial and microelectronic applications but cheaper than gold and silver¹⁸⁻¹⁹. In the applications such as microelectronics, metamaterials and SERS, they all have high demand not only on 2D but also 3D structures¹⁴⁻¹⁷. Photopolymerisation and photoreduction in a single step by TPL have been reported on simple gold-polymer line structures and more studies on the printability of 3D structures, chemical mechanism, optimisation of processing parameters and characterisations on fabricated structures are still missing. Silver and copper nanocomposites have never been manufactured by this method. Therefore, this thesis is based on an investigation of 3D fabricating gold-, silver- and copper-polymer nanocomposites through simultaneous photopolymerisation and photoreduction.

1.2 Aim and Objectives

This PhD thesis aims to investigate the possibility of using simultaneous photopolymerisation and photoreduction to fabricate 3D complex metal-polymer nanocomposites and construct a primary understanding for the fabrication of metal-polymer (gold-, silver- and copper-) nanocomposites. In order to achieve this aim, the objectives are identified as follows:

- (1) To develop suitable formulations for fabricating 2D & 3D gold-polymer, silver-polymer and copper-polymer nanocomposites through simultaneous TPP and TPR.
- (2) To fabricate 2D & 3D metal-polymer nanostructures using suitable processing parameters through two-photon fabrication method.
- (3) To characterise the fabricated microstructures.
- (4) To investigate the relationship between material composition or processing parameters and final properties of the fabricated metal-polymer nanostructures.
- (5) To evaluate the potential applications for the fabricated 2D & 3D metal-polymer nanocomposites.

1.3 Research Concept

In order to additive manufacture metal-polymer nanocomposites with the feature sizes at subwavelength scales through a combination of TPP and TPR, suitable materials and formulations are essential. Material selection was one of the main steps for both printability assessments and applications. Suitable metal salts (gold, silver and copper salts), solvent, high-efficiency photoinitiators and monomers were chosen first. The solubilities of the materials were considered and improved when they were low. The

processing parameters of two-photon fabrication were optimised, and 2D and 3D gold-, silver- and copper-polymer nanocomposites with the feature size of subwavelength were produced. The fabricated structures were characterised by different techniques and their potential applications were evaluated.

1.4 Outline of the Thesis

The thesis consists of the chapters as following:

Chapter 2 Literature Review gave a review of the histories of AM and two-photon fabrication. Previous and up-to-date literature about two-photon fabrication were reviewed, including the concept of two-photon fabrication, materials requirements, fabrication parameters, potential problems and challenges during processes.

Chapter 3 Methodology and Experimental Setup introduced research approaches for this PhD thesis. The details of the AM equipment, material selections and sample characterisation techniques were introduced in this chapter.

Chapter 4 Gold-polymer Nanocomposite presented the results for fabricating of gold-polymer nanocomposites through simultaneous photopolymerisation and photoreduction. Suitable ink formulations were developed. The influences of photoinitiator concentrations, photosensitive dye and laser power on structures' properties were investigated. Further experiments were performed to identify the reduction of gold salt and the presence of gold particles. Potential applications of fabricated gold-polymer composites were discussed.

Chapter 5 Silver-polymer Nanocomposite provided the results for fabricating of silver-polymer nanocomposites through simultaneous photopolymerisation and photoreduction. Water-soluble materials and a phase-transfer protocol using non-water-soluble materials were assessed to fabricate silver-polymer nanocomposites. The effects of photoinitiator concentrations, photosensitive dye and laser power on structures' properties were investigated. The presence of silver NPs and particle size were identified and measured by further experiments. The potential applications of fabricated silver-polymer composites were discussed.

Chapter 6 Copper-polymer Nanocomposite demonstrated the fabrication of copper-polymer nanocomposites through simultaneous photopolymerisation and photoreduction. The reduction of copper salt and the presence of copper particles were verified. The challenges of processes and potential applications were discussed.

Chapter 7 General Discussion discussed the achievements of this thesis. The novelty of the thesis was highlighted. The advantages compared to literature and potential problems of the achievements were discussed. The potential applications of the achievements were discussed.

Chapter 8 Conclusion and Future Work provided the main conclusions of the thesis and suggestions for future work.

2 Literature Review

2.1 Introduction to Additive Manufacturing

Additive manufacturing is also known as rapid manufacturing, rapid prototyping, 3D printing, solid freeform fabrication or direct digital manufacturing²⁰. The official definition of AM by American Society of Testing and Materials (ASTM) standard F2792-12a is as follows:

‘A process of joining materials to make objects from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing methodologies’²¹.

AM was first developed alongside the emergence of Computer Aided Design (CAD) in the 1980s. AM process usually starts with a CAD file for the specific geometry, and then a surface tessellation (STL) file is converted from the CAD file. The STL file is then transferred to a computerised system, and the structure is “sliced” into virtual horizontal layers with different thicknesses by computer software. The structure is finally built up by a manufacturing system layer by layer^{20, 22-23}.

Unlike conventional subtractive manufacturing, AM can fabricate almost any geometry and build complex 3D parts. The main advantages of AM include:

- Design freedom in geometric complexity. Tooling changes are no longer required between design updates. AM techniques combined with CAD software make it possible to create new types of objects with unique material and structural properties²⁴. Complex structures such as channels and lattices

are achievable²⁵. Redesign and optimise geometries can meet functional requirements and reduce material consumptions²⁵.

- Machines and materials for AM are expensive, but current AM can compete with traditional techniques for small to medium batch production of metal parts²⁵. AM is expected to be more economically friendly than at present²⁵. Assembly steps can be reduced or eliminated by AM, which can reduce cost, time and quality problems caused by assembling process²⁵. The production can begin after product design, which can reduce the time delay between design and manufacturing and save cost²⁵. The total annual cost savings of \$170-593 billion through AM in industries in 2025 was predicted²⁶.
- Mass personalisation can be achieved²⁴ and customers' requirements can be fulfilled^{25, 27}.
- Some material waste can be reduced by reusing the materials (i.e. powders and resins) that not used during manufacture. 95-98% recyclability for metal powders was estimated²⁵.
- AM enables the engagement of consumers in the design of products. The emergence of distributed manufacturing and new supply chains can be achieved by AM²⁴.

The first commercial 3D printing system was stereolithography (SL) brought out by a US company 3D Systems²³. The principle relies on solidification of UV curable polymeric resin with UV laser light²⁸. Numerous other AM technologies and systems have been rapidly developed and commercialised since the late 1980s²³. The ASTM has classified AM technologies into seven categories, as shown in Table 2.1. The AM technique used in this PhD thesis, two-photon lithography (TPL), belongs to the vat

polymerisation category. According to the types of feedstock materials, AM could also be classified into liquid-based processes, solid-based processes and powder-based processes. The development of innovative AM techniques has progressed in terms of feature resolutions, manufacturing speed and reliability in recent years. AM provides industries with high potentials for customisation and AM applications have been broadened to aerospace, automobile, biomedical, architecture, electronics and energy fields²³.

Table 2.1 The classification of AM techniques according to ASTM^{24, 29-30}.

Category	Description	Examples
Binder jetting	Powder materials are joined by a liquid bonding agent through selective deposition	Metallic binder jetting, Polymer binder jetting
Direct energy deposition	Thermal energy (laser, electron or plasma arc) is used to fused melt materials being deposited	Laser-based metal deposition (LBMD)
Material extrusion	Materials are selectively dispensed through a nozzle or orifice	Fused deposition modeling (FDM), fused filament fabrication (FFF)
Material jetting	Droplets of build materials are selectively deposited	Inkjet printing, Liquid metal jetting
Powder bed fusion	Thermal energy is used to selectively fuse regions of a powder bed	Selective laser sintering (SLS), Direct metal laser sintering (DMLS), electron beam machining (EBM)
Sheet lamination	Sheets of materials are bonded to form an object	laminated object manufacture, Adhesive lamination
Vat photopolymerisation	Liquid photopolymers in a vat is selectively cured by light-induced polymerisation	Two-photon lithography (TPL), digital light processing (DLP), and stereolithography (SLA))

2.2 Two-photon Absorption

TPL (Two-photon lithography)³¹⁻³², also named multiphoton lithography³³, or direct laser writing^{12-13, 34-47}, is an attractive AM technique owning subwavelength resolution. This technique is based on a two-photon absorption process³⁰. Two-photon absorption (TPA) was theoretically predicted by Maria Göppert-Mayer in 1931 in her PhD thesis⁴⁸. Because high photon intensities were required, TPA was not experimentally demonstrated until 1961 by Kaiser⁴⁹, when the laser was invented. In one-photon absorption, an atom or a molecule is excited by a photon with a frequency of ν_1 from its ground state S_0 to the first excited state S_1 (**Figure 2.1(a)**)⁵⁰. TPA or multi-photon absorption (MPA) is a radiation-matter interaction that an atom or a molecule is excited by two or more photons from a lower ground state S_0 to an excited state S_2 in a single step⁵¹⁻⁵². The energy difference between two states is the sum of the energies of two or more photons⁴⁴. **Figure 2.1(b)** illustrates the energy transition in TPA.

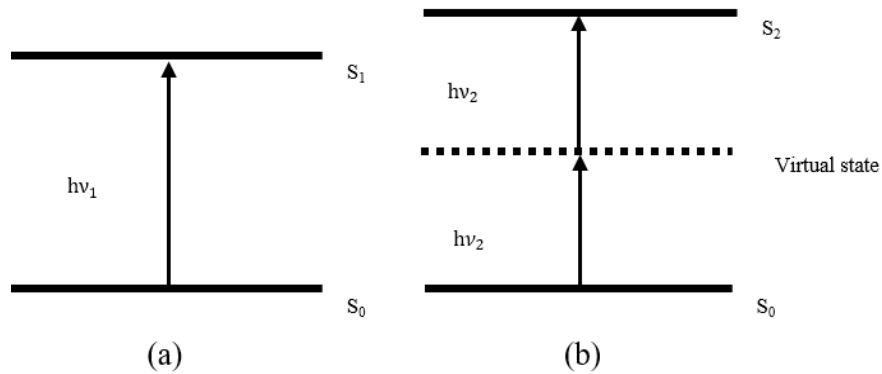


Figure 2.1 Energy transitions in (a) one-photon absorption and (b) TPA.

There are two types of TPA processes: (1) degenerate process and (2) non-degenerate process⁵⁰. In the degenerate process, two photons with the same frequencies are absorbed. While in the non-degenerate process, two photons with different

frequencies are absorbed. The degenerate TPA is more often used in the TPP process⁵⁰. In simultaneous TPA, there is a no real intermediate energy state and TPA exists only if another photon arrives within the virtual state lifetime⁵³. Therefore, high intensities, which can be provided by a focused femtosecond laser, are needed for TPA so that two photons can be absorbed simultaneously⁵³.

TPA is a third-order nonlinear process and the absorption rate is proportional to the square of the light intensity^{50, 54}:

$$\frac{dW}{dt} = \frac{8\pi^2\omega}{n^2c^2} I^2 \text{Im}(\chi^{(3)}) \quad \text{Equation 2.1}$$

where W is the absorption energy, t is the absorption time, n is the refractive index, ω is the incident light optical frequency, c is the speed of light in vacuum, I is the light intensity and $\text{Im}(\chi^{(3)})$ is the imaginary part of the third-order susceptibility.

Absorption cross-section (δ) is the ability to absorb photons and a high cross-section is important for TPA. TPA cross-section is defined by^{50, 54}:

$$\frac{dn_p}{dt} = \delta NF \quad \text{Equation 2.2}$$

where n_p is the number of absorbed photons, N is the number density of absorbing molecules, $F = I/h\nu$ is photon flux of beam. From the relation, $dW/dt = dn_p/dt$,

TPA cross-section is:

$$\delta = \frac{8\pi^2 h\nu^2}{n^2 c^2 N} I^2 \text{Im}(\chi^{(3)}) \quad \text{Equation 2.3}$$

In most cases, TPA cross-section is measured in Göppert-Mayer (GM) unites (1GM = $10^{-50} \text{cm}^4 \text{s/photon} \cdot \text{molecule}$)^{50, 54}. Methods including nonlinear transmission,

two-photon induced fluorescence emission and Z scan measurement are used to measure the TPA cross-section⁵⁰.

The nonlinear property of TPA leads to the excitation being localised within the focal volume of the laser beam. In a single-photon excitation process (for example, UV absorption), the rate of absorption in a transverse cross-section of the laser beam is proportional to the light intensity (photons/time · area) and the number of molecules in the transverse cross-section. The light is absorbed in the first few micrometres of resins, so it is a planar process without localisation (**Figure 2.2 (a)**). In TPA, the rate of absorption is proportional to the square of the light intensity and the number of molecules in the transverse cross-section, so the most excited molecules are in the region where the laser beam is focused the most tightly. (**Figure 2.2 (b)**). Therefore, TPA can be localised at a focal point⁵⁵.

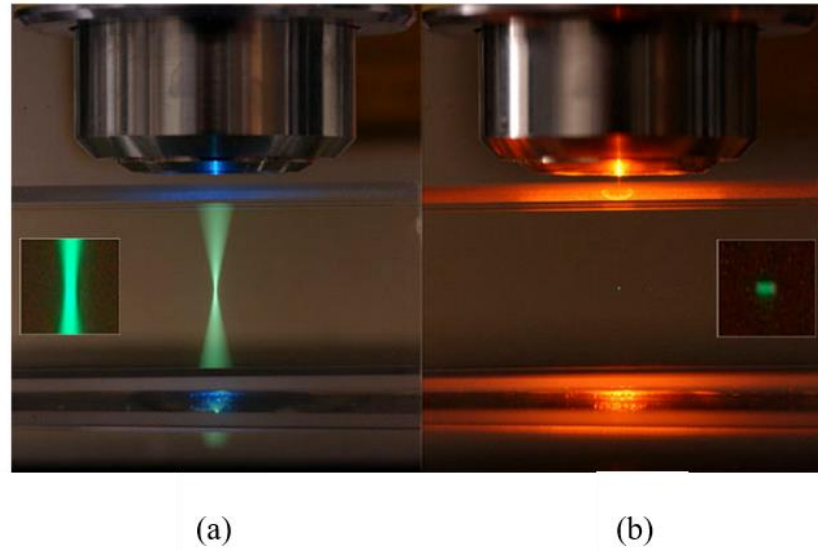


Figure 2.2 Fluorescence images of (a) linear single-photon absorption (The scanning blue (488 nm) laser excites an entire column of the sample) and (b) nonlinear two-photon absorption (The scanning IR (infrared) pulse laser (Zeiss NLO system) excites only a small spot of the sample)⁵⁵.

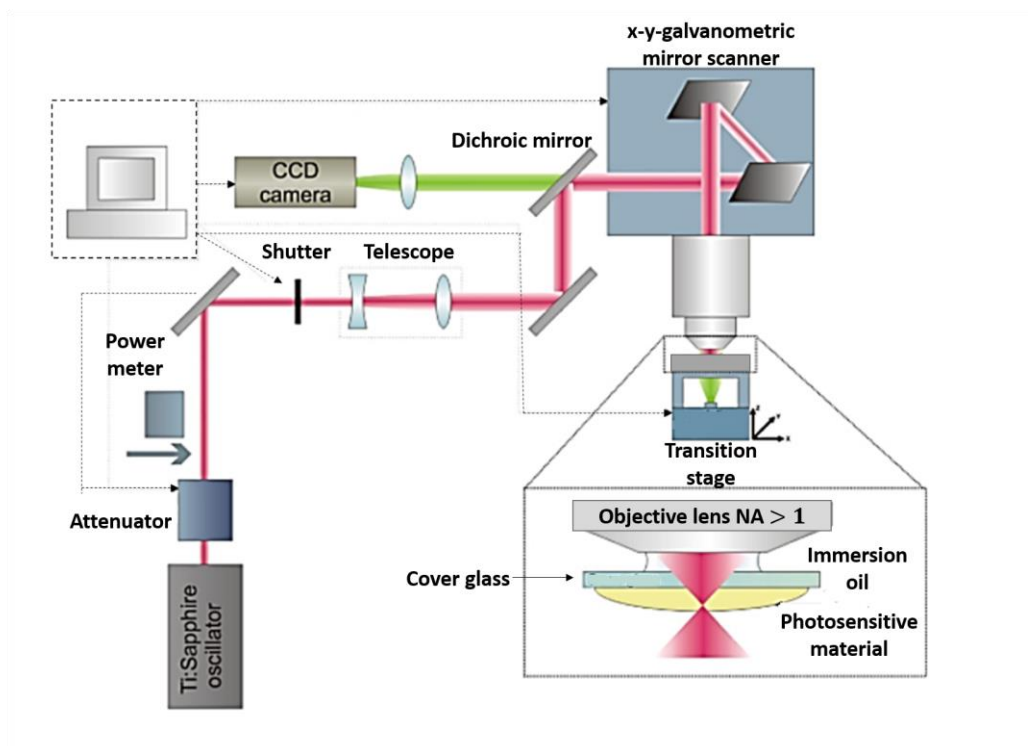


Figure 2.3 A schematic illustration of components of a typical two-photon fabrication system⁵⁶.

Figure 2.3 shows a typical experimental setup for two-photon fabrication including (1) a femtosecond laser; (2) a beam or sample motion system; (3) beam intensity control and shutter; (4) beam focusing optics and (5) a monitoring camera and control software^{44, 56}.

A mode-locked Ti: sapphire laser, also known as Ti: Al₂O₃ laser, with a centre wavelength of 800 nm (near-infrared, NIR) is one of the most common laser sources^{44, 55-57}. A second-harmonic fibre laser with a typical wavelength of 780nm is more often used as it is more reliable and affordable⁴⁴. In general, the laser has a pulse duration of fewer than 200 fs and a repetition rate of 50-80 MHz^{44, 56}. The laser power is adjusted by an attenuator and variable filters⁵⁵⁻⁵⁷. The output laser power ranges from milliwatts to higher than a watt⁵⁵⁻⁵⁷. Beam on-off and exposure time can be controlled by a fast mechanical shutter⁴⁴. An objective with a high numerical aperture (NA) (normally NA of 1.4) is employed to provide high photon intensity^{44, 52, 57}. Numerical aperture is a measure of an objective's ability to gather light, which is defined by:

$$NA = n \times \sin\theta \quad \text{Equation 2.4}$$

where n is the refractive index of the medium in which a lens is working; θ is the maximal half-angle of the cone of light entering or exiting the lens. Immersion oil is used for index matching ($n = 1.52$)⁵⁶. In order to fabricate 3D structures, the focused laser beam or the resin needs to move three dimensionally⁴⁴. In a galvo mode, the fabricated structure is printed layer by layer using an X-Y galvo mirror scanner (X-Y movement). It has high scanning speed and up to m/s can be achieved. Movement in z-axis can be achieved using a piezoelectric stage or a high-resolution linear stage. In a piezo mode, the piezoelectric stage moves in all directions (X-Y-Z

movement) with nm-scale accuracy but slower speed (tens of microns per second). These two modes are both used in practice depending on the application. A charge-couple device (CCD) camera and a video screen are used to observe printed samples during fabrication⁵⁵⁻⁵⁶.

Compared to other micro-fabrication methods, (1) two-photon lithography is able to directly produce 3D structures without a mask, mould or stamp; (2) TPA with long-wavelength laser leads to less absorption and less scattering, which gives a high resolution (subwavelength resolution). The ultrashort laser pulses reduce thermal damage in samples due to their low average power (mW - W); (3) TPL does not need vacuum condition, which makes it easy to operate and maintain⁵⁴.

2.3 Two-photon Fabrication - Polymer

TPP (two-photon polymer) is one of the most well-developed techniques based on TPA (two-photon absorption). The principle of TPP, the materials suitable for TPP and the up-to-date literature about TPP were introduced in this section.

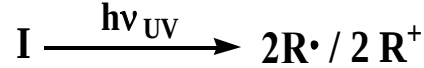
2.3.1 Principle of TPP

TPP was first experimentally reported in 1965 by Pao and Rentzepis⁵⁸. TPP refers to chain-growth polymerisation utilising light to initiate the polymerisation⁵⁹. Both free-radical polymerisation and cationic polymerisation have been reported⁵⁹. Photoinitiators, which are excited by TPA, and monomers or oligomers, which polymerise into solid structures, are the essential components for TPP⁵⁴⁻⁵⁵.

A typical one-photon polymerisation (OPP) process has three steps⁵²:

1. Chain initiation :

Photoinitiators are excited by UV light and free radicals / cationic species are generated in this step⁶⁰.



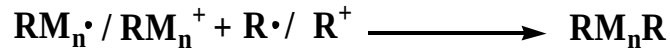
2. Chain propagation:

Polymer chains are created by a series of quick steps of monomer addition over the propagating radicals or cationic species. The main microstructure of polymers is formed in this step⁶⁰.

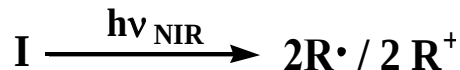


3. Chain termination:

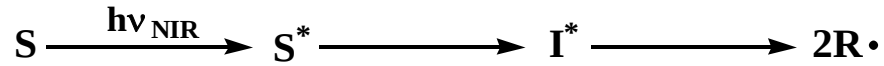
As polymerisation goes on, the concentration of free radicals or cationic species increases while the concentration of monomers reduces. Reactive species meet each other and polymerisation enters termination stage⁶⁰.



In an OPP process, a UV photon is absorbed by the photoinitiator through linear absorption⁵². The UV light is absorbed within the first few micrometres of resins so it is a planar process⁵². In TPP process, two photons of near-infrared (NIR) light are absorbed simultaneously through nonlinear absorption⁵². The first step of TPP is:



Sometimes during the photoinitiation stage, a photosensitiser is employed to absorb photons and then transfer to a photoinitiator to start polymerisation. The process can be described as⁵²:



Other components such as polymerisation inhibitors, solvent and other additives can also be involved in polymerisation⁵⁵.

TPP (two-photon polymerisation) shows advantages compared to OPP (one-photon polymerisation) process⁵²:

- (1) The polymerisation is initiated within the focal volume of the light so TPP is a real 3D process while OPP is a planar process.
- (2) High resolutions of around 100 nm and sub-100 nm feature sizes can be achieved by TPP.
- (3) Complex 3D structures can be fabricated by TPP. Polymerisation processes in the focal volume and complex shapes can be achieved by the movement of substrate or by scanning the beam in 3D trajectories.

2.3.2 Resolution of TPP Process

TPP only starts when the photon density exceeds a threshold value because of radical quenchers in the resin (**Figure 2.4**)^{52, 57, 61}. The structural feature size can be smaller than the diffraction limit if the laser power is just above the threshold value⁵².

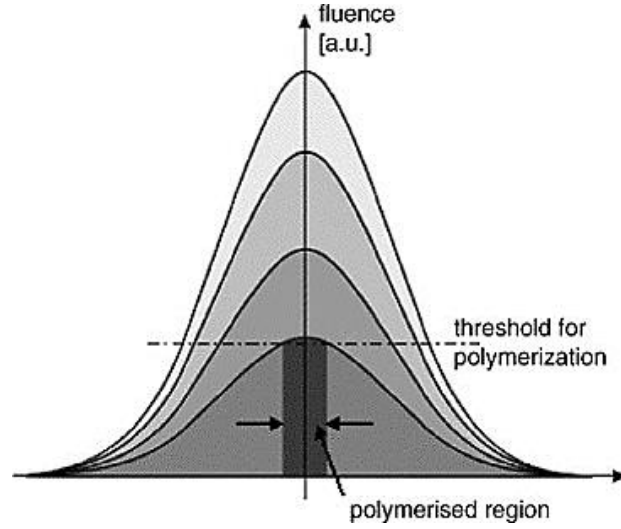


Figure 2.4 Laser focus distribution. Polymerisation only occurs when the laser power is above the threshold value. The structural feature size can be smaller than the diffraction limit if the laser power is just above the threshold value⁵².

By controlling the laser power and the number of applied pulses, the voxel size can be adjusted^{51, 60-61}. The voxel size is able to be predicated if the threshold is known^{52, 61-62}. The voxel sizes include lateral (l) and axial (d) dimensions⁶¹.

When the density of radical particle density $\rho \geq \rho_{th}$ (threshold value), the voxel diameter d is⁶¹:

$$d(N_0, t) = r \sqrt{\ln\left(\frac{\sigma_2 N_0^2 n \tau_L}{C}\right)} \quad \text{Equation 2.5}$$

$$C = \ln[\rho/(\rho - \rho_{th})] \quad \text{Equation 2.6}$$

where N_0 is the photon flux, t is the total processing-irradiation time, r is the distance to the optical axis, σ_2 is the effective two-photon cross-section, n is the number of pluses, τ_L is the laser pulse duration, and ρ_0 is the primary radical particle density.

The voxel length l which is along the beam axis at $r = 0$, is estimated by⁶¹:

$$l(N_0, t) = 2Z_R \sqrt{\left(\frac{\sigma_2 N_0^2 n \tau_L}{c}\right)^{1/2} - 1} \quad \text{Equation Equation 2.7}$$

where Z_R is the Rayleigh length, which is determined by a laser beam.

The estimation of voxel size is based on the assumption of (1) monomers are polymerised as soon as the photon density exceeds the threshold value; (2) photon flux is constant on the optical axis during the laser pulse; (3) losses of free radicals between the laser pulses are ignored⁶¹. From the equations, the lower laser power and shorter irradiation time, which just reaches the threshold value and initiates polymerisation, the more spherical voxel, which is $l/d = 1$, can be achieved⁶².

Apart from the calculation, the voxel size can also be measured experimentally by an ascending method^{55, 63-64}. **Figure 2.5** shows the ascending scan method. In order to retain a structure or a voxel after sample washing, the focal point needs to be partly submerged in the substrate. For this reason, only part of the structure is fabricated above the substrate. Therefore, the accurate measurement of voxel size is difficult⁵⁵. In order to measure the accurate size, an ascending scan is applied⁶⁴. The same voxels are built at different focusing level. Some voxels are only loosely connected to the substrate and topple over after sample development by solvent washing. Finally, a precise voxel size can be measured⁵⁵.

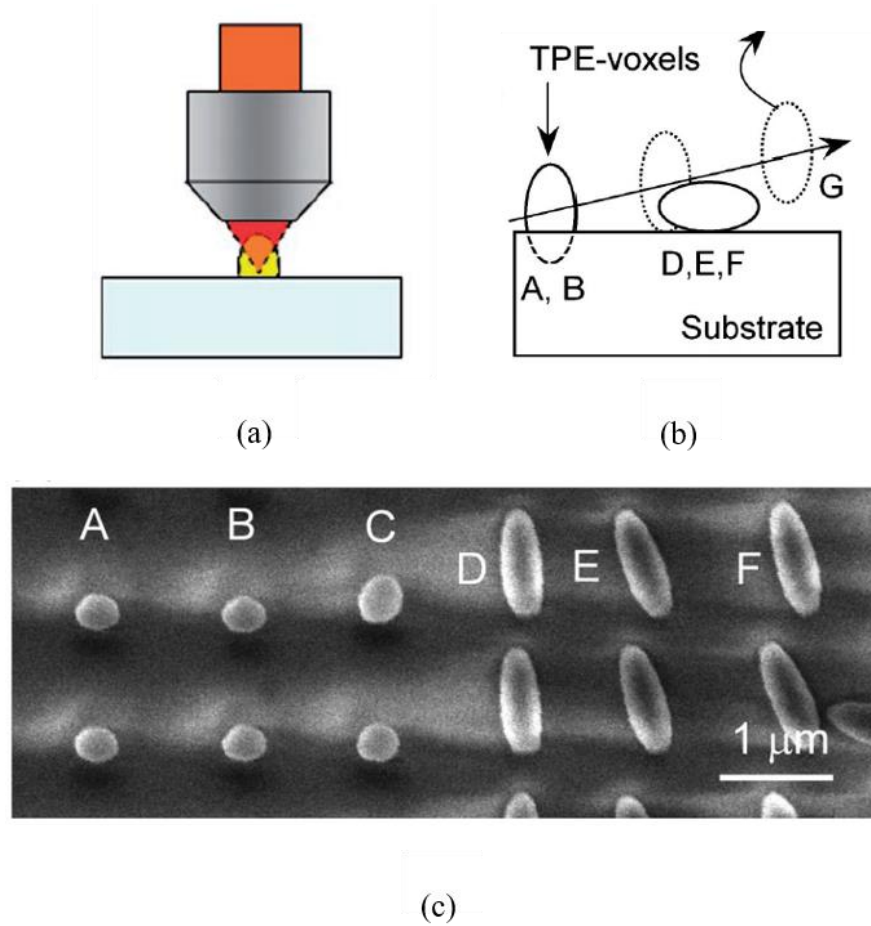


Figure 2.5 The ascending scan method for measuring the precise voxel size. (a) The laser is focused below the structure, so only partial structures were fabricated⁵⁵. (b) Different voxels fabricated using different focus height⁶⁴. (c) SEM images of different voxels using different focus height⁶⁴. Voxels A-C: the focus point is below the substrate so only partly structure is left; Voxels D-F: the fabricated voxels are loosely adhered to the substrate surface and topple down after sample development.

Figure 2.6 shows a comparison between the calculated and experimental measured values of voxels. The measured values fit well to the calculated values. In addition to voxel sizes, the width of lines can also be measured to demonstrate resolution⁵⁷. The resolution of TPP can be improved by controlling the process parameters, including laser power, exposure time (scan speed) and NA (numerical aperture) value of the

objective. Radical quenchers and using efficient photoinitiators can also contribute to reducing feature sizes^{1, 65-70}. The resolution of TPP can be improved by selecting materials and processing parameter. All achievements in resolutions of TPP are summarised in **Table 2.2**. The final voxel size is also determined by many other factors including the concentration of photoinitiator, the radical quantum yield, the material viscosity, the concentration of inhibitors and the shrinkage of materials^{55, 69, 71}.

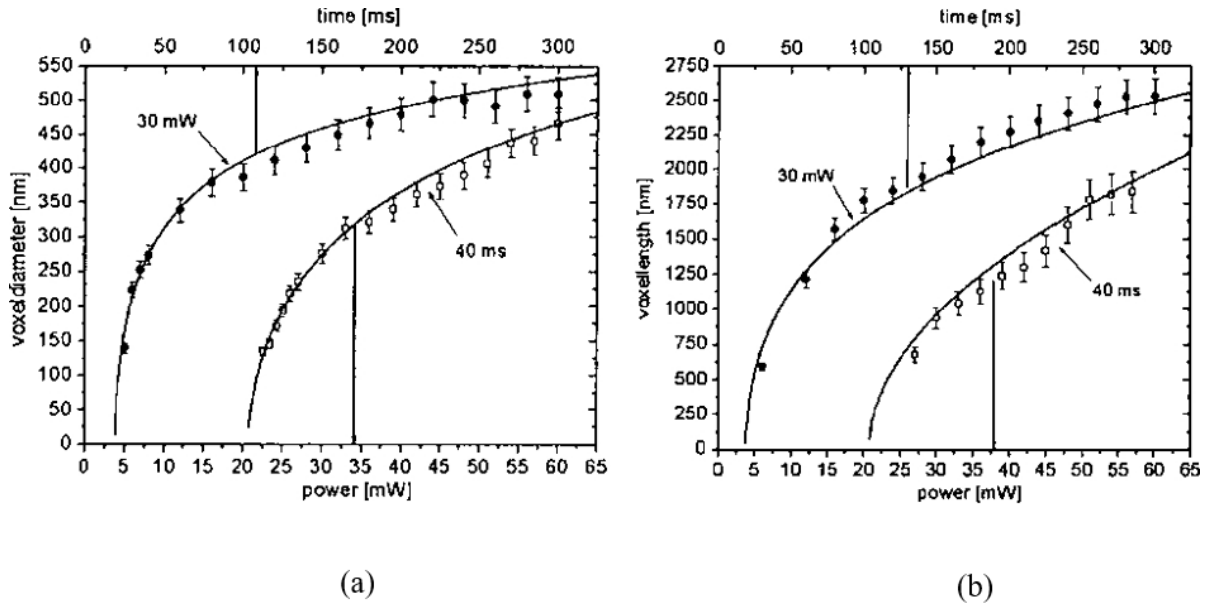


Figure 2.6 The calculated and measured values for the voxel diameter d (a) and length l (b) as a function of laser power (constant irradiation time 40 ms) and irradiation time (constant laser power 30 mW)⁵².

Table 2.2 Summary of the approaches to improve resolution and achievements in resolutions of TPP from literature.

Material	Methods improving the resolution	Achievements	Reference	Year
SCR 500 (Urethane acrylate type monomer)	Reducing exposure time 780 nm, 78 MHz, NA = 1.4, 150 fs	Spatial resolution 120 nm	S. Kawata et al. ⁶⁵	2001
SCR 500	Changing process parameters 35mW laser power, 600 $\mu\text{m/s}$ scan speed 780nm, 80 MHz. NA = 1.45, 80 fs	Line width 23 nm	D. Tan et al. ⁶⁶	2007
SCR 500	Changing process parameters 2.5 mW laser power, 1.07 ms exposure time 780nm, 80 MHz, NA = 1.45, 80 fs	Line width 50nm aspect ratio 1.38	X. Dong et al. ⁶⁷	2008
Blend of triacrylate monomers	Changing process parameters 0.45 μW laser power, 60 $\mu\text{m/s}$ scan speed 520 nm, 1 kHz, NA = 1.4, 100 fs	Line Width 65 nm	W. Haske et al. ¹	2007
MMA (methacrylic acid)	Introducing highly efficient photoinitiator 0.8 mW laser power, 50 $\mu\text{m/s}$ scan speed 800 nm, 80 MHz, NA = 1.42, 80 fs	Lateral spatial resolution 80 nm	J. Xing et al. ⁶⁸	2007
SCR 500	Introducing radical quenchers	Lateral spatial resolution 100 nm	K. Takada et al. ⁶⁹	2005
SCR 500	Introducing radical quenchers	Lateral spatial resolution 96 nm	S.H. Park et al. ⁷⁰	2006

2.3.3 Photoinitiators for TPP

Photoinitiators play a crucial role in TPP. A photoinitiator absorbs two photons to produce active points and initiates the polymerisation process. The requirements for a photoinitiator used in TPP are as follows⁵⁴⁻⁵⁵:

- (1) The photoinitiator should be transparent at the visible and NIR regions so that a laser beam can be focused within the volume of the materials.
- (2) The photoinitiator should have a broad two-photon cross-section (ability to absorb photons), a high radical quantum yield and high-active species generated to make sure the high efficiency of TPP; Normally if any two of the three are large enough, it would be sufficient for TPP.
- (3) The photoinitiator should have good solubility in used solvents and resins for photopolymerisation.

For a photoinitiator in TPP, large two-photon cross-section and high efficiency can reduce the polymerisation threshold, broaden the laser-writing window and decrease the possibility of structural damage caused by high fabrication intensity and long exposure time⁵². Generally, there are two types of photoinitiators: radical and cationic. Radical or cationic photoinitiators generate free radicals or cations upon light irradiation and initiate a polymerisation process⁴⁴.

The majority of TPP developed to date has employed radical polymerisation because of its high reaction rates, ease of processing and wide availability of photoinitiators and monomers^{44, 55}. For TPA, the maximum absorption wavelength is ideal for half of the wavelength of the laser beam⁵². If the fabrication wavelength is within the range of λ_1 to λ_2 , the absorption of a photoinitiator should be within the range of $\frac{1}{2}\lambda_1$ to $\frac{1}{2}\lambda_2$. By two different mechanisms, the radical photoinitiators are classified as type I and type II⁵⁵. For type I photoinitiator, it is cleaved to produce radicals that initiate a polymerisation process⁵⁵. For type II photoinitiator, a co-initiator is involved and the energy is transferred from the main initiator to the co-initiator to create

radicals⁵⁵. The co-initiator is a tertiary amine providing a hydrogen atom to excited photoinitiator exciplex and then two free radicals are formed for a polymerisation reaction⁵⁵. The free radicals generated from the tertiary amine are always more reactive with oxygen than the other radical, so it can help protect the free radical for polymerisation being oxidised during processes⁵⁵.

According to the literature, there are many commercially available photoinitiators for TPP^{13, 61, 65-67, 69-70, 73-79}. **Figure 2.7** shows the UV-visible absorption spectra of commercially common photoinitiators and **Table 2.3** shows TPA cross-sections of these photoinitiators measured by two methods⁷⁴. SCR 500 (Japan Synthetic Rubber Co.) is a commercial TPP resin consisting of urethane acrylate oligomers and photoinitiators: Irgacure 369 and Irgacure 184^{65-67, 69-70, 73}. Irgacure 369 is also a common photoinitiator for Ormocer resins^{61, 75-77}. Irgacure 369 is a type I photoinitiator and its chemical name is 2-benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone⁸⁰. The para-position of the aromatic ring is substituted by a high electron-donating group, dimethylamino, making Irgacure 369 a high initiating efficiency initiator⁸¹. According to literature, Irgacure 369 undergoes mainly α -cleavage that generates benzoyl and benzyl free radicals and a minor β scission upon absorption of light⁸¹(**Figure 2.8**). The free radicals generated from the cleavage reactions then combine with monomers and propagate polymerisation reactions. Other photoinitiators such as Irgacure 819, ITX, Dorocure TPO have been used for TPP with acrylate or methacrylate resins⁷⁸⁻⁷⁹.

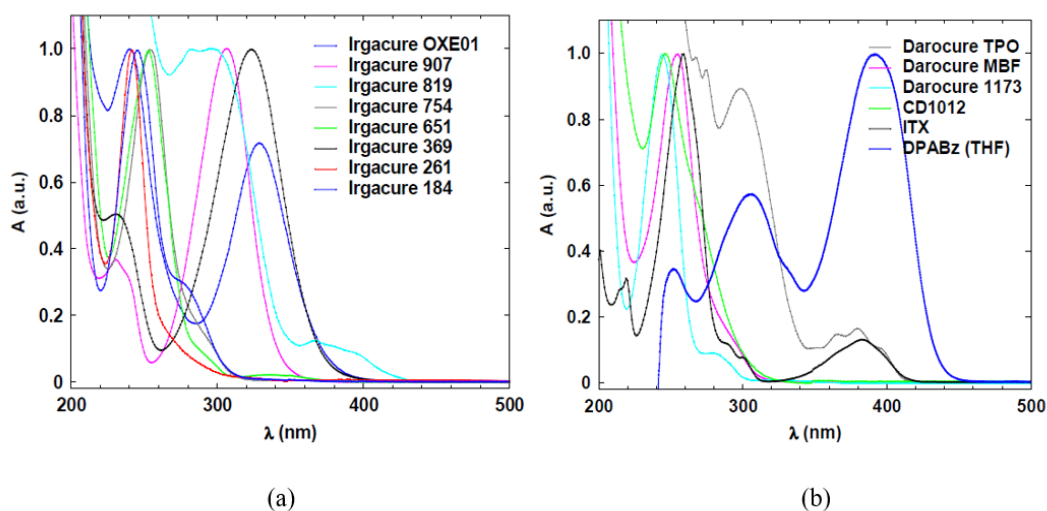


Figure 2.7 Normalised UV-visible absorption spectra of (a) Irgacure series photoinitiators in MeOH; (b) Darocure series, SC1012 and ITS photoinitiators in MeOH; DPABz photoinitiator in THF⁷⁴.

Table 2.3 Peak TPA cross-section for commercial photoinitiators using Z-scan and nonlinear transmission WLC (white-light continuum) pump-probe method⁷⁴.

Compound	λ_{max}	Z-scan		WLC-2PA	
		$\lambda_{\text{max}}^{(2)}$	δ_{meas}	$\lambda_{\text{max}}^{(2)}$	δ_{meas}
Irgacure 184	246	265	23	250	<20
Irgacure 261	242	265	<20	250	<20
Irgacure 369	324	335	7	318	27
Irgacure 651	254	265	28	250	<20
Irgacure 754	253	265	21	250	10
Irgacure 819	295	300	<4	300	<5
Irgacure 907	306	300	4	300	<5
Irgacure OXE01	328	330	31	330	38
Darocure TPO	299	300	<4	300	<5
Darocure MBF	255	265	27	250	<20
Darocure 1173	244	265	<20	250	<20
CD1012	247	265	16	273	14
ITX	382	380	5	377	4
DPABz	390	390	100 (THF)	388	120 (THF)

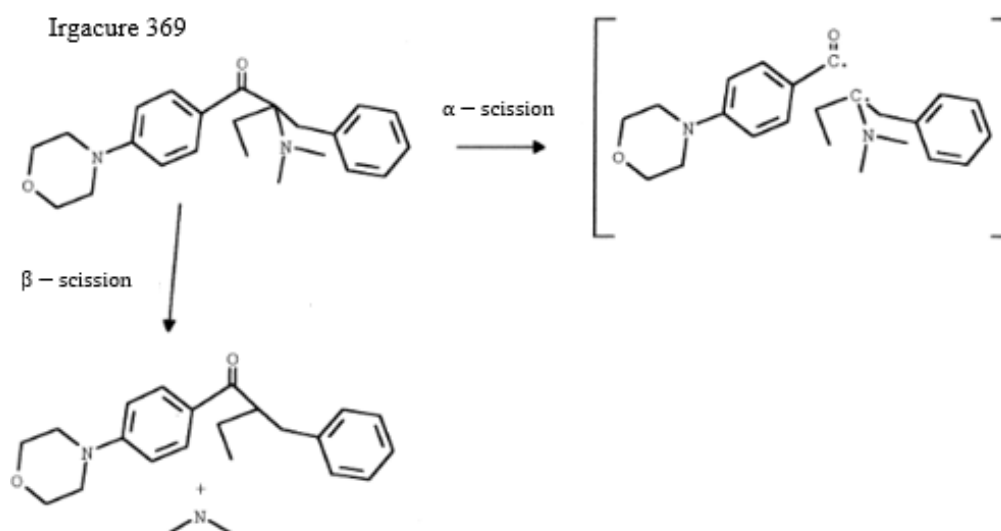


Figure 2.8 Cleavage reactions of Irgacure 369 upon absorption of light⁸¹.

In recent years, many efforts have contributed to synthesise fast and efficient photoinitiators suitable for TPP⁸²⁻⁸³. Some water-soluble photoinitiators, such as Irgacure 2959¹³, which contains water-soluble hydroxyl groups and P2CK or E2CK⁸⁴ which contains water-soluble carboxylic acid sodium salts, have been also reported and used in water-soluble monomers. Irgacure 2959 is a type I benzoin photoinitiator that generates a benzoyl radical and an alkyl radical upon absorption light⁸⁵(**Figure 2.9**). Benzoyl radicals have higher reactivity than alkyl radicals in polymerisation processes⁸⁵. The alkyl radicals that can deliver electrons to electron acceptors such as metal ions have been found useful in the photoreduction of metal ions, gold ions, silver ions and copper ions, for example⁸⁶.

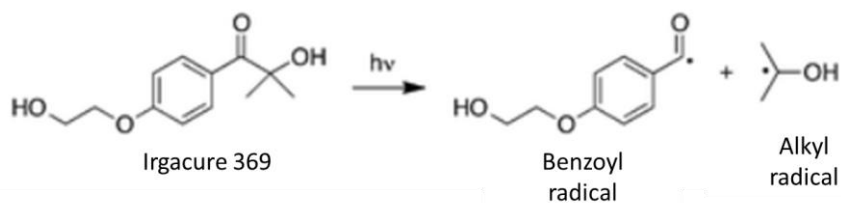


Figure 2.9 Free radicals of Irgacure 369 generated upon absorption of light⁸⁵.

P2CK and E2CK are synthesized water-soluble photoinitiators that consist of dialkylamino groups as electron donors, double bonds as conjugation bridges as well as five or six member rings as an acceptor in the centre (**Figure 2.10**) (D- π -A- π -D)^{84, 87}. Carboxylic acid sodium salts are introduced as water-borne functionalities at the end of amino groups. The long conjugation length and the presence of strong electron donor and acceptor groups, P2CK and E2CK owe large two-photon cross-sections 176 GM and 201 GM, respectively, providing broad processing windows in TPP^{84, 88}.

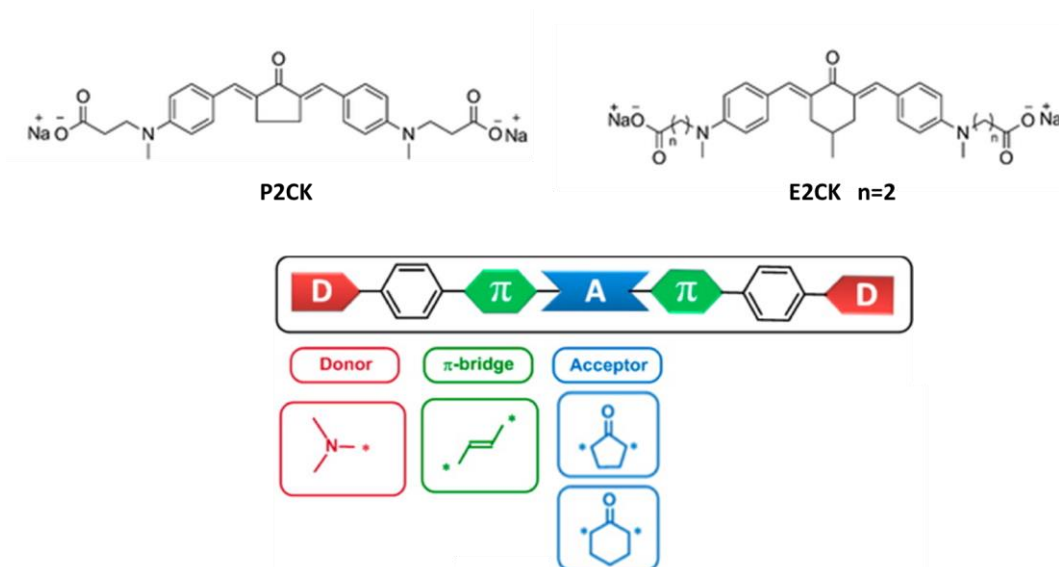


Figure 2.10 Structures of P2CK and E2CK.

Apart from free radicals, a cationic photoinitiator generates a strong photoacid (photoacid generator) upon laser exposure initiating cationic polymerisation⁸⁹. Both commercial (diaryliodonium salt and triaryl sulfonium salt) and custom-made photoacid generators were reported in cationic TPP for epoxy resin such as SU-8⁵⁵.

A series of photoinitiator candidates are available. The TPL used in this thesis was Nnanoscribe (Nanoscribe GmbH Photonic Professional GT) and the wavelength (λ) of the laser beam was 780nm. According to **Figure 2.7**, Irgacure OXE01, Irgacure 819,

Irgacure 369, Darocure TPO, ITX and DPABz all show absorption at 390nm, which is $\frac{1}{2} \lambda$. According to **Table 2.3**, the cross-section values of Irgacure 819, Darocure TPO and ITX are lower than Irgacure OXE01, Irgacure 369 and DPABz. Therefore, Irgacure OXE01, Irgacure 369 and DPABz are three suitable photoinitiators. Because Irgacure 369 is more commercially available, it was chosen as the main photoinitiator in this thesis. Irgacure 2959, P2CK and E2CK were also assessed as water-soluble photoinitiators in this thesis.

2.3.4 Photopolymers and Fabricated Structures

Resins used for TPP are either monomers, oligomers or a mixture of monomers and oligomers. The basic requirements of the resins for TPP include⁵²:

- (1) Being transparent in the visible and NIR region to allow for laser focusing.
- (2) Forming self-support structures with fast curing speed that polymer structures are formed when a laser is applied.
- (3) Strong washout resistance to keep structural integrity after sample development by dissolving fabricated structures and unreacted materials in solvents.
- (4) Minimum shrinkage and resulted distortion of the final build structures.
- (5) The refractive index of the resin should be close to 1.5, which is the refractive index of glass, allowing the laser beam to be easily focused without aberrations.
- (6) Sufficient mechanical properties to maintain structures after curing and sample development.

Most monomers suitable for TPP are acrylates and methacrylates⁹⁰. There are various monoacrylates and multi (meth) acrylates with different molecular weights available

on the market today. The chemical structures of acrylate and methacrylate groups are shown in **Figure 2.11**. They are easily processed with a high polymerisation rate⁹⁰. In general, polymethacrylates have a higher glass transition temperature (T_g), higher stiffness, higher tensile strength and lower elongation while polyacrylates are softer, more rubbery and with lower tensile strength and higher elongation if they have similar chemical structures⁹⁰. The reason is that methyl groups affect the rotational mobility of the polymer chains⁹⁰. The polymerisation rate of acrylates is often higher than methacrylates⁹⁰. Functionality is the number of polymerisable groups per molecule. Higher functionality gives a higher reaction rate because of the higher concentrations of reacting sites⁹⁰. Shrinkage is the main drawback of free radical polymerisation⁹⁰. Shrinkage causes a large build-up of internal stress and dimensional changes⁹¹. The double bonds in monomers are converted to single covalent bonds during polymerisation. Therefore, the total volume of materials changes from the van der Waals distance to the shorter single bonds distance resulting in shrinkage⁹⁰. A higher degree of functionality and higher molar mass produce higher shrinkage results⁹⁰. However, shrinkage of monomers with high functionality ($f \geq 3$) is comparable to (sometimes even lower than) monomers with low functionality because mobility of large network chains are limited (vitrification phenomena)⁹¹. For example, TMPTA (trimethylolpropane triacrylate), a triacrylate monomer shows the same shrinkage (12%) with TPGDA (tripropylene glycol diacrylate), a diacrylate monomer⁹¹. Therefore, in order to improve the reaction rate, a high degree of functionalities are preferred but the shrinkage needs to be considered and assessed.

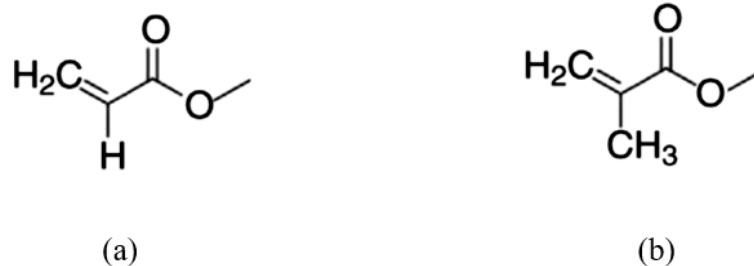


Figure 2.11 Chemical structure of (a) acrylate and (b) methacrylate groups⁹⁰.

Some resins for TPP have been already commercialised, including acrylic-based and epoxy-based resins. The achievements of these materials in fabrication structures by TPP are summarised in **Table 2.4**. **Figure 2.12** shows fabricated structures using acrylic resins as the monomers. The complex interpenetrating microcoils⁵⁵, a cantilever⁵⁵, a micro-bull⁶⁵, a chain with interlocking rings⁹² and two pairs of pyramids of different height⁷⁹ are shown great structural complexity and high resolution.

Table 2.4 Summary of commercially available resins used for TPP.

Resin	Type of material	Examples of achievement
SCR 500	Urethane acrylate	3D micro-bull sculpture ⁶⁵ Woodpile photonic crystal structure ⁹³
Nopcocure 800	Acrylic acid ester	Micro gear-wheel ⁹⁴
IP-G 780	Acrylic photoresist	Ionically conductive polymer composites ³²
IP-L 780	Pentaerythritol triacrylate	
IP-Dip	A mixer of diacrylate (confidential formulation)	
IP-S	Epoxy-based resin	Microneedle ⁹⁵
Ormocers	Silicate inorganic-organic hybrid material	Woodpile photonic crystal structure ^{61, 76-77} Scaffold application ⁷⁵
SU-8	Epoxy-based resin	Micro-optical elements ⁹⁶ Ultra high aspect ratio ^{89, 97} Woodpile photonic crystal structure ⁷⁷ Scaffold application ⁷⁵

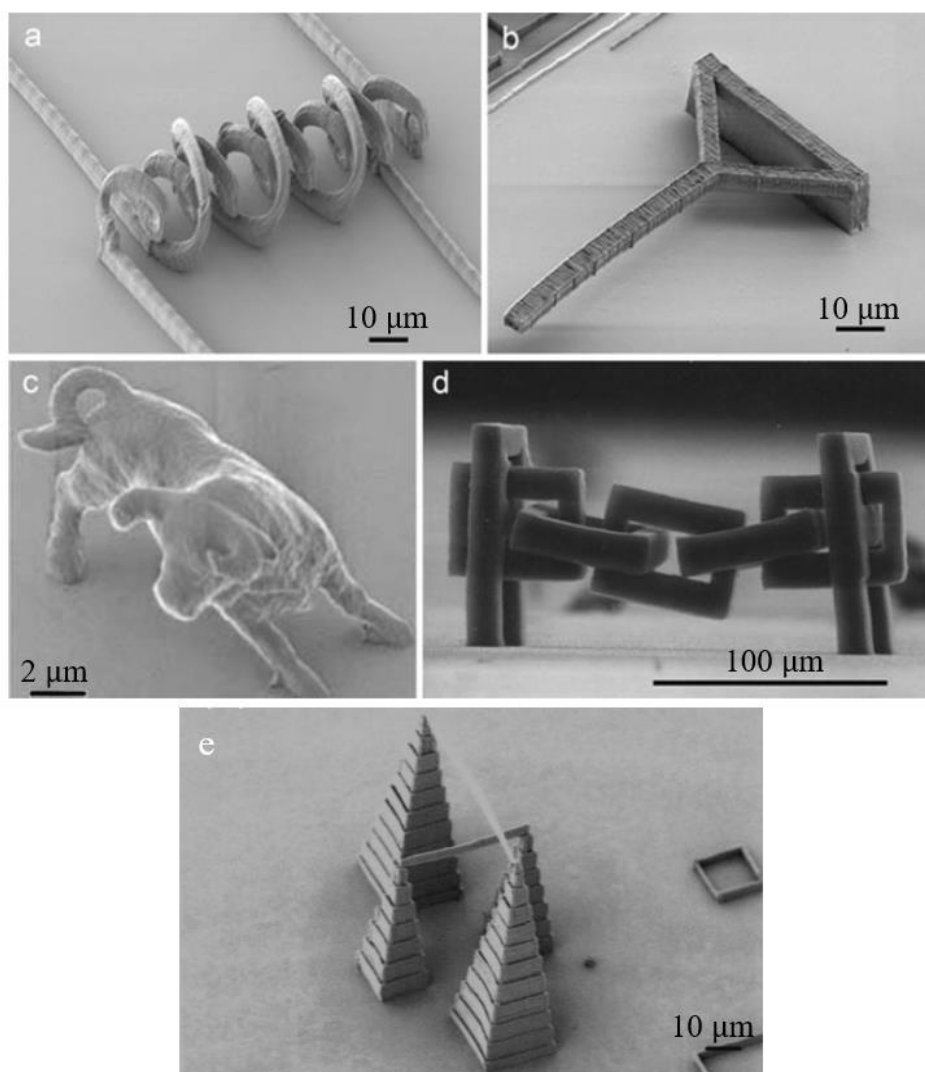


Figure 2.12 SEM images of fabricated structures using acrylic monomers. (a) Interpenetrating microcoils⁵⁵ (b) a cantilever⁵⁵ (c) a microbull⁶⁵ (d) a chain with interlocking rings⁹² (e) two pairs of pyramids of different height⁷⁹.

Ormocer material is a silicate inorganic-organic hybrid that has been used in TPP⁴⁴. This organically modified ceramic material is found usefully to be used in photonic applications and biomedical applications⁴⁴. Ormocers consist of silicones, organic polymers and glasses/ceramics (shown in **Figure 2.13**). By modifying chemical structures, the property of an ormocer material becomes adjustable and controllable⁹⁸.

Figure 2.14 shows the multifunctional precursors that are used for material processing

and the influence on its properties. Commercial ormocers are viscous liquid that can be solidified by crosslinking the organic chains without any pre-treatment⁹⁸. Ormocers exhibit excellent physical, chemical, mechanical and optical properties⁴⁴. The major applications of ormocers are photonic crystal woodpile structures, biomedical micro-devices and medical implants⁴⁴. **Figure 2.15** shows a woodpile structure and micro-needles fabricated using ormocers by TPP. Ormocer provides a large degree of variability on material optical, chemical and mechanical properties so it is a good candidate of material selection.

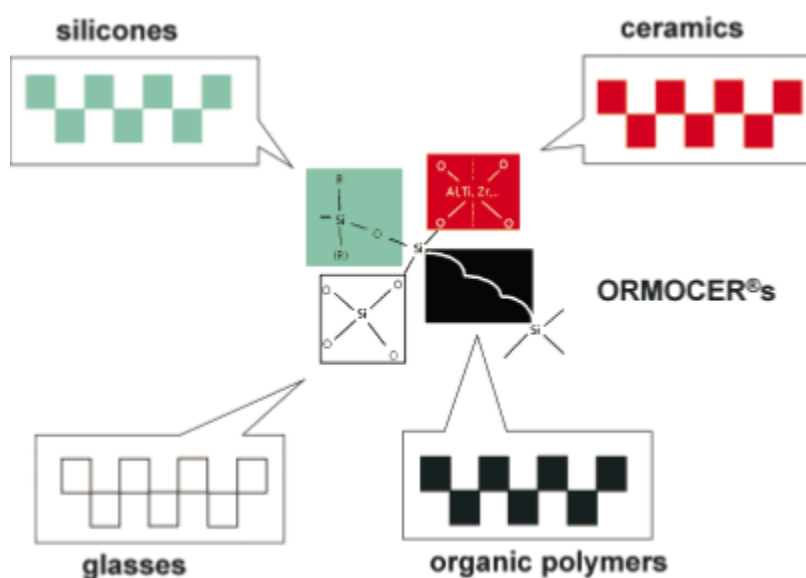


Figure 2.13 Relationship of hybrid polymers (Ormocers) with silicones, organic polymers, and glasses/ceramics⁹⁸.

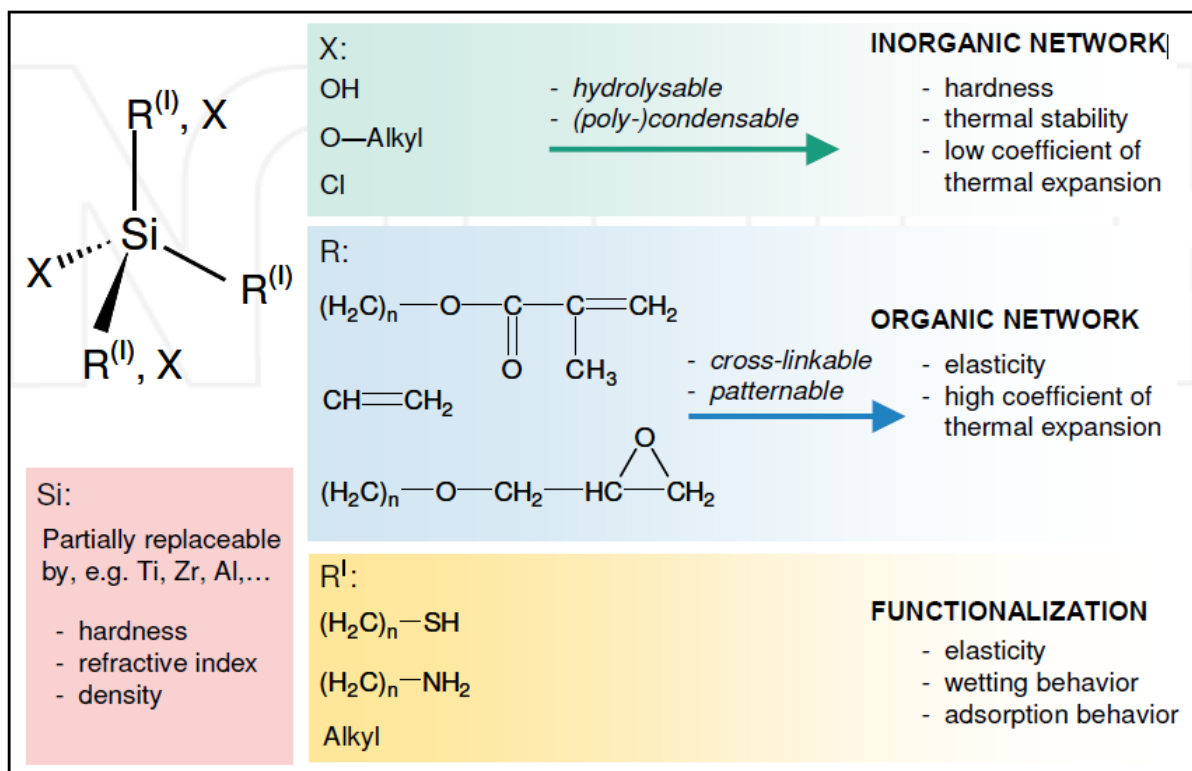


Figure 2.14 Multifunctional precursors for ormocer synthesis and their influence on resulting material properties⁹⁹.

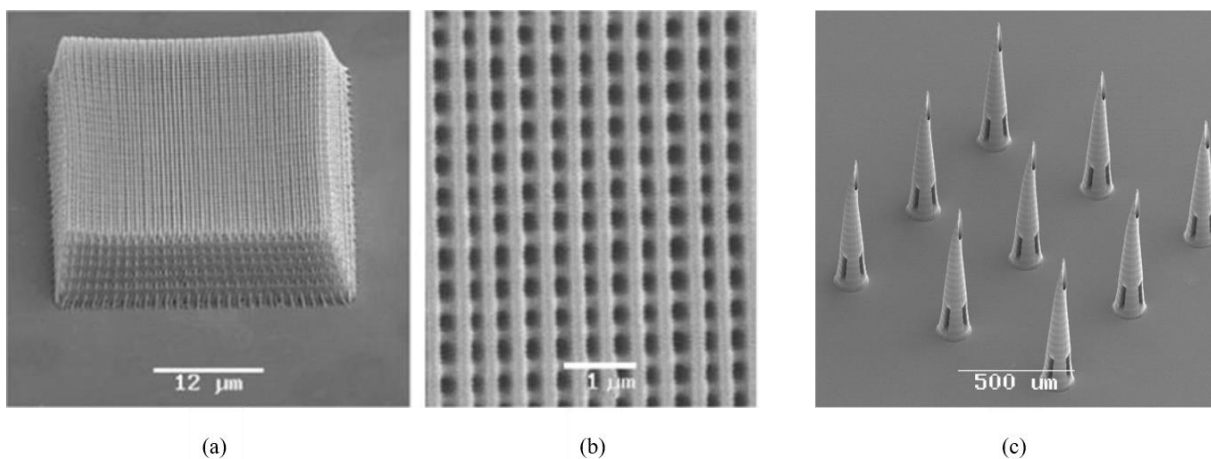


Figure 2.15 SEM images of TPP (a)-(b) woodpile structures⁷⁷ and (c) micro-needles¹⁰⁰ using ormocers.

SU-8 is an epoxy-based resin that contains eight epoxy groups and triaryl sulfonium salt (photoacid generator) (**Figure 2.16** (a)). It is polymerised by cationic

polymerisation. Upon exposure to a light beam, a strong acid is generated as a result of a photoacid generator and then initiate the crosslinking of the epoxy networks by the opening of the epoxy groups⁸⁹. **Figure 2.16** shows the process of SU-8 polymerisation. It needs an additional post-baking step to achieve the high crosslinking density^{52, 89}. SU-8 gives high chemical and thermal resistance due to its high epoxied functionality and crosslinking density (glass transition temperature $T_g > 200^\circ\text{C}$ and degradation temperature $T_d \sim 380^\circ\text{C}$ when SU-8 is fully crosslinked). SU-8 is mostly used in the fabrication of MEMS because it can produce a structure with a high aspect ratio. A 50:1 ultra-high aspect ratio has been achieved by Teh et al.⁸⁹ by using a low NA (numerical aperture, $\text{NA} = 0.3$) objective.

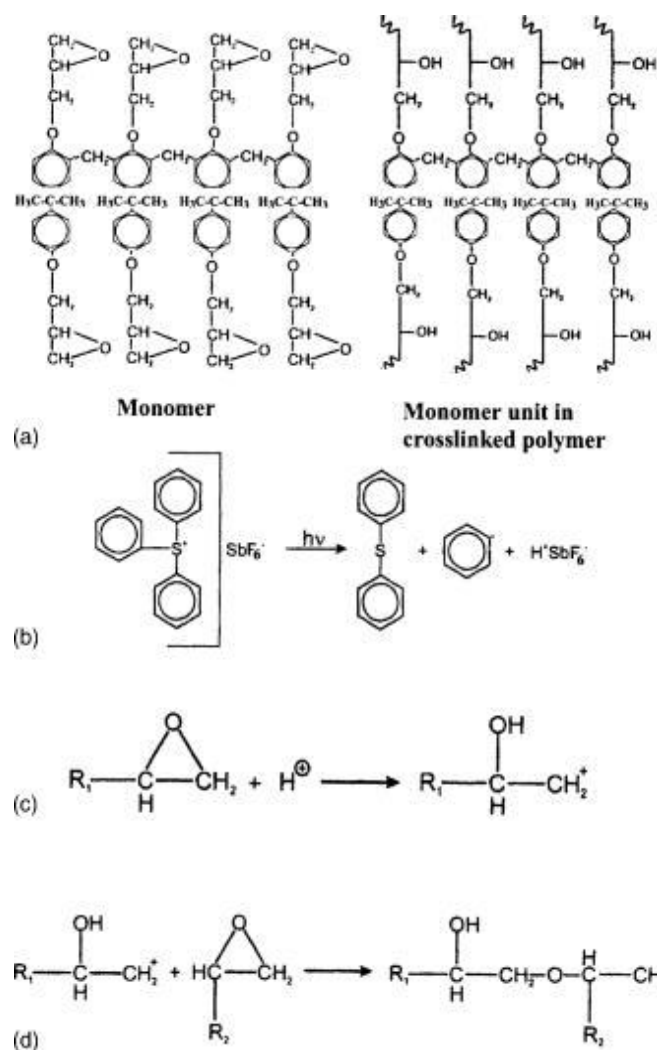


Figure 2.16 (a) The chemical structure of SU-8 (b) Generation of acid upon laser exposure from cationic photoinitiator (c) Initiation of polymerisation by opening the epoxy groups (d) Chain propagation of the cationic polymerisation^{89, 101}.

Apart from the materials themselves, the laser power and laser scanning speed are the main processing parameters that affect the qualities of the fabricated structures. Fan et al.¹⁰² and Li et al.^{84, 87} reported the concept of processing windows of the materials that are suitable for two-photon polymerisation. A series of independent structures that were fabricated using an increasing laser power and scanning speed were compared and classified based on the structural qualities (shown in **Figure 2.17**). It

was shown that the quality of the fabricated depended on the laser power and writing speed. The structures could keep structural geometry as designed only when the values of laser power and scanning speed were in a certain processing window (green area in **Figure 2.17**). Therefore, the successful fabrication of structures by two-photon fabrication relies on the selection of suitable materials, processing parameters, and also structural design.

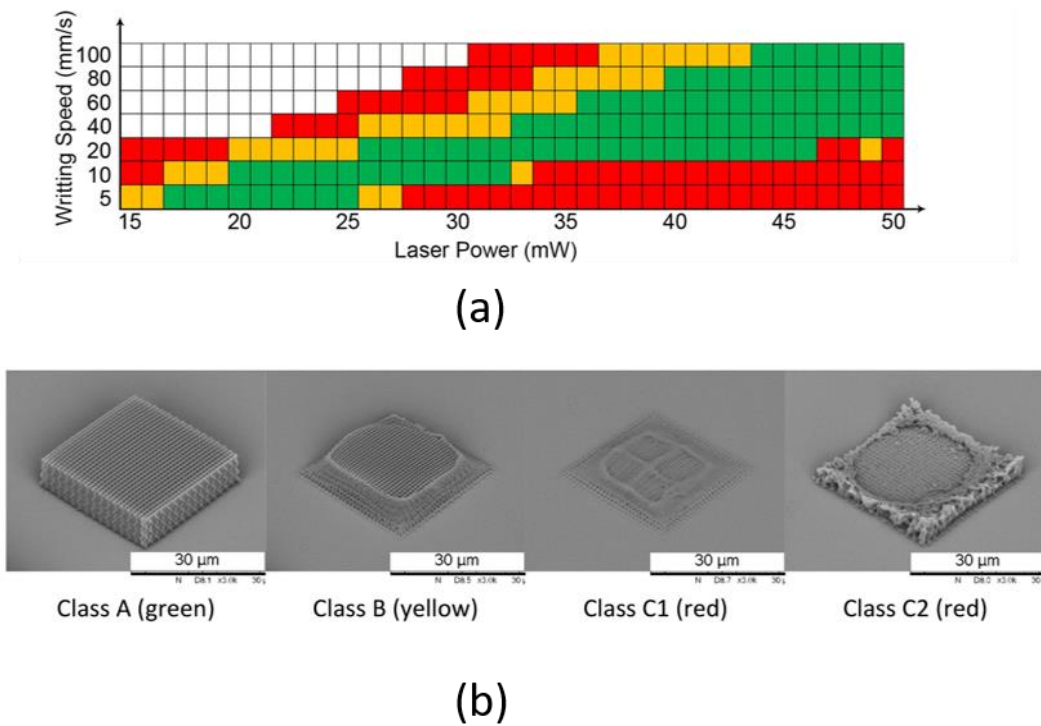


Figure 2.17 Processing windows in screening test with different scanning speeds and laser power using a formulation of PETA/Irgacure 369, the qualities of structures were classified and marked using different colours. (b) Classification of the structures by the typical quality of their appearances. Green – Class A; Yellow – Class B; Red – Class C; white – Class D¹⁰².

In summary, there are a variety of monomers suitable for TPP processes. The majority of TPP developed to date has employed radical polymerisation because of its high reaction rates, ease of processing and wide availability of photoinitiators and monomers compared to cationic polymerisation^{44, 55}. Therefore, radical polymerisation was used in this thesis. Many acrylate or methacrylate-based monomers are available. In this thesis, acrylate monomers with multifunctional groups were selected due to their high polymerisation efficiency⁹⁰. Ormocer is a good candidate for monomers polymer resin. But since this thesis a primary study on TPL fabrication of metal-polymer composites, ormocer was not used. If any special properties such as high thermal conductivity or high hardness are required, ormocer could be considered. The effect of processing parameters, such as laser power and scan speed, were studied.

2.4 Two-photon Fabrication – Metal

In addition to polymers, micro/nano metallic structures fabricated by TPL have been studied. Metals have unique properties, including electromagnetic field enhancement, catalysis, photoemission, and electronic conductivity¹⁰³⁻¹⁰⁶. They have promising applications in many fields such as metallic photonics, plasmonics, metamaterials, electronics, SERS (surface-enhanced Raman scattering) and bio-sensing^{12, 41, 107-109}. TPL (two-photon lithography) provides opportunities to fabricate complex metallic structures in subwavelength scales¹¹⁰. In general, there are four methods to fabricate the metallic structures using TPL¹¹¹: (1) Direct deposition of metals either from solution or polymer matrices; (2) metallic coating onto 2D or 3D polymer surface; (3) inversion method; (4) simultaneous photopolymerisation and photoreduction process. In this section, the four techniques were reviewed and discussed. The applications of

metallic structures fabricated by TPL were reviewed and the challenges and future perspectives in this area were discussed.

2.4.1 Direct Deposition of Metals

Direct deposit metal either by photoreduction of metals ions or photodecomposition of metal-containing materials from solution or polymeric matrices shows a great simplicity in metallic structure processing by TPL (two-photon lithography) because metal structures are formed in a step¹¹¹. According to the literature, there are three types of photoreduction mechanism: (1) non-photosensitised reduction¹¹²; (2) using a dye as a photosensitiser^{111, 113} and (3) using a photoinitiator or photoacid generator to generate radicals^{1312, 31, 112}.

Non-photosensitised reduction means that a metal source is directly photoreduced or fused by the absorption of photons¹¹². For the TPR with a dye, two photons are absorbed simultaneously and then the electrons transfer from the lowest unoccupied molecule orbital level to the metal ions and generate metal atoms. The generated metal atoms could contribute to nucleation or charge recombination^{111, 113}. **Figure 2.18** (a) illustrates the photoinduced electron transfer from the dye molecules to silver ions for the reduction of silver ions. The sensitiser that helps absorb photons may not necessarily be consumed and acts as a catalyst to enhance the formation of metal atoms⁴⁶. Contrary to dyes, photoinitiators generate radicals¹³ or photoacids^{12, 31, 114} leading to metal reduction.

Two-photon reduction is defined in three steps: (1) nucleation due to the reduction of metal ions; (2) the growth of metals seeds to NPs; (3) the aggregation of NPs to form final patterns. (**Figure 2.18** (b))¹¹¹.

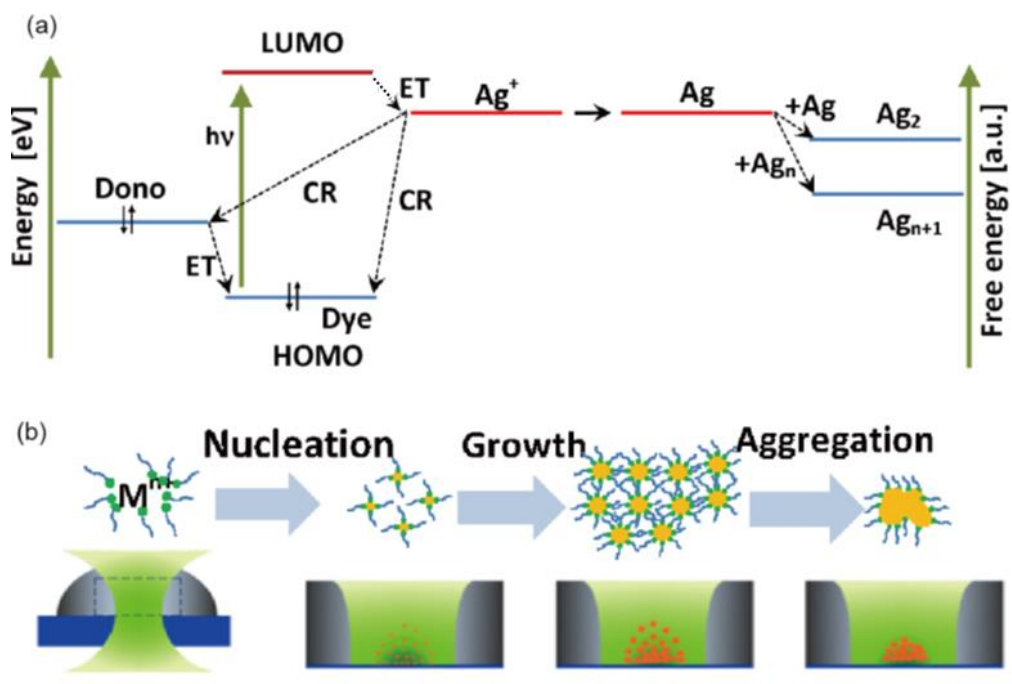


Figure 2.18 (a) The basic scheme of photoinduced electron transfer from the dye to silver ions for silver reduction. Ag^+ for silver ions; Ag for silver atoms; ET for electron transfer; CR for charge recombination; HOMO for the highest occupied molecular orbital; LUMO for the lowest unoccupied molecular orbital. (b) Three steps of photoreduction process: (1) nucleation (2) growing (3) aggregation^{107, 111}.

A summary of past works on TPR of metals is shown in **Table 2.5**, including the materials used, the processing parameters and the achievements. Tanaka et al.¹¹² fabricated of 2D and 3D metallic microstructures using directly two-photon-induced metal reduction. Silver nitrate ($AgNO_3$) and gold chloride ($HAuCl_4$) were reduced directly from the metal-ion aqueous solution. **Figure 2.19** (a-b) shows the fabricated

2D silver and gold double ring structures. The structures had low resistivity, which was only a few times larger than bulk metal. A 3D silver gate structure (**Figure 2.19** (c)) was obtained by two-photon reduction by precise control of the laser power and scanning speed. The research showed that the relationship between line width and laser power were not linear. The complicated structure can be only obtained using suitable laser power and scanning speed. It was found that the top of the structure needed higher laser power (laser power: 29.8 mW for top, 18.8 mW for the bottom, scanning speed: 24 μ m/s) as the reduction rate in the solution was lower than at the glass-solution boundary.

Table 2.5 Summary of past work on direct TPR of metals.

Materials	Achievements	Beam information	Reference	Year
AgClO ₄ in silicate sol-gel matrix	Photo-reduction of AgClO ₄	800 nm, 1kHz, 120 fs	P-W. Wei et al. ¹¹⁵	2000
AgBF ₄ + dye + PVK	100 µm high metallic structures	760 nm, 82 MHz, 120 fs	F. Stellacci et al. ¹¹⁶	2002
Gold salt in PVA film	Grating structure mean particle size 106 nm	780 nm, 82 MHz, 80 fs	K. Kaneko et al. ¹¹⁷	2003
AgNO ₃ solution + PVP	Silver lines then coated with copper	780 nm, 76 MHz, 250 fs	T. Baldacchini et al. ³⁴	2005
AgNO ₃ solution + coumarin 440 (dye)	Silver dots, wires and mesh structures	800 nm, 82 MHz, NA = 1.42, 80 fs	A. Ishikawa et al. ⁹	2006
AgNO ₃ solution / HAuCl ₄ solution	Silver and gold double ring structure 3D silver gate	800 nm, 80 MHz, NA = 1.42, 80 fs	T. Tanaka et al. ¹¹²	2006
AgNO ₃ + PVP film	Silver lines	790 nm, NA = 0.75, 100 fs	C. N. LaFratta et al. ³⁸	2006
AgNO ₃ + PVP film	Silver lines Pyramidal microstructure	752 nm, 76 MHz, NA = 1.25, 200 fs	S. Maruo et al. ⁴⁰	2007
HAuCl ₄ solution (PVP as a dispersant)	Particle size 3nm	780 nm, 10 Hz, NA = 0.5, 100 fs	T. Nakamura et al. ¹¹⁸	2008
HAuCl ₄ solution + Ru (II) dye in PSS matrix	Metallic grids	740 nm, 82 MHz, NA = 1.25, 100 fs	L. Vurth et al. ¹⁰	2008
HAuCl ₄ solution in PSS matrix	Gold lines, woodpile structure	740 nm, 82 MHz, NA = 1.25, 100 fs	N. Tosa et al. ¹¹⁹	2008

Ag ions + NDSS (surfactant)	Silver lines (Line width 120nm) Free-standing pillar Silver-pyramid array	800 nm, 80 MHz, NA = 1.4, 80 fs	Y-Y. Cao et al. ¹⁰⁷	2009
Ag ions + fatty salt (surfactant)	Silver lines (line width 285 nm)	800 nm, 80 MHz, NA = 1.4, 80 fs	Y-Y. Cao et al. ¹²⁰	2009
Ligands attached Ag NPs	a subwavelength resolution mesh structure	800 nm, 76 MHz, 130 fs	W. J. Kim et al. ¹²¹	2011
AgNO ₃ + PVP	Lines, helix, pillar and cubic structures in PVP matrix	800 nm, NA = 1.3, 100 fs	N. Tsutsumi et al. ¹²²	2011
Gold nanodots	Lines and 2D structures electronic resistivity $5.5 \times 10^{-8} \Omega\text{m}$	800 nm. NA = 1.35, 120 fs	B-B. Xu et al. ¹²³	2012
AgNO ₃ solution + coumarin 440 (dye) + NDSS	2D silver mesh 3D silver cup Line width 120nm	800 nm. 82 MHz, NA = 1.42. 80 fs	A. Ishikawa et al. ¹¹³	2012
AgNO ₃ + PVP	Silver dots 300 nm	795 nm, 11 MHz, NA = 0.8, 50 fs	K. Vora et al. ¹²⁴	2012
HAuCl ₄ + ionic liquid	Gold lines (Line width 228 nm) electronic resistivity $16.5 \times 10^{-8} \Omega\text{m}$ 2D structures	780 nm, 80 MHz, NA = 1.45, 80 fs	W-E. Lu et al. ^{39, 125}	2013
AgNO ₃ solution + surfactant + dye	silver nanodots 22 nm	800 nm, 80 MHz, NA = 1.4, 140 fs	Y-Y. et al. ³⁵	2013
HAuCl ₄ + TPO (photoinitiator) + CTAB (capping agent)	Gold blocks for SERS	780nm	I. Izquierdo-Lorenzo ³⁶	2014

Ag NPs	Silver lines	800 nm, NA = 1.45, 120 fs	H. Wang et al. ⁴⁷	2015
AgNO ₃ + gelatin	3D photonic structure	795 nm, 11MHz, NA = 0.8, 50 fs	S. Y. Kang et al. ³⁷	2015
Modified Au NPs	Au square patterns	700 nm, 80 MHz	L. Stolzer et al. ¹²⁶	2015
	Au KIT logo		D. Naumenko ⁴⁷	2016
	SERS substrates			
AgNO ₃ + NDSS + HHMP (dye)	2D c-shape arrays	532 nm, 50 MHz, NA = 1.4, 270 fs	S. Tabrizi et al. ⁴⁵	2016
HAuCl ₄ / AgClO ₄ solutions + surfactant	Au and Ag NPs	800 nm, 1kHz, 90 fs	N. Nakashima et al. ¹²⁷	2016

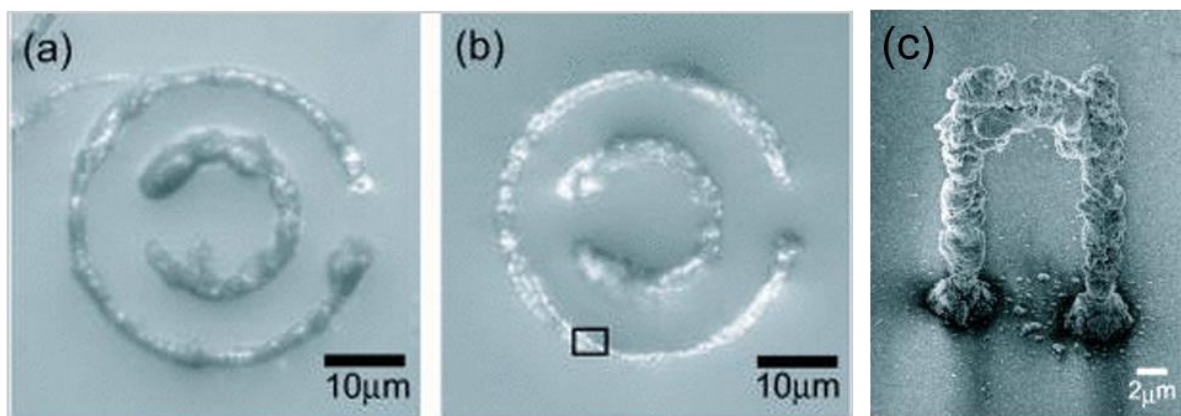


Figure 2.19 (a) Optical microscope image of a silver double ring structure fabricated by 2 photon metal reduction (b) Optical microscope image of a gold double ring structure fabricated by 2 photon metal reduction (c) SEM image of a 3D silver gate fabricated by 2 photon metal reduction. width: 12 μm ; height: 16 μm ; line width: 2 μm .

A two-photon sensitive dye, coumarin 440, was found helpful to improve the reduction properties of silver ions in aqueous solution⁹. Low laser power was required to trigger the reduction of silver ions by excitation of a sensitive dye. The minimum wire width of 400 nm (**Figure 2.20** (a)) was achieved using a low laser power of 4.32 mW and a scanning speed of 50 $\mu\text{m}/\text{s}$. They pointed out that the local heating could not be avoided because the laser beam needs to be focused on the surface of fabricated structures. For that reason, using a dye with low processing laser power can help suppress the local heating and improve the quality of the 3D silver structure. In addition, a ruthenium (II) dye¹⁰ as a photoinitiator was found useful to reduce gold ions. Laser power was reduced from 30mW to 5mW and thus reduced the thermal effect. $[\text{Ru}(\text{bipy})_3]^{2+}$ has a large two-photon cross-section and it strongly absorbs the IR light and results in a triplet metal-to-ligand charge-transfer (3MLCT) excited state,

which transfers electrons, and locates electrons on bipy ligands to help gold reduction^{10, 128}. Both 2D and 3D silver structures were fabricated by using two-photon sensitive dyes to help metal reduction^{45, 113}. (**Figure 2.20** (b)-(d))

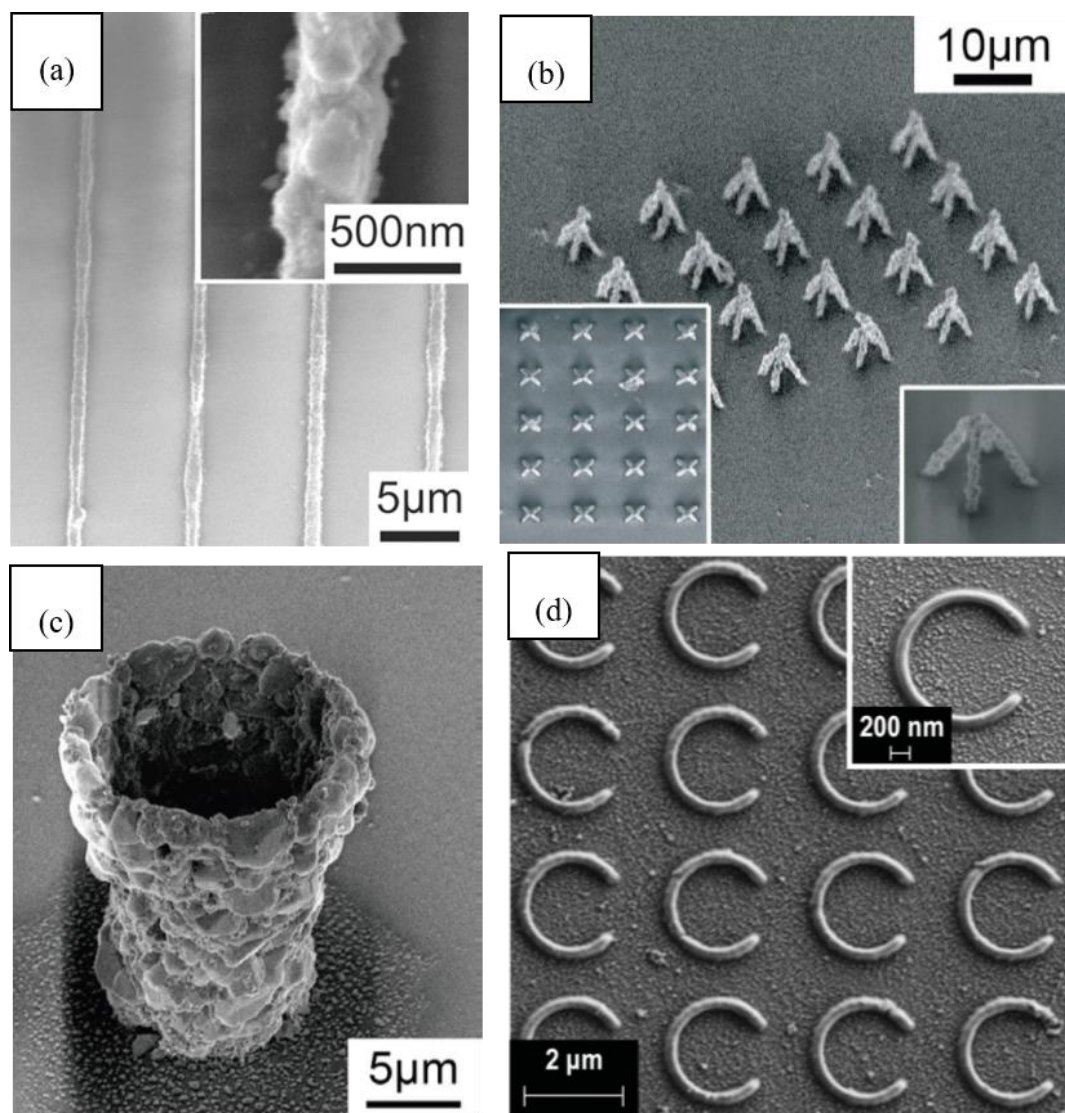


Figure 2.20 (a) SEM image of a silver wire fabricated with coumarin 440 as a 2-photon sensitive dye⁹; (b-c) 3D silver pyramids and silver cup fabricated with coumarin 440 as a 2-photon sensitive dye and NDSS as a surfactant¹¹³; (d) silver c-shape arrays fabricated with HHMP as a 2-photon sensitive dye and NDSS as a surfactant⁴⁵.

Apart from using a dye, photoinitiators have also been used to reduce metal sources. Lorenzo et al.³⁶ presented a 3D Au nanostructure using direct laser writing that can be applied as substrates for Surface-Enhanced Raman Spectroscopy (SERS). The gold NPs were produced by radical-mediated TPR that biphenyl- (2,4,6-trimethylbenzoyl)-phosphine oxide (TPO) was used as a radical photoinitiator to reduce gold chloride (HAuCl₄), a hexadecyltrimethyl ammonium bromide (CTAB) was used as a capping agent and propanediol was used as a solvent. The NPs only formed when the laser power above the threshold and the first layer of NPs were produced slowly. After the first layer, the photoreduction became violent due to the local heating near the laser focus. **Figure 2.21** shows the Au-NP based structures.

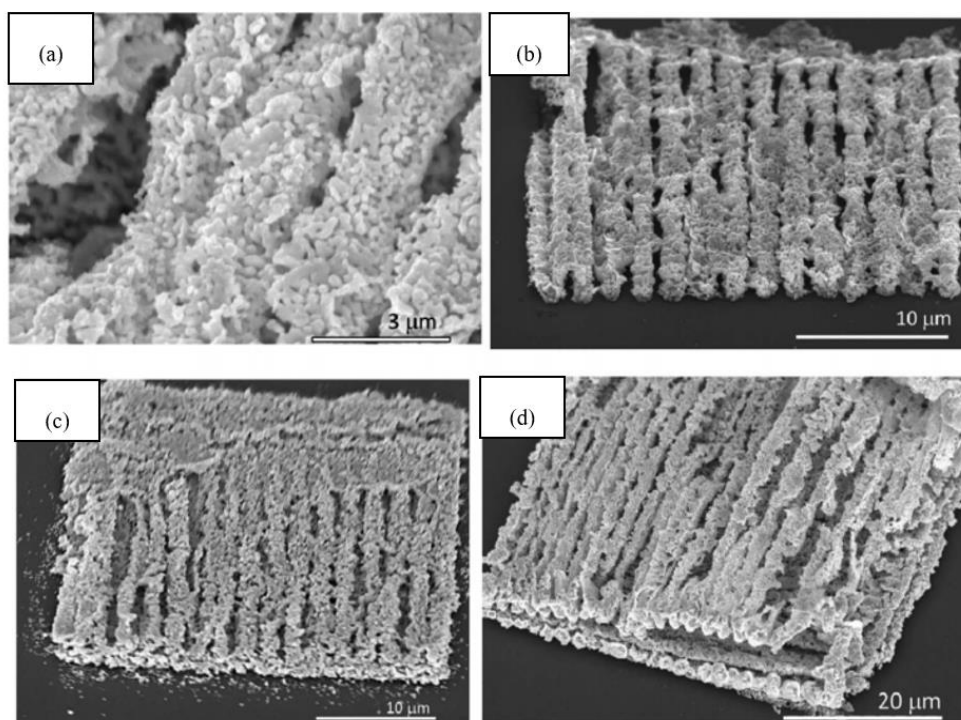


Figure 2.21 SEM images of Au-NPs based structures. (a) line structures (b) Single-layer structure consisting of lines (c) single woodpile structure (d) triangular-based

prism³⁶.

However, direct two-photon deposition of metals from solution generally involves isolated metal nanoparticle aggregation; thus, it is difficult to control the metallic structure. The structures were granular and rough. Therefore, it is challenging to control 2D structures and to build 3D structures⁵⁵. Cao et al. indicated that using NDSS¹⁰⁷ or fatty acid¹²⁰ as surfactants helps obtain a smaller feature size around 100nm. A 3D standing pillar with a line width of 180 nm was achieved. (**Figure 2.22** (a)) The NDSS surfactant inhibited the unwanted growth of the metal NPs upon laser exposure so that the feature size could be controlled. **Figure 2.22** (b) illustrates the two-photon metal reduction processes with and without the surfactant, NDSS. At stage one, silver ions were reduced and silver seeds were formed during laser irradiation. After that, the NPs grew up at stage two. The particles had different sizes and shapes without NDSS while the particles were more uniform by adding NDSS. Finally, the aggregation of the NPs tends to form the final structures. Ionic liquid works by a similar mechanism and refines surface morphology^{39, 125, 127}. A 228 nm width gold line and U-shape gold resonance rings (**Figure 2.23**) on glass substrate were obtained³⁹.

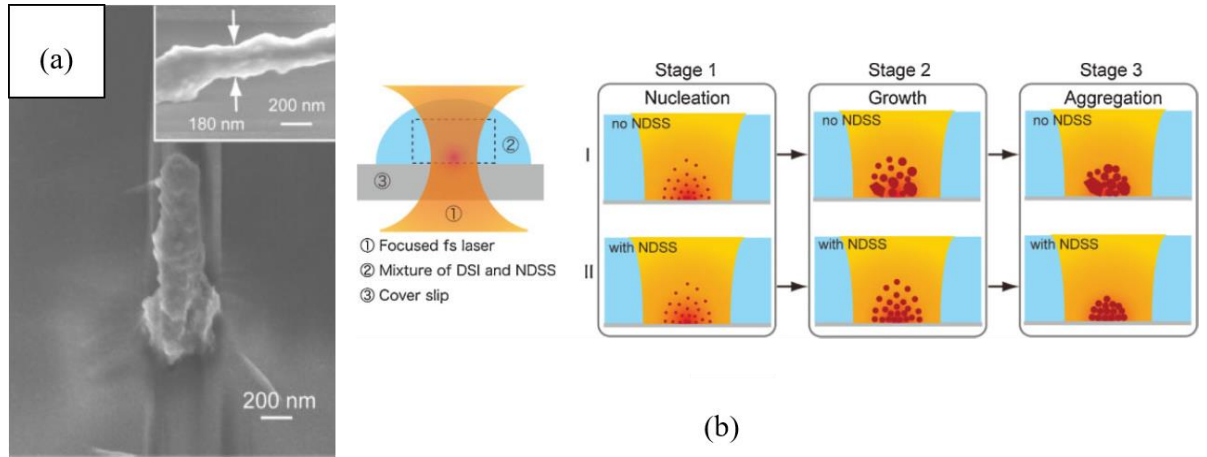


Figure 2.22 (a) SEM image of a free-standing silver pillar made through two-photon reduction with NDSS as a surfactant (b) Schematic illustration of the formation of silver patterns with/without NDSS by two-photon reduction process¹⁰⁷.

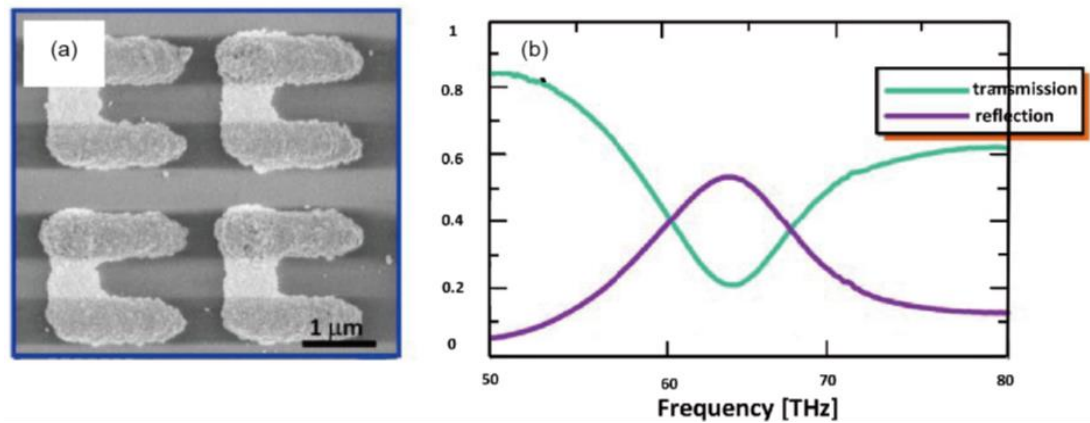


Figure 2.23 (a) SEM image of the u-shape gold resonance rings on glass substrate, which was fabricated by amino-terminated ionic liquid assisted two-photon reduction. (b) Measured transmission and reflection spectra for the metamaterials with x-polarized illumination³⁹.

Apart from the direct reduction of metals from metal solution, suspending the metal atoms in a transparent matrix to deposit metals is another technique. Wu et al.¹¹⁵ firstly demonstrated the method. They suspended AgNO_3 in a porous silicate sol-gel matrix

and then the silver was written directly into the interior of the sol-gel matrix by TPL. The method produced discrete silver particles with the sizes from 40 to 50 nm. Stellacci et al.¹¹⁶ used a solvent-soluble silver salt (AgBF_4) and ligand-coated silver NPs as metal seeds in polyvinyl carbazole (PVK) as a host polymer matrix. The deposition was initiated by a TPA photoreducing dye. A 3D stack-of-logs structure was fabricated. After removing the matrix, the structure was deformed but it was still freestanding. The conductivity was three orders of magnitude lower than bulk silver. Besides, copper and gold patterns were also written in poly (methylmethacrylate) (PMMA). Silver nitrate in a thin polyvinylpyrrolidone (PVP) film³⁴ and gold ion-doped polyvinyl alcohol (PVA) film¹¹⁷ were also employed to fabricate metallic gratings by two-photon photoreduction. However, the structure formed is granular after removing the polymer matrix³⁴. The conductivity of the silver/PVP line was enhanced by electroless deposition of copper³⁸. **Figure 2.24** illustrates the procedure of metallic structures fabricated using silver/PVP films by TPL. Sample liquid containing silver nitrate and PVP are preheated at 110 °C for 10 mins. Then silver ions are reduced and structure is shaped by femtosecond pulsed laser beam. Finally, PVP and unreacted materials are removed by rinsing in ethanol. Later, Maruo and Saeki⁴⁰ fabricated not only silver lines but also a 3D pyramidal model and a hybrid structure consisting of polymer and silver lines (**Figure 2.25**) by using silver ion-doped PVP films. The high resistivity of $3.48 \times 10^{-7} \Omega\text{m}$ was achieved. This 3D direct laser writing method has potential application in 3D electrical wiring of electronic devices and MEMS devices.

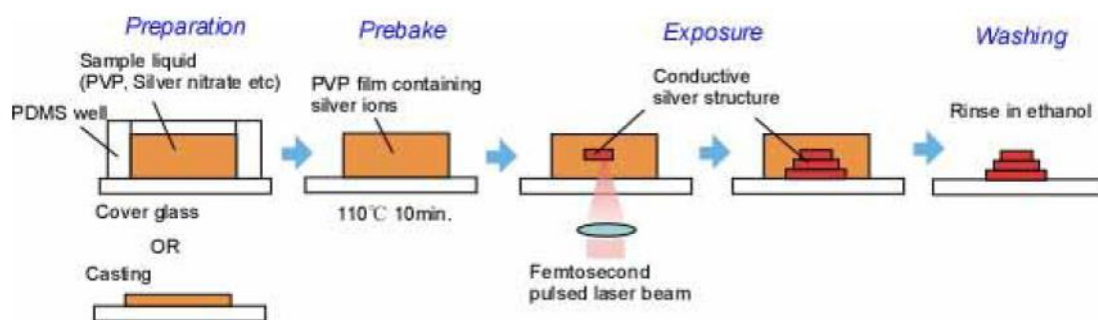


Figure 2.24 Illustration of 3D laser writing of metallic microstructures using Ag/PVP films⁴⁰.

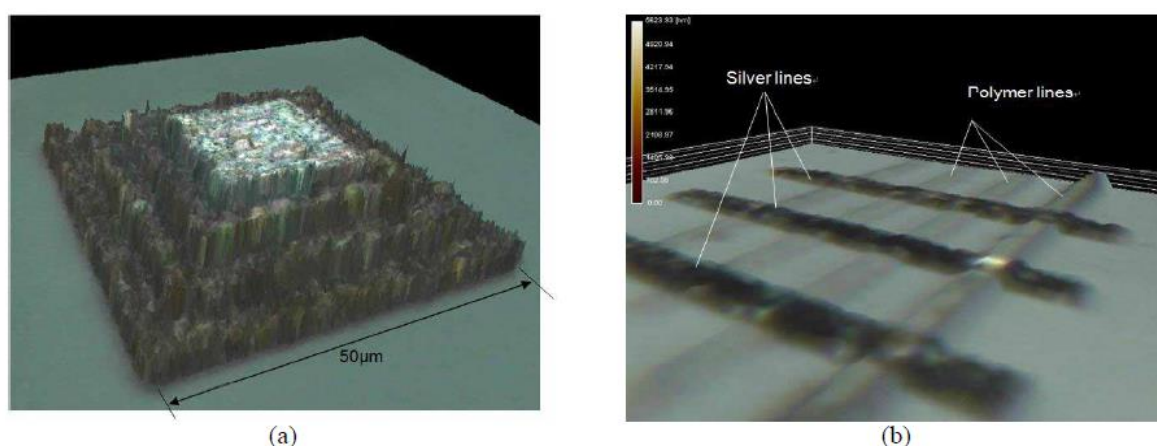


Figure 2.25 Pyramidal microstructure (a) and hybrid microstructure consisting of silver and polymer lines (b) fabricated using silver ion-doped PVP films by 2-photon reduction⁴⁰.

3D gold structures were also fabricated by a two-photon reduction in a polymer matrix. Gold salt (HAuCl_4) was dispersed in polystyrene sulfonate (PSS) as a polymer host.^{10, 119} After the writing of gold structures, the polymer matrix was washed with isopropanol and ethanol. The metal growth is likely to happen in the metal nucleation centres only when the energy is high enough¹¹⁹. When the laser power is low (10 and 20 mW), the growth does not happen even if the laser beam is focused on the generated

gold particles. But if the laser power is high (40 mW), the gold particles grow rapidly when the laser beam interacts with nucleation centres leading to a larger feature size (about five times wider than 10 and 20 mW, the authors did not measure line widths). It indicates that the quality and size of metallic structures are closely associated with the processing condition such as laser power and scanning speed. However, the fabricated 3D woodpile structure in their work was only observed during writing processes but disaggregated after removing the unreacted matrix by the washing process. Direct deposition of metals by TPL is a simple process, but it is challenging to control metal particles, to form a smooth surface on structures and to fabricate structures with complex shape.

2.4.2 Metallic Coating onto 2D or 3D Polymer Surface

The second method is combining two-photon fabrication and metallic coating to fabricate metallic nanostructures. 2D and 3D metallic nanostructures were fabricated through TPP followed by selective electroless plating (EP)^{41, 43, 129-139}. A thin silver, gold or copper film was deposited on the surface of the polymer structures fabricated by TPP. Using silver EP as an example¹³³, the glass slide was treated to be hydrophobic to avoid metal depositions. The styrene-modified SCR500 polymeric structures were fabricated by TPP and surface-modified using SnCl₂ to increase silver nucleation and adhesion. Finally, silver was coated on the surface of the polymeric structures by EP method. **Figure 2.26** illustrates the process details. The conductivity of the coated structure was only five times lower than bulk silver¹³³. **Figure 2.27** (a) shows a self-standing microspring array that coated with silver. **Figure 2.27** (b) and (c) show an uncoated polymer microspring and silver-coated microspring by EP.

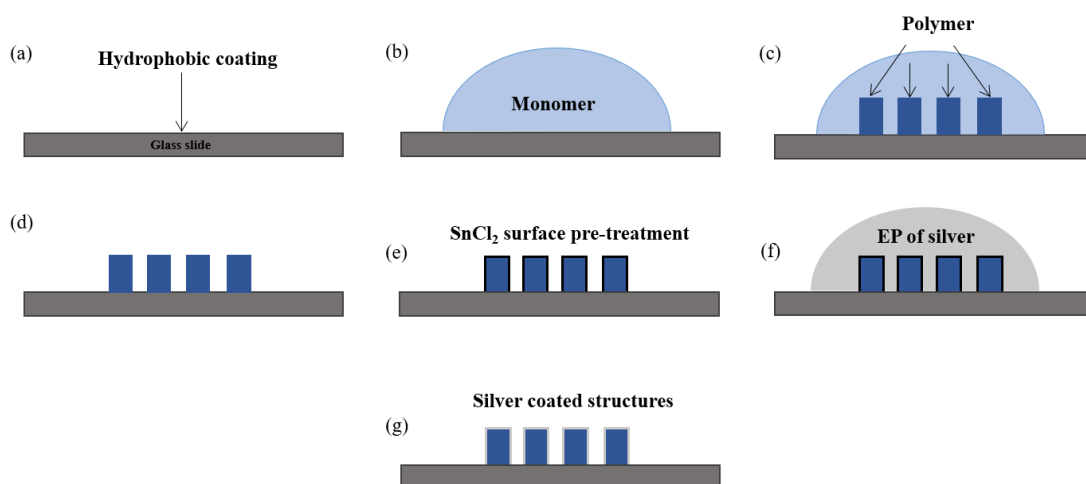


Figure 2.26 Selective EP to fabricated metallic structures (a) Hydrophobic coating of glass slide that silver can be selectively reduced onto the polymeric microstructures (b) Monomer resin is dropped onto the glass slide (c) TPP (d) Removal of unpolymerised resin (e) SnCl_2 surface pre-treatment to improve metal deposition (f) EP of silver (g) Washing of the sample¹³³.

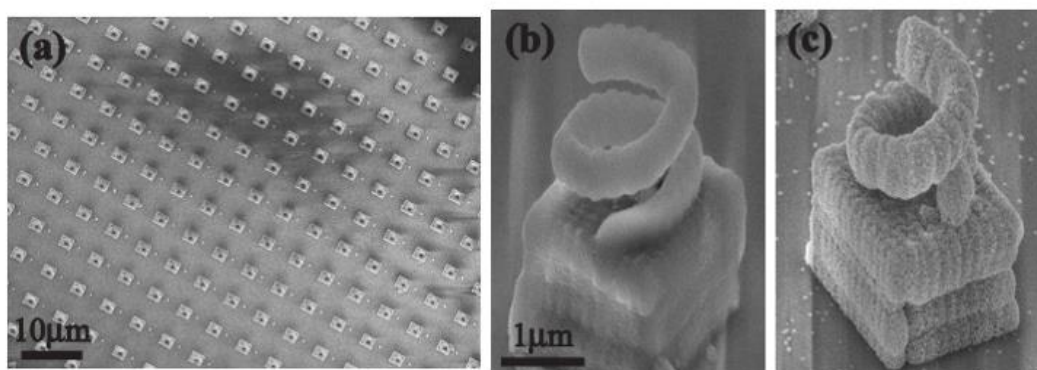


Figure 2.27 (a) $78 \times 58 \mu\text{m}^2$ 3D microspring array that coated with Ag by EP (b) An uncoated microspring consisting a cube ($2\mu\text{m}$ size) and a spring (height $2.2\mu\text{m}$, inner diameter $1\mu\text{m}$) (c) A silver coated microspring by electroless plating¹³⁰.

Antonello et al.¹³⁹ reported an improved method for the electroless silver deposition by adding Arabuc Gum, a complexing agent for silver. They deposited a thin and smooth silver layer onto the surface of 2D diffraction and sinusoidal plasmonic gratings which have potential applications in optics and plasmonics. Gold^{131, 138}, copper¹³⁴ and nickel¹³⁶ have also been used as a metallic coating on polymers by EP method. Chemical vapour deposition (CVD) is another method to deposit a metal layer onto a TPP polymer structure which allowed high-temperature processing^{42, 140}. Recently, some new approaches using different chemical methods such as photothermal-reaction-assisted TPL¹²¹ and two-photon induced photocleavage of organic monolayers¹⁴¹ have also been reported.

2.4.3 Inversion Method

Most TPP uses negative photoresist, which is soluble to the organic developer solvent before polymerisation and polymerises upon light exposure becoming insoluble to developer solvent. Positive photoresist works in the opposite way: it changes chemically and/or structurally upon light exposure and becomes more soluble to an organic developer after polymerisation. An inversion method using a positive photoresist to fabricate metal nanostructures was reported by Gansel et al.¹⁴² The process is illustrated in **Figure 2.28**. A positive photoresist (10 μm thick) was spun onto a 25-nm thin film of conductive indium-tin-oxide (ITO), which was evaporated as the cathode onto a glass substrate. After two-photon fabrication and solvent development, an array of air helices in a block of polymers was left. Gold was then plated in an electrolyte and polymer was removed by plasma etching. Finally, a square array of free-standing 3D gold helices was obtained. However, this method is time-consuming in sample preparation and sample development.

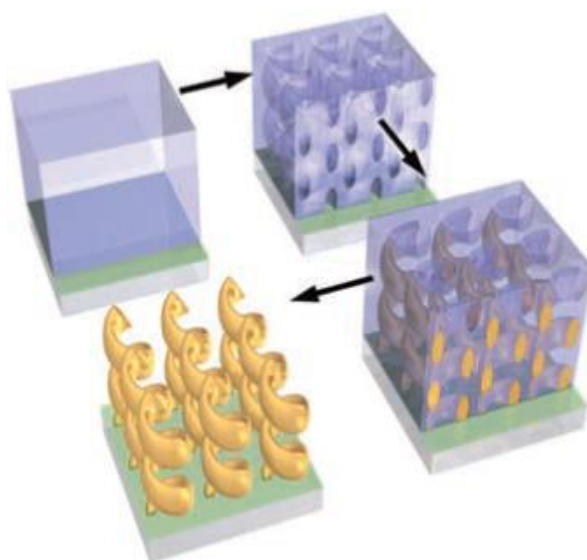


Figure 2.28 Illustration of inversion method to fabricate gold helices structures¹⁴².

2.4.4 Simultaneous Photopolymerisation and Photoreduction

A new method using simultaneous photopolymerisation and photoreduction to fabricate metallic nanostructures has been reported^{12, 31, 114}. Direct photoreduction of metal ions leads to high surface roughness and low-quality metal structure that has granular metal particles¹¹⁰. Direct photoreduction from matrix produces discontinuous aggregated nanoparticles¹¹. Deposition of a thin metal layer on a TPP polymer structure requires multi steps¹¹⁰. A surface treatment is always required¹¹⁰. A homogeneous coating is difficult to achieve, especially in the case of complex 3D structures¹¹⁰. The inversion method is complex in-process and difficult to control. Shukla et al.^{12, 31} fabricated gold-SU-8 nanocomposites by two-photon simultaneously induced gold salt reduction and polymerisation. 10 wt% gold salt was added in their formulation. A higher metal loading, 40 wt% was also achievable by this method. The gold-doped polymer lines were as narrow as 200 nm. Gold NPs around or even less than 50 nm were embedded within the polymeric structures. **Figure 2.29** shows the

process details. SU-8 including a photoacid generator, PC2506, and a two-photon dye, AF380 together with a gold precursor, $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, were spin-coated on a glass slide. Upon laser exposure, the two-photon sensitive dye absorbed energy and transferred energy to the photoacid generator. Cationic polymerisation was initiated when the laser intensity was high enough to generate a strong acid. Meanwhile, the presence of photoinitiators PC2506 helped gold ion reduction. The free radicals from photoinitiators and byproducts reduced gold ions. **Figure 2.30** illustrates the proposed mechanism of this process.

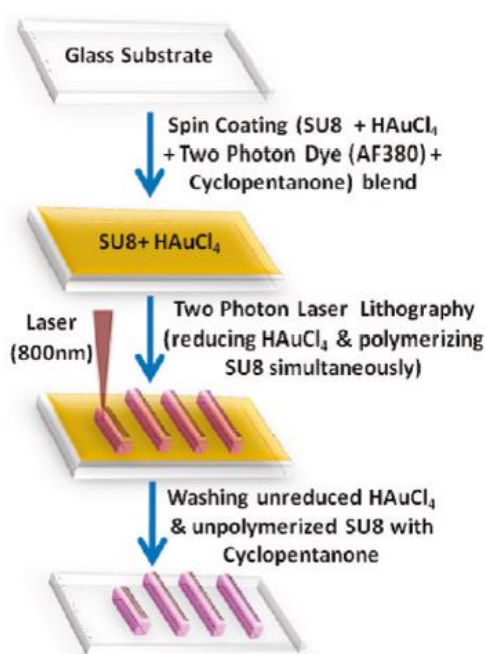


Figure 2.29 Simultaneous photo-polymerisation of SU-8 and photoreduction of gold salt¹².

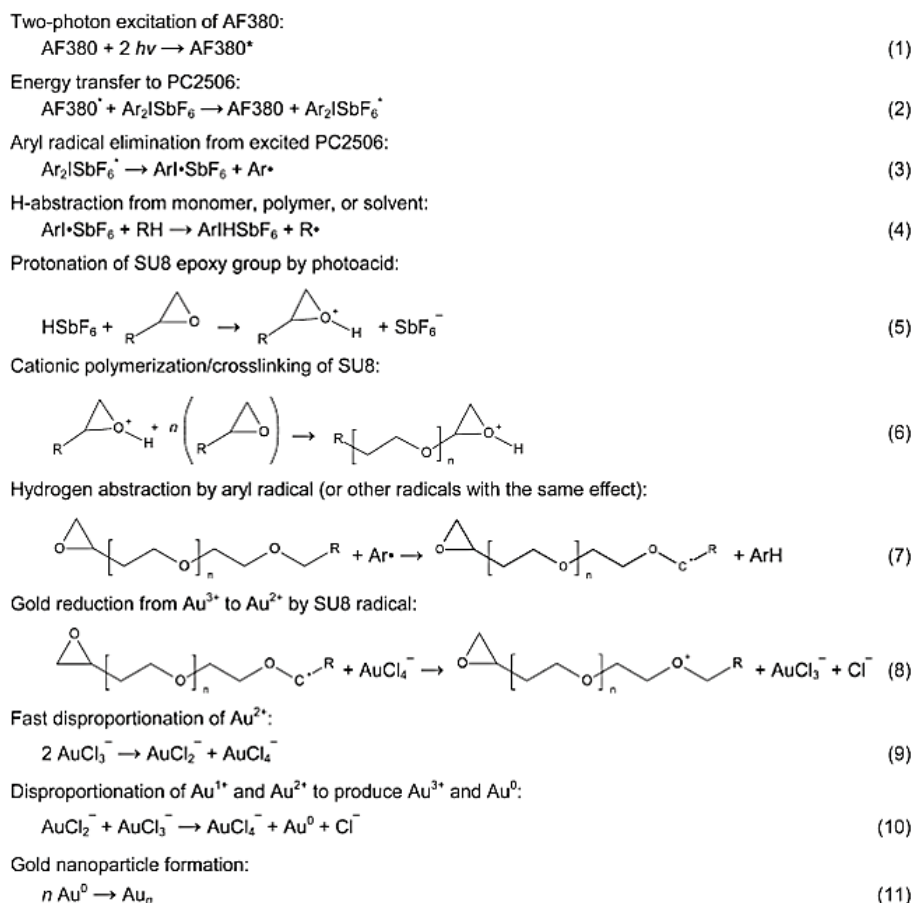


Figure 2.30 Proposed mechanism of simultaneous photo-polymerisation of SU-8 and photoreduction of gold salt¹².

There was a competition between gold reduction and photoinitiation because both these processes consume free radicals. Therefore, a large amount of photoacid generator was needed to achieve simultaneous photoreduction and photopolymerisation. **Figure 2.31** (a) shows the SEM image of polymer/gold lines fabricated at 50mW and a backscattered electron (BSE) image in the lower right inset shows the presence of gold NPs within the polymers. Some bridging lines were between two lines when they were close (**Figure 2.31** (a) top left inset). **Figure 2.31** (b) shows the polymer/gold line that was fabricated at lower power, 20mW. At low

laser power, the gold particles were in the centre of the line, where the intensity of the laser was the highest. Energy-dispersive X-ray spectroscopy (EDS) in **Figure 2.31** (c) shows the presence of gold in the structure. No chlorine was detected by EDS, which indicated the full reduction of gold ions. 2D structures, including grating structures and planar chiral nanostructures, were produced by simultaneous photoreduction and photopolymerisation. This novel method has the potential for the fabrication of real 3D metamaterials with low-cost and high-throughput in a single step. However, no 3D structures were fabricated by using SU-8 and gold salt^{12, 31, 114}.

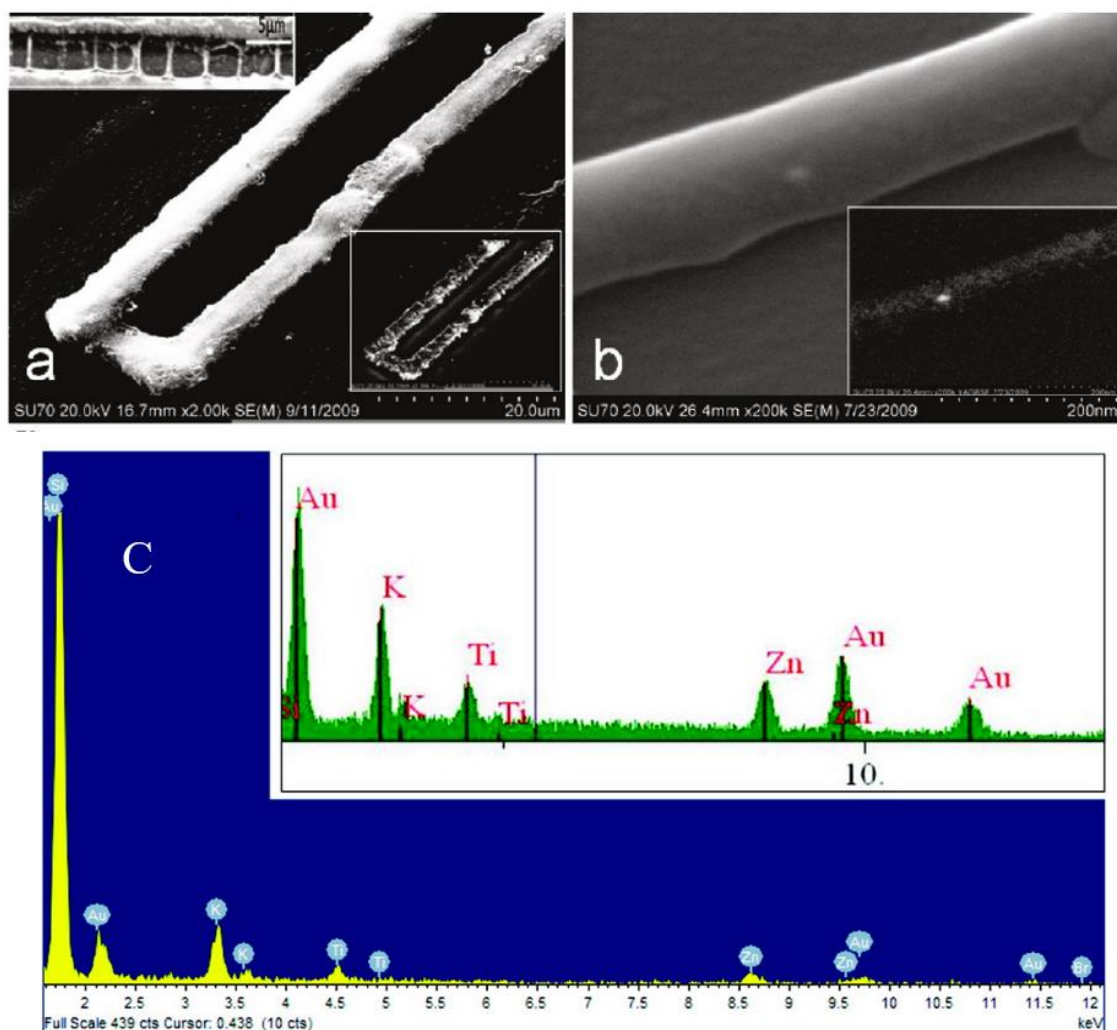


Figure 2.31 (a) SEM image of the polymer/gold lines fabricated at 50mW (top left inset: bridging when the distance of two lines was 4 μm; bottom right inset: BSE image shows gold NPs) (b) SEM image of the polymer/gold line fabricated at 20mW (inset: BSE image shows gold NPs) (c) EDS spectra of the polymer/gold structures¹².

The method was further developed by Blasco et al.¹³ who employed acrylate-functionalized poly(ethylene glycol) derivative (PEG-triacry) as an oligomer, Irgacure 2959 as a photoinitiator and gold chloride as a metal source. **Figure 2.32** (a) illustrates the polymerisation of oligomers and photoreduction of gold salt. After fabrication, the

gold particles were wrapped by polymer chains. The bridge-like structure was fabricated via simultaneous photopolymerisation and photon reduction of gold. (**Figure 2.32 (b)**)

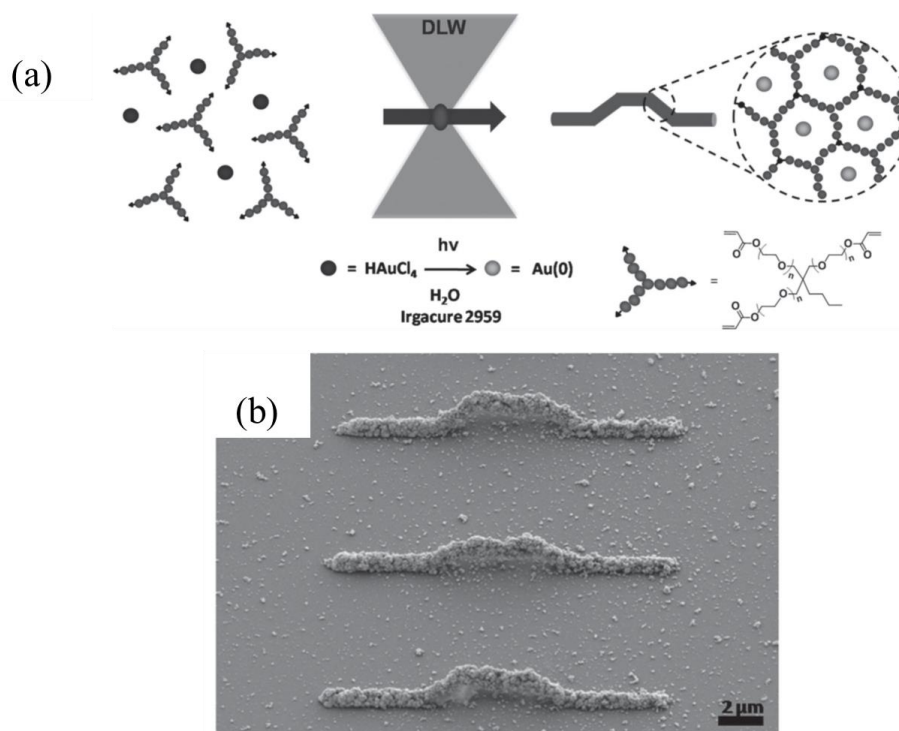


Figure 2.32 (a) Schematic illustration of the simultaneous photo-polymerisation of oligomers and photoreduction of gold salt; **(b)** SEM image of the fabricated bridge-like gold-polymer structures¹³.

According to the literature^{12, 31, 114}, simultaneous photopolymerisation and photoreduction shows excellent potential for the fabrication of complex 3D metallic structures with high resolution. Unlike direct deposition of metals, this technique is easier to control metallic particles by using polymers as a dispersing agent. Compared to metallic coating or the inversion method, simultaneous polymerisation and photoreduction is simpler and forms a structure in a single step.

2.5 Applications of Metallic Nanostructures via Two-photon Fabrication

By taking advantage of the subwavelength resolution of two-photon fabrication, metallic micro/nanostructures fabricated by two-photon fabrication have a great potential to be used in many applications including microelectronics, optical devices, catalysis, microfluidics chips, microsensors etc.^{12, 41, 107-109, 111}.

2.5.1 Microelectronics

Conductive nano/microstructures, of which conductivity is close to the respective bulk materials, are desired in microelectronics^{46, 110}. Tanka et al.¹¹² fabricated silver lines using TPA (two-photon absorption)-induced photoreduction of silver ions. Silver ions were reduced in a single step via TPA process and the average resistivity of the silver lines was $5.30 \times 10^{-8} \Omega\text{m}$, which is 3.3 times higher than that of bulk silver ($1.59 \times 10^{-8} \Omega\text{m}$). Later, the surface smoothness of silver and gold lines was improved using surfactants and the metal particle sizes were reduced to tens of nanometers.^{39, 107, 120} The conductivity of fabricated gold lines ($16.5 \times 10^{-8} \Omega\text{m}$) was the same order as that of bulk gold³⁹. However, rough surface and even discontinuous structures make it challenging to produce complex structures that restrict the applications of direct photoreduction of metal ions. Photoreduction of metal ions in a polymer matrix makes it possible to make complex metallic structures. However, it is difficult to obtain continuous metal structures and metal particles cannot maintain the structure after removing polymer matrix³⁹. In order to fabricate continuous metallic structures, Maruo et al.⁴⁰ improved the concentration of silver nitrate in PVP

(polyvinylpyrrolidone) polymer films from 3.8 wt% to 7.3 wt%. A silver line with a resistivity of $3.48 \times 10^{-7} \Omega\text{m}$ was measured, which was about 22 times higher than that of bulk silver. However, it is challenging to maintain metallic structures after removing the polymer matrix. Metal coating on polymeric structures fabricated via TPP has been reported a useful approach to fabricate 3D metal structures¹¹⁰. Formanek et al.¹³³ used SnCl_2 as an adhesion agent to promote the silver deposition on two-photon polymerised structures. The resistivity of $8.2 \times 10^{-8} \Omega\text{m}$ was measured, which was five times larger than that of bulk silver. A 16-turn copper-coated inductor (200 μm in length and 24 μm in diameter) was fabricated by Farrer et al.¹³¹ by using the selective electroless copper plating method (**Figure 2.33**). However, the measured resonance frequency was six decades lower than their expectation. Metallisation by metallic coating can produce 3D structures, but a surface modification is always necessary¹¹⁰. The effect of metallisation relies on the surface-functionalisation process of polymer structures fabricated through TPP (two-photon polymerisation). In addition, the density and distribution of the functionalised sites on polymers are difficult to control, especially for complex 3D structures. Therefore, uniform metal deposition is challenging. The simultaneous polymerisation and photoreduction in a single step provides another route to fabricate metallic structures. Blasco et al.¹³ used Irgacure 2959 as a photoinitiator to form radicals that polymerised acrylate functionalised oligomers and reduced gold precursor (HAuCl_4) at the same time. The fabricated gold lines were annealed at 200°C for 10 min and the conductivity of the annealed gold lines was $2.2 \times 10^6 \text{ S/m}$, which is about 20 times lower than that of bulk gold ($4.1 \times 10^7 \text{ S/m}$). High resistance (in the order of $\text{M}\Omega$) of the gold lines before annealing is because of isolated gold particles in nonconductive polymers. Oligomers acted as a binder to bind gold particles and the chains of oligomers

separated particles. Using single monomers to replace oligomers is promising to generate more uniformly distributed metal particles and improve conductivity. Moreover, the strategy of simultaneous polymerisation and photoreduction is promising to fabricate complex 2D and 3D structures. Therefore, it is a potential approach and a good candidate to fabricate microelectronic devices.

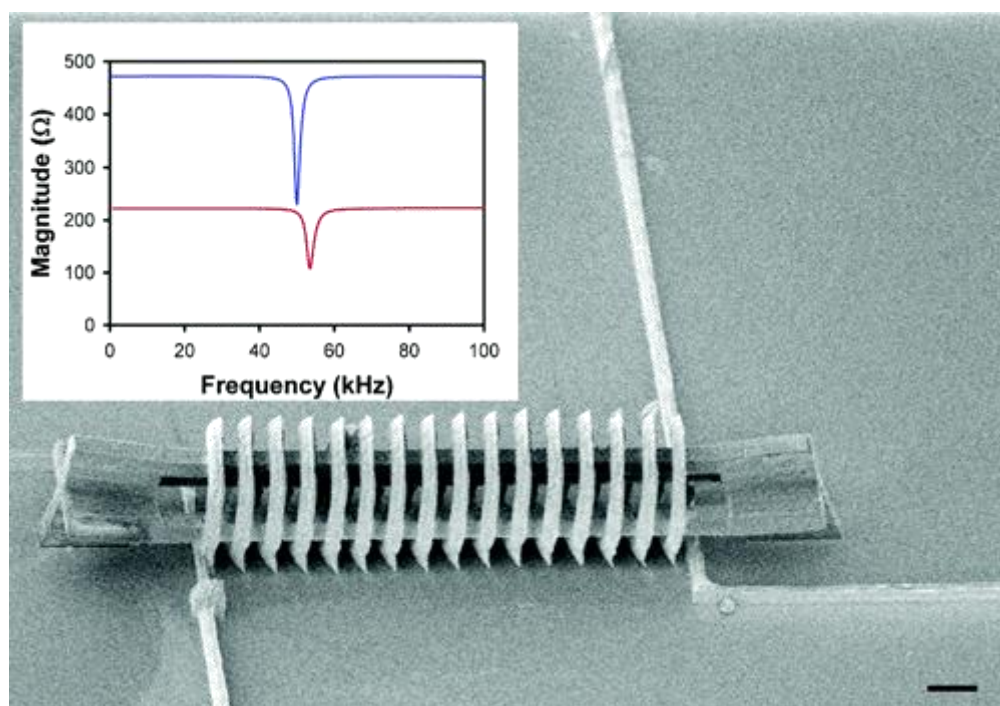


Figure 2.33 SEM image of a copper-coated inductor through two-photon polymerisation (TPP) and electroless copper plating¹³¹.

2.5.2 Metamaterials

Two-photon lithography (TPL) is also a promising technique in fabricating designed optical metallic nano/microstructures such as metamaterials¹¹⁰. Metamaterials are artificially produced periodic structures with precise shape, geometry, size, orientation and arrangement^{98, 131}. The size and spacing are much smaller than the wavelength of interests^{110, 143}. By using different metamaterial designs, some

properties different from their intrinsic material properties can be obtained, for example, manipulating electromagnetic radiation by blocking, absorbing, enhancing or bending waves¹¹⁰.

Metals such as gold, silver and copper have been important materials throughout history¹⁴⁴⁻¹⁴⁵. Apart from reflecting light, their applications have been explored in electronics, catalysis and structural materials and when these metals are fashioned into structures with nanosize ranges, some interesting interactions between metals and light are performed known as plasmonics^{144, 146}. In plasmonics, metal nanostructures convert light into localised electric fields or guide light to desired locations in nanometer-length scale^{144, 146}. At a specific frequency, the oscillation of electrons is in resonance with the incident light, which is so-called localised surface plasmon resonance (LSPR)^{144, 147}. By artificially building metallic nanostructures, plasmonic metamaterials can perform attractive optical phenomena such as guiding and controlling light¹⁴⁴.

Because of the ability to produce high-resolution structures without a mask, TPL becomes a promising candidate for fabricating metallic features for plasmonic metamaterial design. Ishikawa et al.^{113, 148} demonstrated plasmonic metamaterials consisting of 2D silver rod pair array operating at far-infrared frequencies (18 THz) fabricated by direct deposition of silver ions through TPA (two-photon absorption). **Figure 2.34** (a) shows SEM images of the fabricated silver rod pair array. **Figure 2.34**(b) illustrates the process that when incident polarized light goes through the array at the incident angle of θ , the magnetic field perpendicular to the x-y plane is proportional to $\sin \theta$. Strong magnetic excitation of the magnetic resonances was

observed by increasing the incident angle θ . **Figure 2.34** (c) shows the relationships between the incident angle and the transmittance at 18 Hz for both rod pair array and single rod array. The transmission spectra measured at $\theta = 45^\circ$ is also shown in the inset. The transmission shows different at 18 Hz. When operating at 18Hz, the transmittance of the single rod array remained constant at around 65% indicating that the single rod array does not have any interaction with the magnetic field while the rod pair array decreased from 70% to 20% with the increasing incident angle indicating the increase of the magnetic field that interacts with the rod pair array. Silver C-shape arrays (**Figure 2.20** (d)) were also made by Tabrizi et al.⁴⁵ by silver ion reduction. The array structure was responsive to external light polarization and tunable in a broad dynamic range by changing processing parameters⁴⁵. 2D gold U-shape resonance rings on a glass substrate (**Figure 2.23** (a)) was fabricated by Lu et al.³⁹ through direct reduction of gold ions in aqueous solution and an electric resonance around 65 THz for a polarization wave was observed (**Figure 2.23** (b)) suggesting TPL could provide high potential for metamaterial devices.

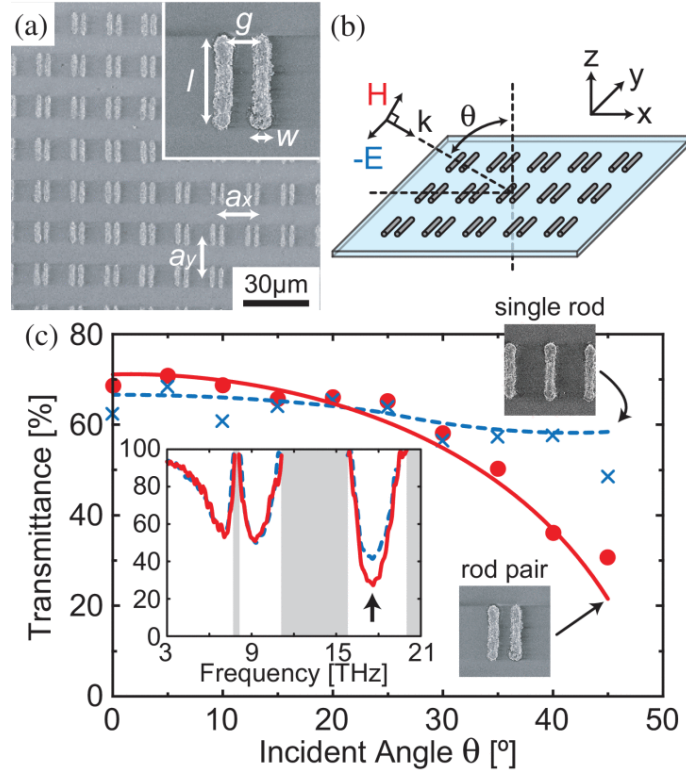


Figure 2.34 (a) SEM image of a silver rod array fabricated by TPL. $a_x = a_y = 15\mu\text{m}$, $l = 10\mu\text{m}$, $w = 1.5\mu\text{m}$ and $g = 4\mu\text{m}$. (b) Optical setup for measuring the magnetic resonance of the rod pair array by changing the incident angle θ of polarized light. (c) The relationship between the measured transmittance of the rod pair array and the single rod array and different incident angle θ . The inset is the transimmission spectra measured at $\theta = 45^\circ$.

Apart from 2D structures, by combining TPP (two-photon polymerisation) of polymers and silver chemical vapour deposition, a 3D metallic metamaterial operating at near-infrared frequencies was reported by Ma et al..¹¹⁰ **Figure 2.35** shows the cross-section image of the fabricated structure and the thickness of deposited silver was about 5 nm. The optical characterization was in good agreement with theory and anticipated magnetic resonance in a selected frequency range was observed

demonstrating the successful fabrication of a magnetic metamaterial. A 3D standing U-shaped array structure was proposed by Wang et al.¹⁴⁹ and it was built by TPP followed by sputtering coating gold. By tuning the polarization of incident light, the structure could act as a mirror that reflects light completely or a light absorber that neither transmits nor reflects light. The standing U-shaped structure allowed easier dissipation of generated heat because resonance occurs in the free space between the standing tines. This type of structure can be used as a detector for the polarization of light.

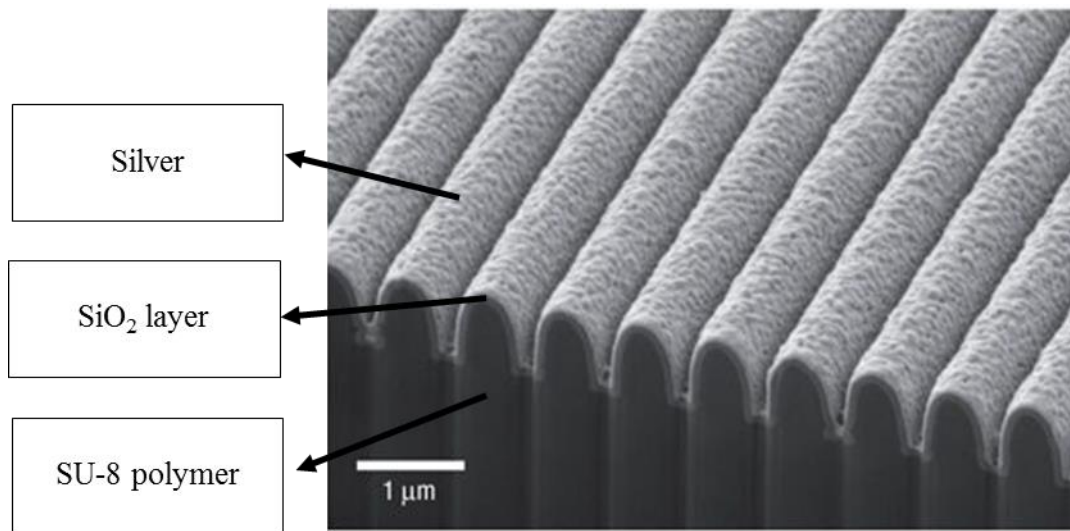


Figure 2.35 The cross-section (cut by a focused-ion beam) image of a 3D metamaterial fabricated by combining TPP and silver chemical vapour deposition¹⁴⁹.

Chiral structures are objects that display no mirror symmetry plane⁴³. Chiral structures can produce intriguing optical properties, for example, circular dichroism, which is the differential absorption of left- and right-hand circular polarized light or optical rotation, which is the rotation of linearly polarized light as it passes through a chiral materials¹⁴³. Many chirality phenomena are existing in native species such as the vivid

colours of butterfly wings are produced by gyroid nanostructures^{143, 150}. However, the optical activities of natural materials usually are weak. Chiral metamaterials are a subset of metamaterials and have attracted attention because they can offer stronger optical activity, which brings a variety of applications such as broadband circular polarization devices¹⁴² and asymmetric transmission for detection of chiral molecules¹⁵¹⁻¹⁵³. By designing 3D metallic structures (e.g., dimensions, angels and number of helices etc.) combined with theory and electromagnetic simulation, TPL provides an open route to produce chiral metamaterial structures due to its precise process and high resolution. Some 3D helix array^{142, 154} (**Figure 2.36** (a) and (c)) or “twisted omega particle”⁴³ (**Figure 2.36** (b)) metallic nanostructures were fabricated by TPL and tested as chiral metamaterials, which showed different optical performance between left- and right-handed circularly polarized light. Metallic coating onto polymeric structures from TPL or the inversion method has been used in the literature^{43, 142, 154}. Compared to these methods, simultaneous photopolymerisation and photoreduction is a simpler and more straightforward way and holds great promise for the development of novel 3D metamaterials.

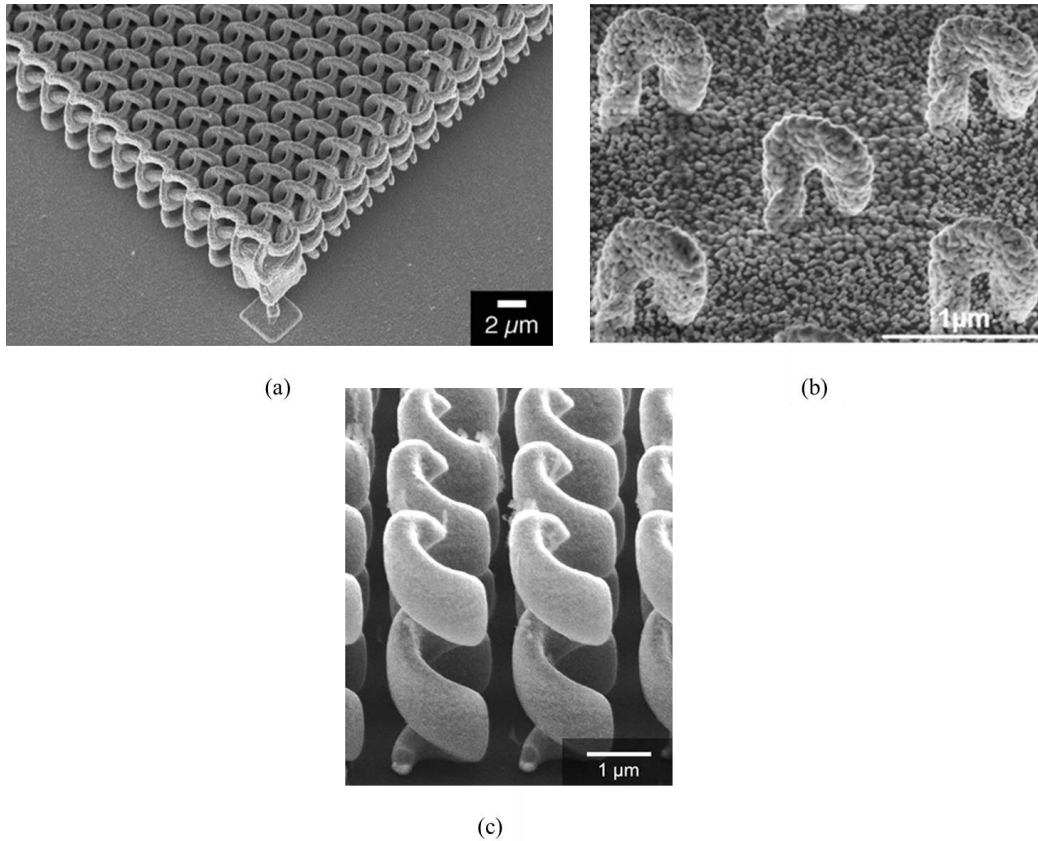


Figure 2.36 3D chiral metamaterials fabricated by TPL. (a) Chiral crystals fabricated by TPL followed by electroless silver plating¹⁵⁴; (b) Chiral “twisted omega particles” fabricated by TPL followed by electroless silver plating⁴³; (c) Chiral helix array structure fabricated by the inversion method introduced in Section 2.4.3¹⁴².

2.5.3 Other applications

Metallic nano/microstructures are also developed and used in SERS (surface-enhanced Raman scattering) devices and microfluidic chips^{15-17, 36, 155}. Raman scattering is a technique which can provide fingerprint information on various molecules by detecting the vibration of each functional group of a molecular¹⁴⁻¹⁵. However, Raman scattering suffers from a very low sensitivity¹⁴⁻¹⁵. The sensitivity

can be enhanced by the SERS technique, which relies on the LSPR (localised surface plasmon resonance) generated from noble metal nanostructures such as silver and gold¹⁴⁻¹⁵. Therefore, TPL fabricated metal nanostructures are a candidate for SERS applications. By employing direct deposition metal through TPR (two-photon reduction), silver¹⁵⁻¹⁷ and gold^{36, 155} nanostructures were fabricated and used as SERS substrates for enhancing Raman scattering. Research also found that 3D gold nanostructure showed higher sensitivity of SERS spectra than 2D³⁶. Nevertheless, 3D metal structures fabricated through direct deposition of metal ions are challenging.

When metallic structures are fabricated in microfluidic chips, they can be used in real-time detection of on-chip chemical reactions. It is achievable in TPL because structures can be written on a no flat surface but it is challenging for traditional technologies such as lithography or imprinting¹¹⁰. Xu et al.¹⁵ fabricated silver SERS substrates by direct deposition of silver ions in microfluidic channels at different positions and monitored chemical reactions by Raman spectra. Therefore, metallic composites made through simultaneous photopolymerisation and photoreduction may provide more possibilities in SERS and sensors applications.

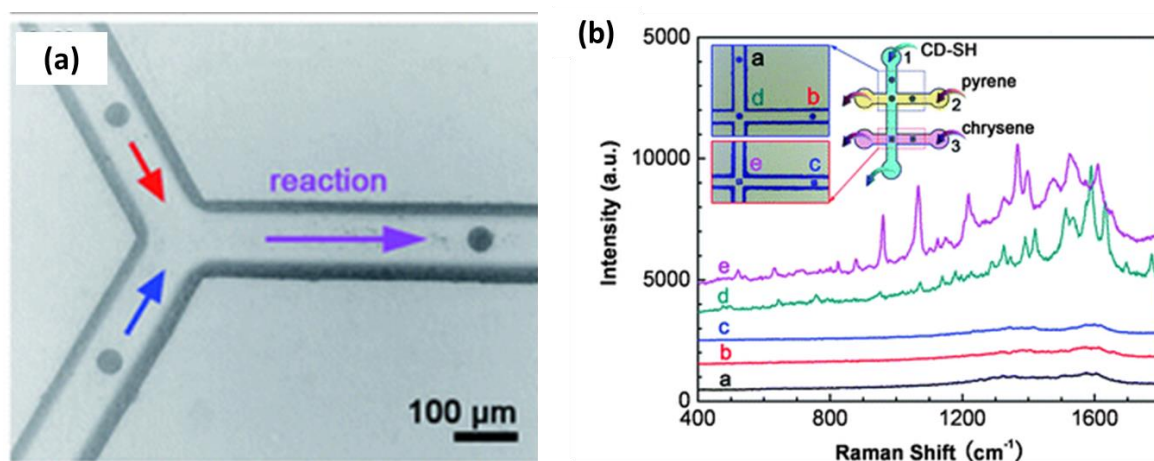


Figure 2.37 (a) Silver SERS substrates fabricated by TPR at different positions of a microchannel; (b) Raman spectra measured on silver SERS substrates at different positions to monitor chemical reactions¹⁵.

2.6 Summary

TPL is an AM technique that can directly produce 3D structures without a mask, mould or stamp with subwavelength resolution⁵⁴. Polymeric two-photon fabrication has been studied in recent years and there are many kinds of monomers and photoinitiators available. Metallic nano/microstructures fabricated by TPL is still new in this area. Selecting and optimising processing methods and materials have not been fully accomplished yet. Therefore, an in-depth investigation is necessary.

Metallic structures fabricated by TPL have been mostly reported by direct deposition of metal ions from solution. Metallic dots, lines and some simple 2D structures can be directly written by photoreduction. However, many applications such as microelectronic^{131, 156} like 3D inductors and microwires, metamaterials^{43, 142, 149, 154} like photonic crystals and chiral structures, and some SERS substrates³⁶, require 3D structures. The rough surface and even discontinuous structures generated through

this method make it challenging to produce complex structures. Direct deposition of metal ions in a polymer matrix is possible to fabricate complex metallic structures but the structures are difficult to be maintained after removing polymer matrix³⁹. Electroless plating on polymeric structures fabricated by TPP (two-photon polymerisation) is another method that has been mostly reported. But they always need a surface treatment and uniform coating is challenging especially for complex 3D structures¹¹⁰. Multiple steps of inversion method make a process complex and time-consuming. Simultaneous photoreduction and polymerisation open a way to solve all the problems mentioned above. The method has just been reported so a comprehensive studying of the method is worthwhile. The ability to fabricate 3D complex metallic microstructures needs to be assessed.

Gold nanocomposites fabricated through simultaneous photopolymerisation and photoreduction have been reported in 2D, but no 3D structures have been produced yet^{12, 31, 114}. The characterisations of reduced Au NPs (gold nanoparticles) such as particle size and chemical state, which can help understand the mechanism of the process, were not demonstrated in any previous literature. Au NPs are attractive because they have high chemical and physical stability and the optical properties related to LSPR (localised surface plasmon resonance) can be used in metamaterials and SERS materials¹⁴⁻¹⁵. The extinction band of LSPR is absent in both small NPs ($d < 2$ nm) and the bulk material¹⁴⁻¹⁵. Apart from size, shape, solvent, surface ligand and temperature all affect their optical properties¹⁵⁷⁻¹⁵⁸. Therefore, the characterisations of fabricated Au NPs on size and shape were required in this thesis. In photopolymerisation and photoreduction, there is a competition between gold reduction and photoinitiation because they all consume free radicals. The suitable

amount of photoinitiator was essential to be tested and decided. Using ruthenium (II) photosensitive dye was found very useful to reduce gold ions so it was also added in formulations¹⁰.

Apart from gold, silver and copper nanoparticles and their nanocomposites are promising candidates in the field of metamaterials due to their LSPR behaviour¹⁹. Ag NPs (silver nanoparticles) have also been used in SERS application¹⁵⁻¹⁷. Cu NPs (Copper nanoparticles) have received much attention due to their high electrical conductivity and low cost¹⁸. Silver and copper nanocomposites have never been fabricated through simultaneous photopolymerisation and photoreduction before and their printabilities were assessed in this thesis. Silver nitrate is highly soluble in water but is poorly soluble in most organic solvents¹⁵⁹. Therefore, a suitable selection of monomers, photoinitiators, solvents and photosensitive dyes was a crucial step for the fabrication of silver-polymer objects. Coumarin dye was reported as a photosensitive dye helpful to improve the reduction properties of silver ions in aqueous solution⁹ so it was added in the formulations for silver nanocomposites.

In conclusion, 2D and 3D gold-, silver- and copper-polymer nanocomposites fabricated through simultaneous photopolymerisation and photoreduction remains worthwhile and useful for studying, developing and evaluating applications.

3 Methodology and Experimental Setup

3.1 General Research Approach

In order to fabricate metal-polymer nanostructures by simultaneous TPP and TPR, suitable formulations need to be obtained. A suitable polymer resin for TPP was determined first. The polymer resin consists of monomers and photoinitiators. Photosensitive dye and solvent may also be needed. Then metal salts (gold, silver and copper salts), monomers, photoinitiators, photosensitive dyes should be well dissolved in a solvent. Bubbles or agglomerated particles should be avoided in case of local heating and structure failure. Appropriate selection and percentage of materials are important to printability, processing parameters and final properties. The final structures fabricated using different formulations and processing parameters were characterised to better understand the processing mechanisms and structural properties. The general research approach is summarised in **Figure 3.1**.

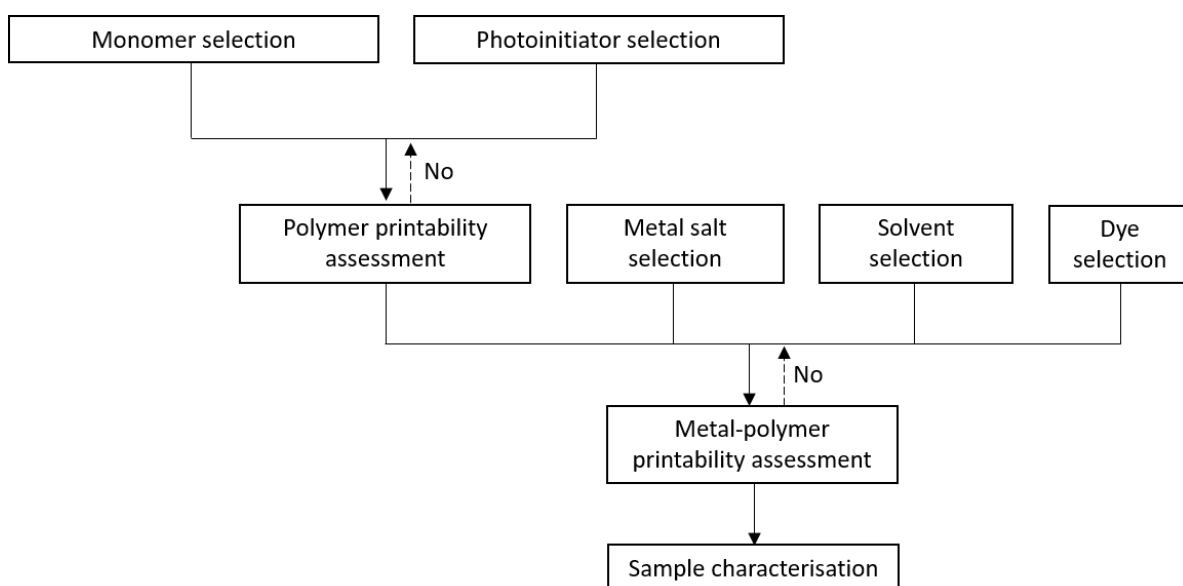


Figure 3.1 Flow chart illustrates the research approach.

3.2 Materials Selection

3.2.1 Materials for Gold-polymer Nanocomposite

Photoresist IPL-780 (Nanoscribe GmbH Photonic Professional GT, Germany) is a commercial resin suitable for the TPL system used in the thesis, Nanoscribe (Nanoscribe GmbH Photonic Professional GT, Germany). According to its MSDS (material safety data sheet), the main composition of IPL-780 is pentaerythritol triacrylate (PETA(> 95%) as a monomer and 7-(Diethylamino)-3-(2-thienylcarbonyl)-2H-1-benzopyran-2-one (DETC) (< 5%) as a photoinitiator. It was chosen as a polymer resin¹⁶⁰. Apart from IPL-780, two more monomers are candidates if TPL-780 is not suitable for making metal-polymer nanocomposites. According to the literature^{44, 55}, the majority of TPP developed to date has employed radical polymerisation because of its high reaction rates, ease of processing and wide availability of photoinitiators and monomers. In this thesis, tri-acrylate based monomers, PETA (pentaerythritol triacrylate)) (Sigma-Aldrich, UK) and TMPTA (trimethylolpropane triacrylate) (TMPTA) (Sigma-Aldrich, UK), were selected due to their high polymerisation efficiency. As discussed in section 2.3.3, Irgacure 369 (2-benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone) (Sigma-Aldrich, UK) was chosen as a photoinitiator because its absorption peak covers $\frac{1}{2} \lambda$ of the laser beam, which means Irgacure 369 can be excited to initiate polymerisation when a 780 nm laser is applied. Gold chloride is the most common gold salt materials used in two-photon reduction (TPR) according to the literature^{10, 36, 39, 112, 118-119, 125, 127} so it was chosen as a raw material in simultaneous photopolymerisation and photoreduction. Adding Ruthenium (II) was found useful to reduce gold ions¹⁰ so tris(2,2' -bipyridyl)

dichlororuthenium(II) hexahydrate (bipy) (Sigma-Aldrich, UK) was used as a photosensitive dye. The chemical structures are shown in **Figure 3.2**. Ethanol was employed as a solvent for both the ruthenium (II) and gold (III) chloride hydrate. All materials choices are summarised in **Table 3.1**.

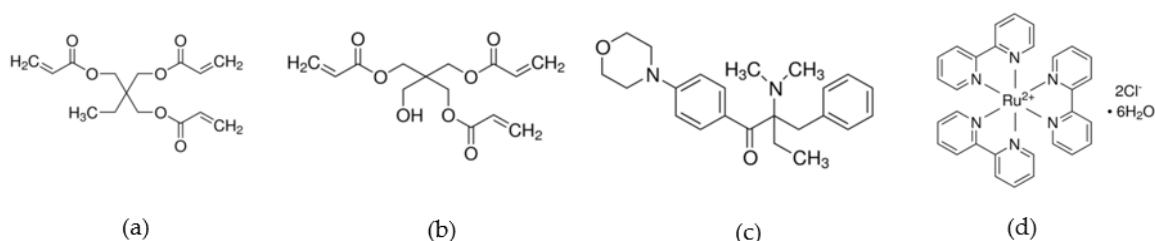


Figure 3.2 Chemical structures of (a) trimethylolpropane triacrylate (TMPTA) (b) pentaerythritol triacrylate (PETA) (c) 2-benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone (Irgacure 369) and (d) Ruthenium (II) complex.

Table 3.1 Material choices for gold-polymer nanocomposite

	Polymer resin		Metal salt	Dye	Solvent
	Monomer	Photoinitiator			
Choice 1	IPL-780		gold (III) chloride hydrate	Ruthenium (II)	Ethanol
Choice 2	PETA	Irgacure 369	gold (III) chloride hydrate	Ruthenium (II)	Ethanol
Choice 3	TMPTA	Irgacure 369	gold (III) chloride hydrate	Ruthenium (II)	Ethanol

3.2.2 Materials for Silver-polymer Nanocomposite

According to literature, the most common silver sources used in TPR is silver nitrate^{9, 34-35, 37-38, 40, 45, 112-113, 115, 120, 122, 124}. Silver nitrate is highly soluble in water but is poorly soluble in most organic solvents¹⁵⁹. Therefore, water-soluble photoinitiators and monomers for two-photon fabrication were considered first. Water-soluble PEGDA (poly (ethylene glycol) diacrylate) (1000 M_w) (Sigma-Aldrich, UK) was first used as an oligomer. Commercial photoinitiator Irgacure 2959 (2-hydroxy-4'-(2-

hydroxyethoxy)-2-methyl-propiophe) (Sigma-Aldrich, UK), P2CK and E2CK synthesised according to the literature⁸⁴ (The University of Nottingham) were chosen as water-soluble photoinitiators.

Another route was to use a phase transfer method to extract silver ions into an organic solvent such as toluene¹⁶¹. PETA and Irgacure 369 can be dissolved in toluene and mixed with silver ions. This phase transfer was achieved by mixing an aqueous solution of silver nitrate with an ethanol solution of dodecylamine (DDA)(Sigma-Aldrich, UK) and then the silver ions were extracted into toluene phase. A silver-DDA complex was formed in the process and the non-polar tail of DDA made the complex dissolvable in non-polar toluene solvent. Research showed that Coumarin 30 (3-(2-N-Methylbenzimidazolyl)-7-N,N-diethylaminocoumarin or Coumarin 515) (Sigma-Aldrich, UK) promote the silver reduction in aqueous solution⁹ so it was added in the formulations for fabricating silver-polymer nanocomposites.

The chemical structures of PEGDA, Irgacure 2959, P2CK, E2CK, Coumarin 30 and DDA are shown in **Figure 3.3**. All materials choices are summarised in **Table 3.2**.

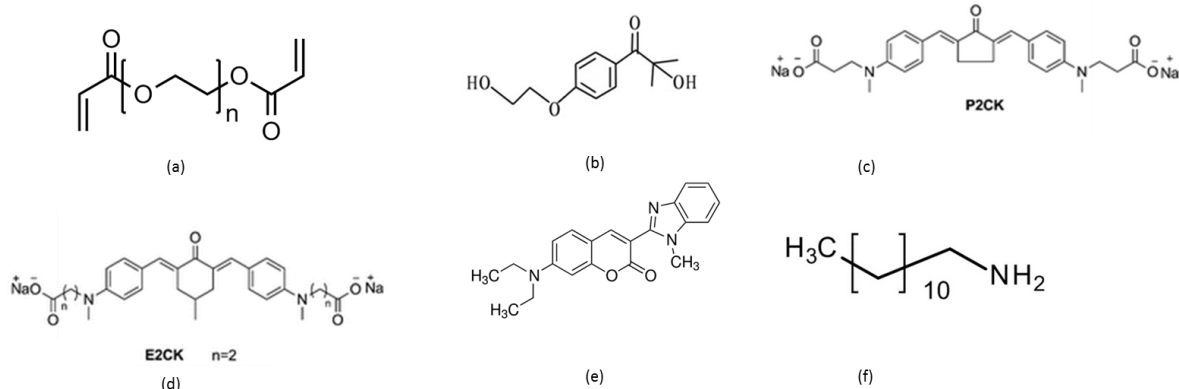


Figure 3.3 Chemical structures of (a) PEGDA (b) Irgacure 2959 (c) P2CK (d) E2CK (e) Coumarin 30 and (f) DDA.

Table 3.2 Material choices for silver-polymer nanocomposite

	Polymer resin		Metal salt	Dye	Solvent
	Monomer	Photoinitiator			
Choice 1	PEGDA	Irgacure2959	Silver nitrate	Coumarin 30	water
Choice 2	PEGDA	P2CK	Silver nitrate	Coumarin 30	water
Choice 3	PEGDA	E2CK	Silver nitrate	Coumarin 30	water
Choice 4	PETA	Irgacure 369	Silver nitrate + DDA	Coumarin 30	toluene

3.2.3 Materials for Copper-polymer Nanocomposite

Photoreduction of copper ions has not been reported yet by two-photon lithography. Literature has shown that copper ions with a photoinitiator were photoreduced to copper NPs by UV irradiation¹⁶². Therefore, using an ethanol solution of CuCl₂ (Sigma-Aldrich, UK) as a copper source, Irgacure 369 as a photoinitiator and PETA a monomer was assessed. Another route was to use a phase transfer method to extract copper ions into an organic solvent toluene¹⁶¹. According to the literature¹⁶¹, copper (II) sulfate pentahydrate (Sigma-Aldrich, UK) was used as the metal salts and toluene was chosen as a solvent for extracted copper ions, which was a similar approach to

the silver work. PETA, Irgacure 369 and Coumarin 30 were used for fabricating copper-polymer nanocomposites. DDA and ethanol were used to help transfer copper (II) sulfate pentahydrate from water to toluene. All materials choices are summarised in **Table 3.3**.

Table 3.3 Material choices for copper-polymer nanocomposite

	Polymer resin		Metal salt	Dye	Solvent
	Monomer	Photoinitiator			
Choice 1	PETA	Irgacure 369	Copper (II) chloride	Coumarin 30	ethanol
Choice 2	PETA	Irgacure 369	Copper (II) sulfate + DDA	Coumarin 30	toluene

3.3 TPL - Nanoscribe

A commercial TPL facility, Nanoscribe (Nanoscribe GmbH Photonic Professional GT, Germany) (**Figure 3.4**), was utilised for the two-photon fabrication in this thesis. The system is driven by a NIR fibre laser at a 780 nm central wavelength, 80 MHz repetition rate and a 120 fs pulse duration. The laser beam was focused using an oil immersion objective lens (1.4 NA, 63 × , 190 μm WD (working distance)). Nano/microstructures were built by moving the sample position in the XY plane using a galvo mirror and in the Z-direction using a piezoelectric actuator to move the objective. The laser power was varied between 10 and 50 mW and the scan speed was 10,000 μm/s.

System: Photonic Professional GT

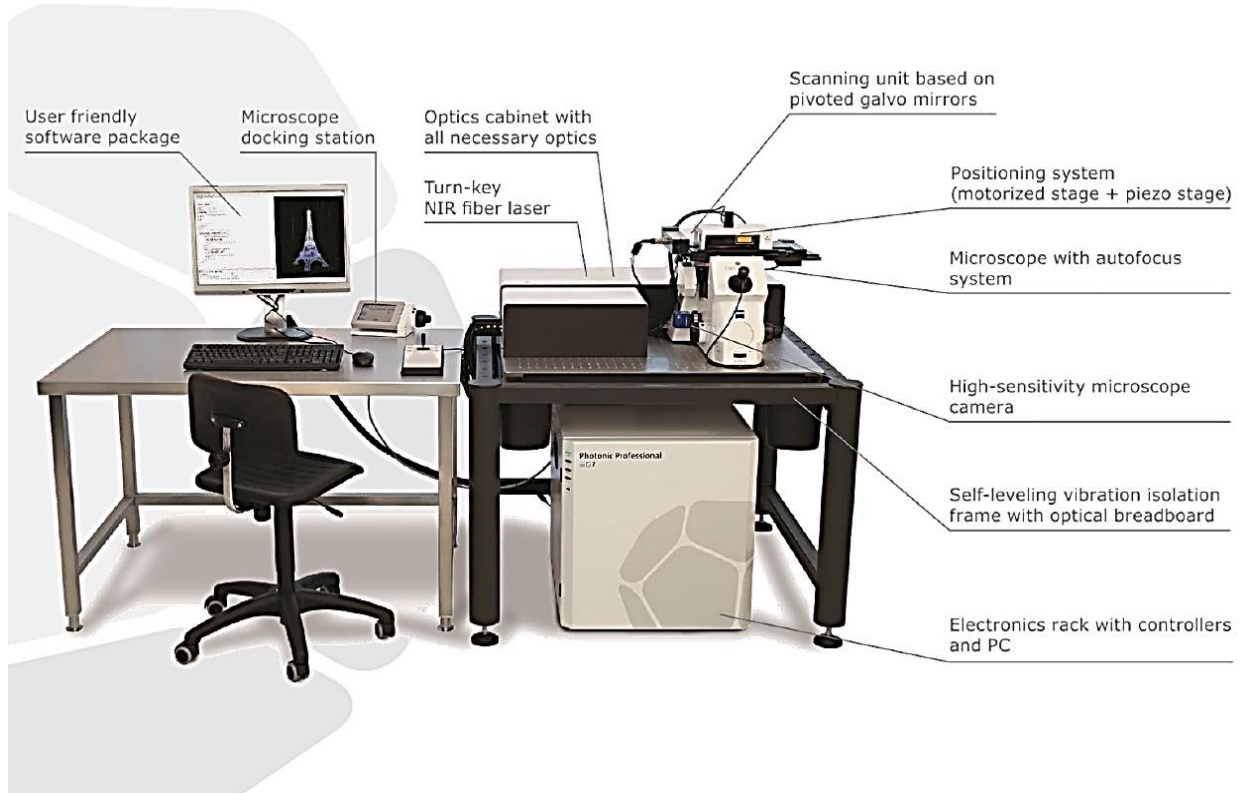


Figure 3.4 Commercial TPL system – Nanoscribe

There are three steps for the fabrication process of Nanoscribe system: (1) Structure design; (2) Materials loading; (3) Two-photon structure fabrication.

(1) Structure design

The structures can be written by a scripting language containing a list of coordinates in their commercial software DeScribe Nanoscribe (Nanoscribe GmbH Photonic Professional GT, Germany) (an example shown in **Figure 3.5**). Otherwise, the .stl file of a CAD structure can be converted to .gwl file using DeScribe software. The structure is sliced into several layers by choosing slicing distance and each layer is filled with lines by choosing hatching distances, contour count and hatching angles

(**Figure 3.6**). The writing code can be then generated automatically. If the slicing distance and hatching distance are bigger than the line width, printing is failed because lines can not be fused¹⁶³. If the slicing distance and hatching distance are small and the laser power is low, no polymerisation is initiated¹⁶³. If the slicing distance and hatching distance are small and the laser power is too high, polymer starts to boil¹⁶³. Therefore, to compare different formulations at the same conditions, all the slicing and hatching distances were fixed at 200 nm (smaller than printed line width), the contour count was set at one and hatching angle was 0°¹⁶⁴ and the formulations were assessed with different laser power.

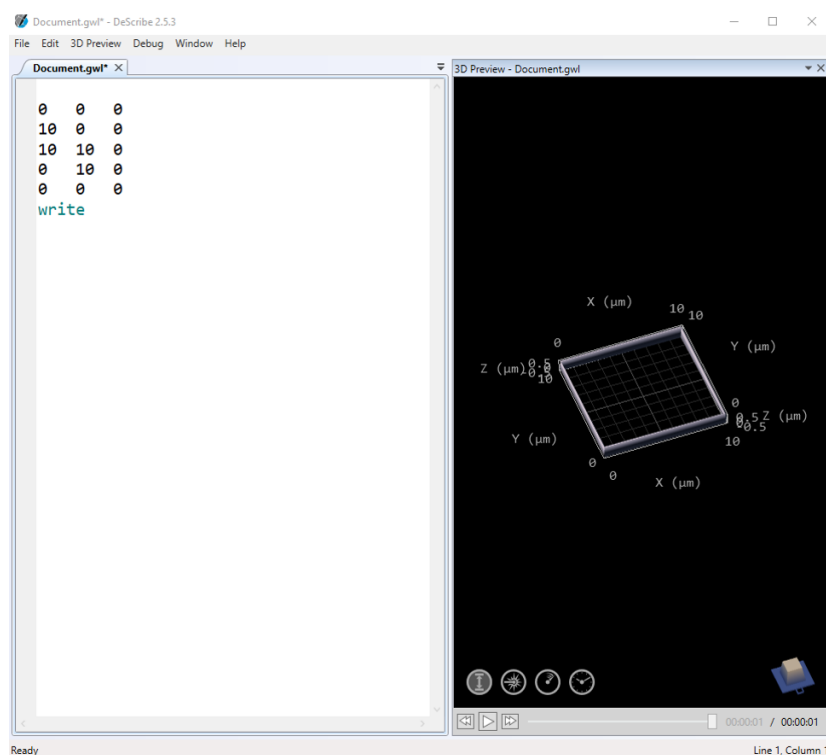


Figure 3.5 An example of writing code containing a list of coordinates by DeScribe software.

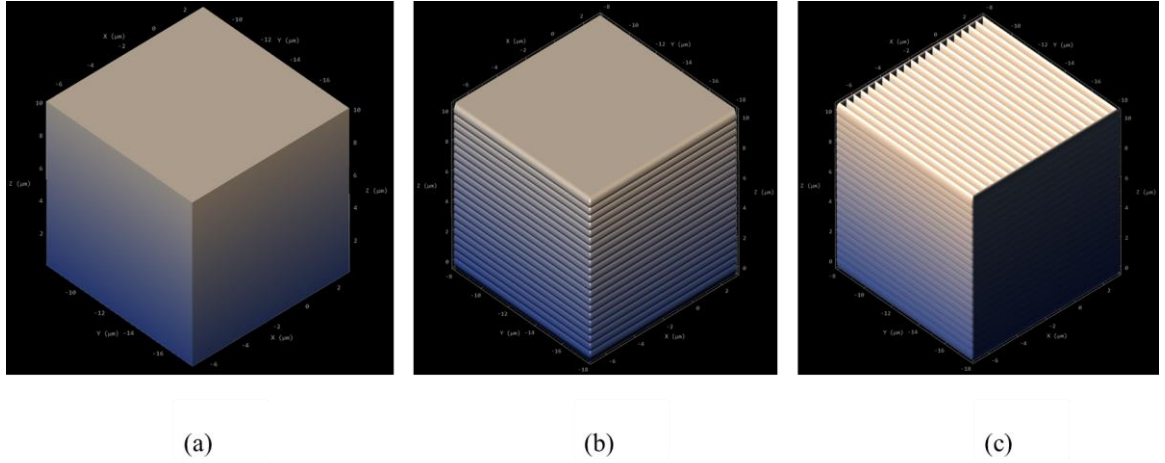


Figure 3.6 A cubic structure is converted to .gwl file (Nanoscribe's general writing language) for Nanoscribe fabrication using DeScribe software. (a) Initial STL file; (2) The cubic structure is sliced in several layers; (c) Each layer is filled with lines.

(2) Materials loading

One or two drops of the materials for two-photon fabrication were loaded onto a glass slide and one or two drops of immersion oil were dropped on the other side of the glass siled (**Figure 3.7** (a)). The glass slide was then mounted on the sample holder shown in **Figure 3.7** (b) and (c). Finally, the sample holder was inserted into the Nanoscribe system (**Figure 3.7** (d)).

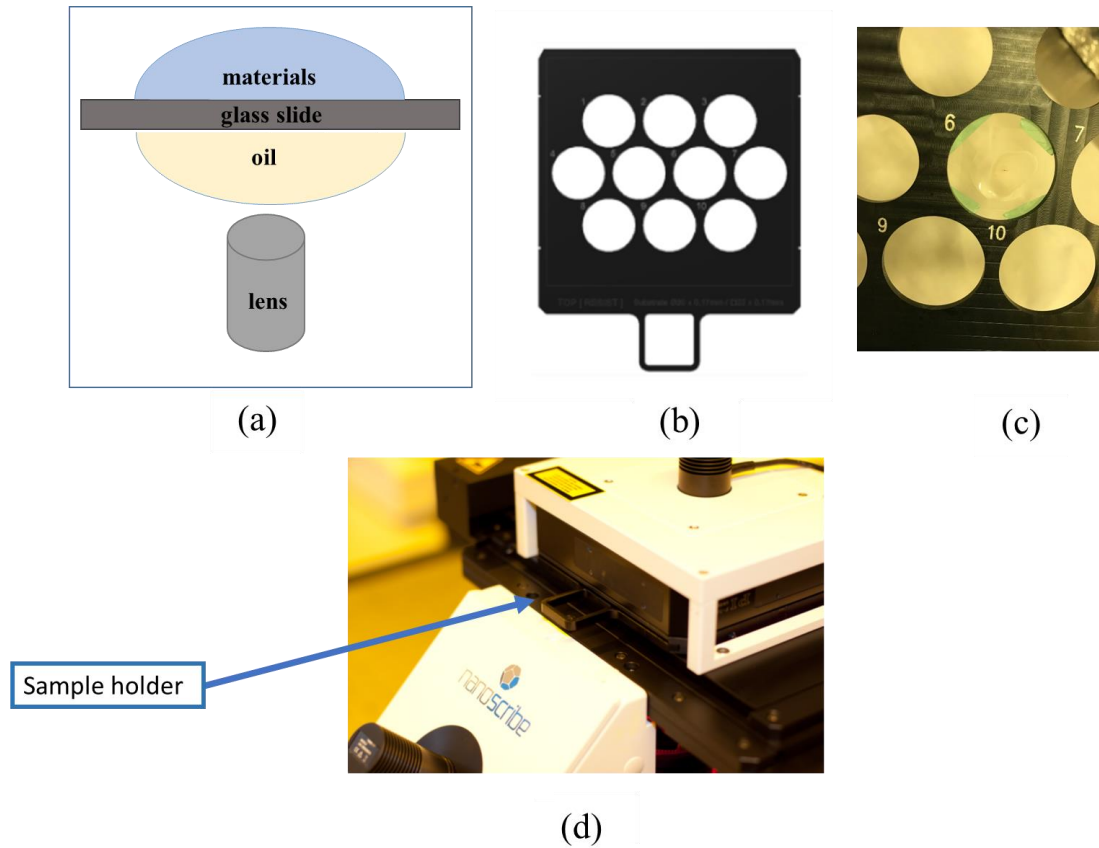


Figure 3.7 Illustration a general procedure of materials loading before two-photon fabrication. (a) one or two drops of materials (blue) for two-photon fabrication is loaded onto a glass substrate. One or two drops of immersion oil (yellow) were dropped on the other side of glass slide; (b) The sample holder for Nanoscribe system; (c) The glass slide loaded with materials and immersion oil is mounted on the sample holder; (d) The sample holder is inserted into the Nanoscribe system.

(3) Structure fabrication

In two-photon fabrication processes, several factors were chosen. The scan speed of galvo mode ranges from 1000-20000 $\mu\text{m/s}$. In a galvo mode, the structure is fabricated layer by layer using an X-Y galvo mirror scanner (X-Y movement) (**Figure 3.8** (a)). Movement on the Z-axis is controlled by a piezo stage. Laser intensity can

be adjusted by two parameters: laser power and power scaling. Parameter laser power (%) represents the percentage of reference power. Power scaling ranges from 0.00 to 1.00 or higher. Writing laser power = laser power $\times$ power scaling $\times$ 50 mW. In this thesis, power scaling was fixed at 1.00 and writing laser power was adjusted by different values of 'laser power'. Max power can be obtained from the calibration value. In this thesis, the power scaling was set at 1.00. The writing laser power is adjusted by changing laser power (%). The interface can be found automatically. 'FindInterfaceAt' is a parameter that adjusts the focusing position. The value must equal to or higher than 0. When the value is 0, the focusing position is the interface between the glass and resins. When the value is 0.5, the piezo stage moves 0.5 μm (**Figure 3.8(b)**). In this thesis, the value of 'FindInterfaceAt' was set to 0.5 in order to make sure that fabrication starts underneath the glass slide so that the fabricated structure stuck tightly onto the glass slide. **Figure 3.9** is an example of writing code for galvo scanning mode.

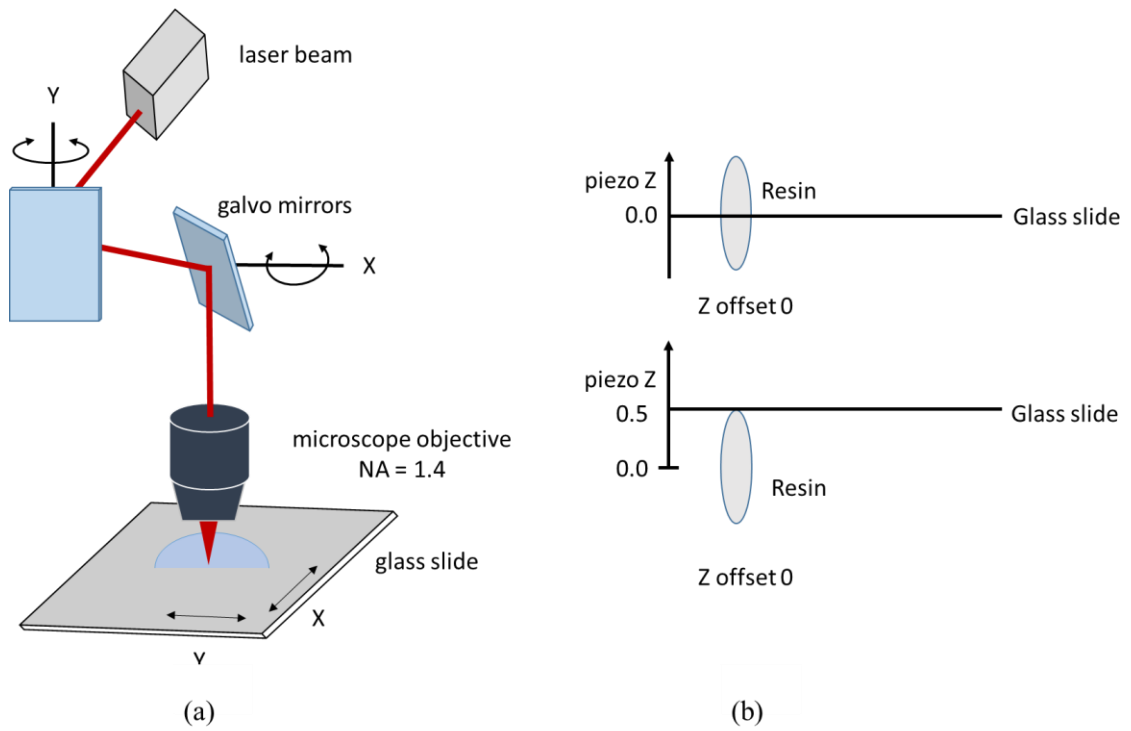


Figure 3.8 (a) Galvo scan mode. X-Y movement of laser is controlled by adjusting galvo mirrors; (b) The voxel position with different values of FindInterfaceAt parameter when Z offset is 0. Upper: when the value of FindInterfaceAt is 0. Lower: when the value of FindInterfaceAt is 0.5. The height of voxel is assumed 1 μm .

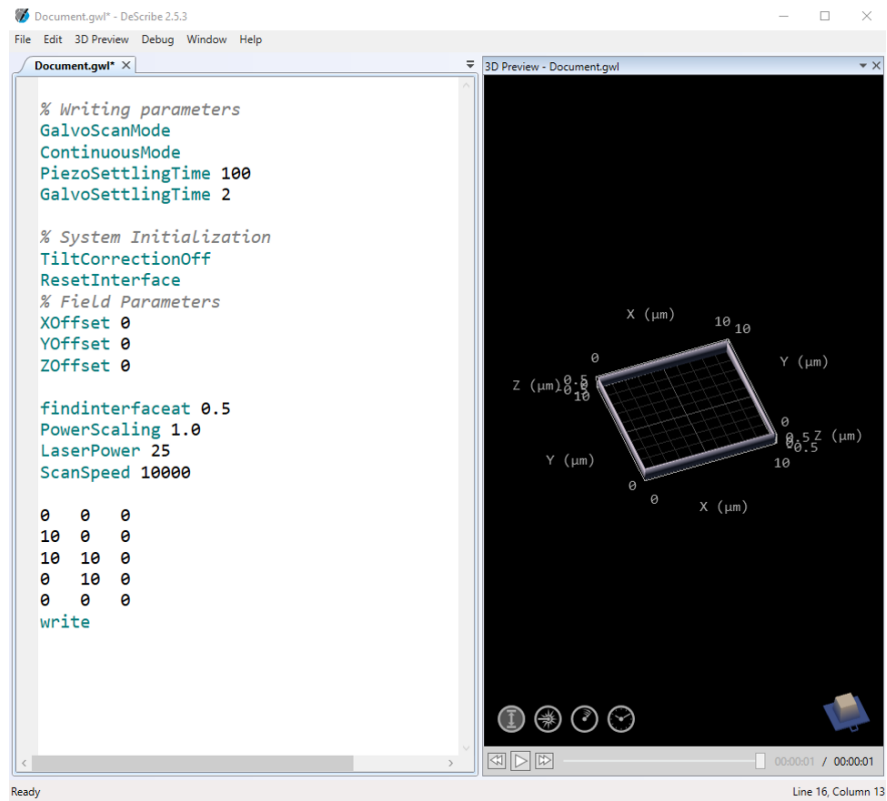


Figure 3.9 An example of writing code for galvo scanning mode.

3.4 Sample characterisation

All characterisation methods used in this thesis are introduced in this section. The names of techniques and the purpose of each technique are summarised in **Table 3.4**.

Table 3.4 *Sample characterisation methods in this thesis.*

Technique	Equipment	Purpose
UV-vis spectroscopy	Varian Cary 50 (Varian Inc., United States)	Obtain optical absorption spectra of raw materials
ICP-AES (Inductively coupled plasma atomic emission spectroscopy)	Perkin Elmer Optima 2000 (PerkinElmer, United States)	Measure phase transfer efficiency of metal ions
SEM & EDX (Scanning Electron Microscopy & Energy-dispersive X-ray Spectroscopy)	• TM3030 (Hitachi, Japan) • XL30(Philips, Netherlands) • 7100F FEG-SEM (JEOL ltd., Japan)	• Structure imaging • structure measurement such as line width • NP characterisation • Element identification
Raman Spectroscopy	LabRAM HR Evolution (Horiba, Japan)	Obtain Raman spectra of structures before and after printing to measure the degree of conversion
XPS (X-ray photoelectron spectroscopy)	Axis Ultra DLD (Kratos, UK)	Identify elemental composition and chemical state, etc.
TEM (Transmission electron microscopy)	JEM-2100F (JEOL ltd., Japan)	NP characterisation

3.4.1 Ultraviolet-visible Spectroscopy

Ultraviolet-visible spectroscopy (UV-vis) or UV-vis spectrophotometry refers to the absorption or reflectance in the ultraviolet-visible spectral region providing the absorption or reflectance spectra of a material. π -electron (double or multiple bonds) transitions or n-electron (lone pairs) transitions can be triggered when imparted with energy in the form of ultraviolet or visible light. Those electrons can be excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). UV-vis spectrophotometer generally records the percentage of absorption (Absorbance) by a sample at different wavelengths (λ). The instrument is composed of a light source, a diffraction grating in a monochromator and detectors. A sample solution is in a transparent cuvette container that allows radiation to pass over^{14, 165}.

The optical absorption spectra of the raw materials used in this thesis were measured by a Varian Cary 50 UV-vis spectrophotometer (Varian Inc., United States). The raw materials were diluted in isopropanol separately and then filled in the quartz cuvettes required for the spectrophotometer.

3.4.2 Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)

ICP-AES was used to measure the phase transfer efficiency of metal ions in this thesis.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) also known as inductively coupled plasma optical emission spectrometry (ICP-OES), is an analytical technique that is the most universally used in the multi-element analysis¹⁶⁶. It consists

of ICP (nebulizer, spray chamber and torch) and an optical spectrometer (**Figure 3.10**). Small mist droplets of samples less than 5µm are generated by a spray chamber and a nebulizer¹⁶⁶. The ICP quart torch with argon gas flow is used to create and sustain a plasma. When the torch is turned on, an intense oscillating electromagnetic field is formed within the radio-frequency coil connecting to a radiofrequency generator. The electrons of argon atoms are stripped off to form argon ions and the ions collide with other argon atoms to form a stable and high-temperature plasma (6000 to 10000K). When sample droplets entered the plasma, they evaporate and the valence electrons or atoms are excited and then emit photons, which are detected by the optical spectrometer. Therefore, the concentration of elements can be obtained and analysed¹⁴.

166-168

In this PhD thesis, Perkin Elmer Optima 2000 ICP-AES instrument (PerkinElmer, United States) in radial mode equipped with an S10 autosampler was. A certified 1000 ppm (+/- 5 ppm) Ag calibration standard in 2 % HNO₃ was used and seven solutions were independently volumetrically prepared in order to give a suitable range of eight standards for calibration (100 ppm, 60 ppm, 40 ppm, 20 ppm, 10 ppm, 0.1 ppm, 0 ppm) together with a known concentration standard to be used for quality control purposes (5 ppm). After calibration, the concentration of aqueous silver ion solution before and after phase transfer were measured and the transfer efficiency (TE) of metal ions was calculated.

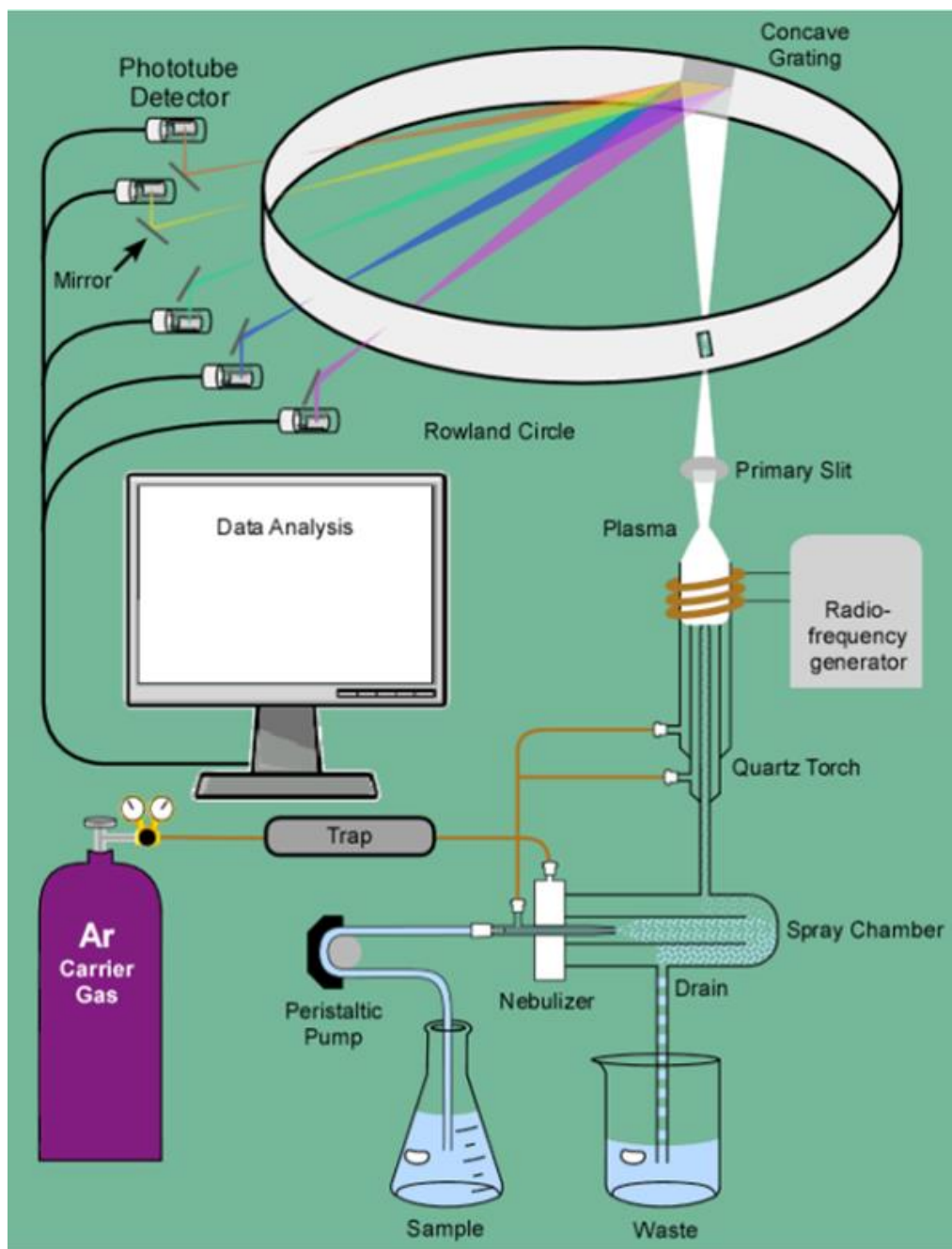


Figure 3.10 An illustration of a basic ICP-AES system¹⁶⁶.

3.4.3 Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray Spectroscopy (EDX)

SEM is an electron microscope technique that images the surface topography of a sample and provides information on composition. Electrons are emitted from an electron gun and interact with samples to produce various types of signals including secondary electrons (SE), backscattered electrons (BSE), transmitted electrons, electron-beam-induced current, cathodoluminescence and x-rays (**Figure 3.11**). In SE mode, the SE can be ejected quickly due to its low energy from a few nanometres to the sample surface. Therefore, the images obtained from SE offers a high resolution of surface topography. The resolution of 5-20 nm could be achieved. While BSE is the electrons reflected or back-scattered from the sample due to elastic scattering. Due to different sizes of the atom nucleus, the number of BSE shows different; thus, BSE images provide the information of material composition by different brightness and contrast. In SEM, the penetration depths are affected by electrons accelerating voltage. The higher voltage leads to deeper penetration-depth. Nonconductive samples are generally coated with conductive materials in case of accumulation of electrostatic charge^{165, 169-170}.

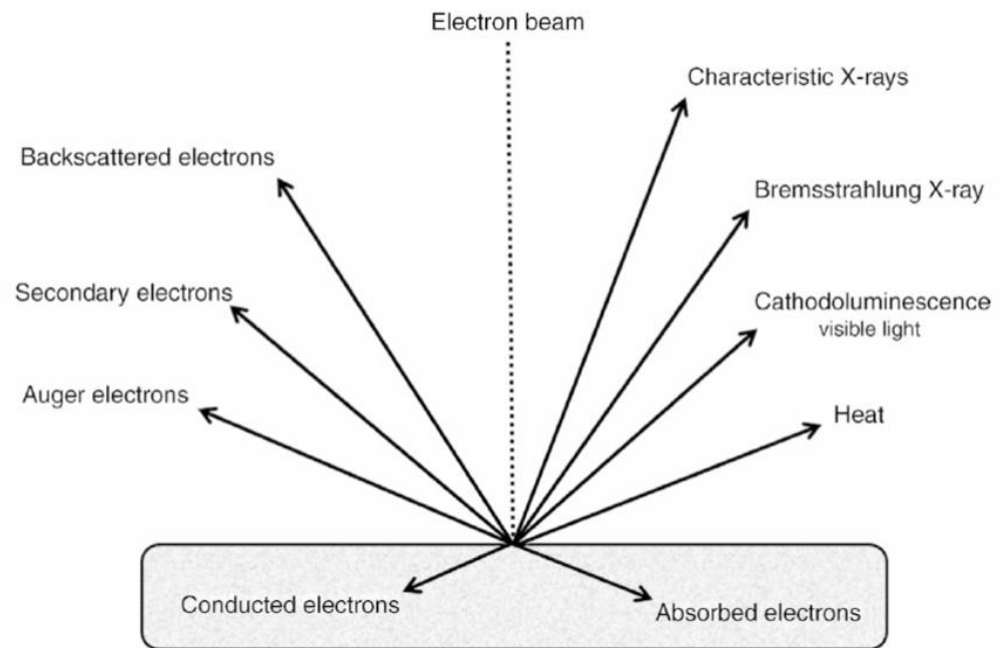


Figure 3.11 Main signals emitted due to the interaction between the electron beam and a sample by SEM^{165, 170}.

Energy-dispersive X-ray spectroscopy (also referred to as EDX or EDS) is an analytical technique used with SEM for chemical analysis of a sample. It is a qualitative and quantitative technique that detect the chemical composition of a sample. When the electron beam penetrates the outer shell and excites the electron in the inner K shell, the excited electron is ejected and an electron-hole is created (**Figure 3.12**). An electron from the outer shell then fill the hole and the energy difference between two shells may be performed by X-ray emitting. By detecting the X-ray signals, the chemical composition can be analysed because elements have a certain energy difference between the two shells¹⁷⁰.

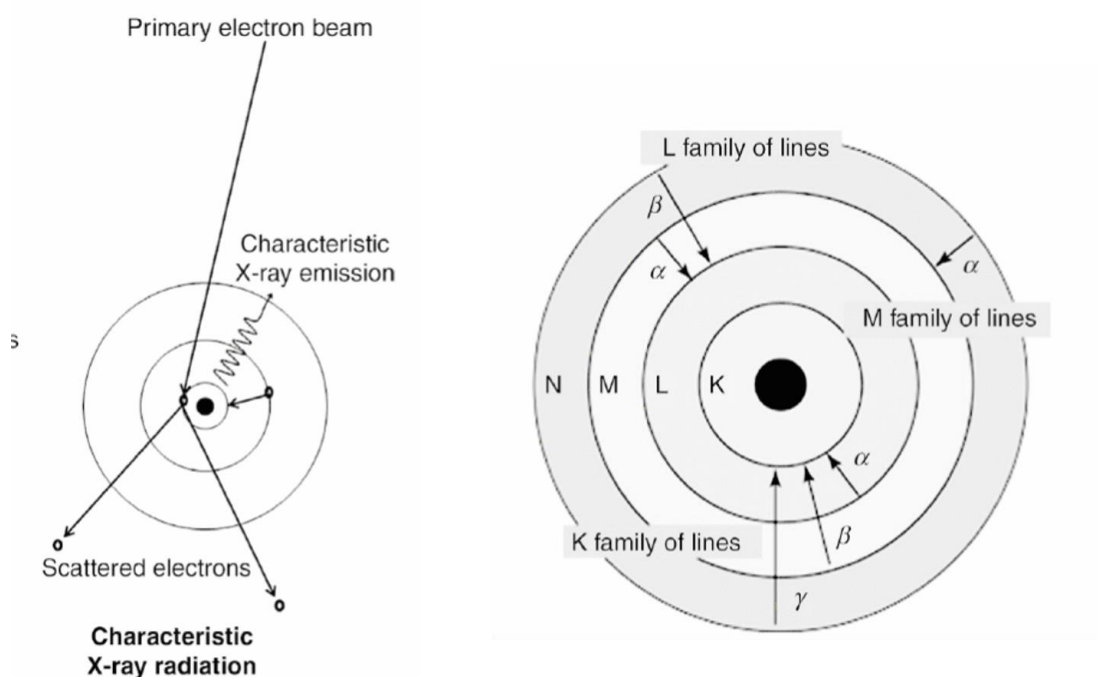


Figure 3.12 (a) The principles in forming X-ray emitting and (b) the illustration of K, L and M shells and α , β , γ and δ electronic transitions of each element^{165, 170}.

In this thesis, both SE and BSE modes were applied. The fabricated structures were sputter-coated with Carbon, Platinum or Iridium and examined by three SEMs (**Table 3.5**)

Table 3.5 SEMs used in this thesis

SEM systems	Coating materials	Details of SEMs and applications
TM3030 (Hitachi, Japan)	Platinum	Tabletop SEM for structure imaging Maximum magnification: 60,000×
XL30(Philips, Netherlands)	Carbon	Printed linewidth measurement Resolution: 5.0 nm at 1 kV; 2.0 nm at 30 kV
7100F FEG-SEM (JEOL Ltd., Japan)	Iridium	Nanoparticles characterization Resolution: 3.0 nm at 1 kV; 1.2 nm at 30 kV

Hitachi TM3030 SEM (Hitachi, Japan), a tabletop SEM, was used to obtain basic structure imaging. XL 30 SEM (Philips, Netherlands) was used to obtain higher resolution images and measure line width. 7100F FEG-SEM (JEOL Ltd., Japan) was employed to image metal NPs in fabricated structures because it enables the highest possible resolution of 2-3 nm. All three SEM equipment was with energy-dispersive X-ray spectroscopy (EDX) that could do elemental analysis. Quanta200 FIB-SEM (focused ion beam SEM) (FEI, United States) was utilised to cut the fabricated nanostructures and prepare samples for Transmission electron microscopy (TEM).

3.4.4 Raman Spectroscopy

Raman spectroscopy was used to characterise polymerisation processes by calculating the degree of conversion of carbon double bonds. Raman spectroscopy is a scattering technique based on the Raman Effect and able to observe the vibration of a molecule.¹⁴ A beam of monochromatic light is introduced and focused on a sample¹⁴. A part of the light is scattered to elastic scattering (Rayleigh scattering) or inelastic scattering (Raman scattering). The shifts in wavelength depend on the chemical structure of a molecule¹⁴.

A schematic diagram in **Figure 3.13** illustrates the Rayleigh scattering and Raman scatterings. Rayleigh scattering involves a scattering that the energy of scattered light is equal to the incident light, while a loss or gain of energy by vibration in the molecule in Raman scattering¹⁴. By detecting Raman scattering, the chemical bonding and chemical structure can be confirmed because the chemical bonds vibrated at specific frequencies^{14, 171}.

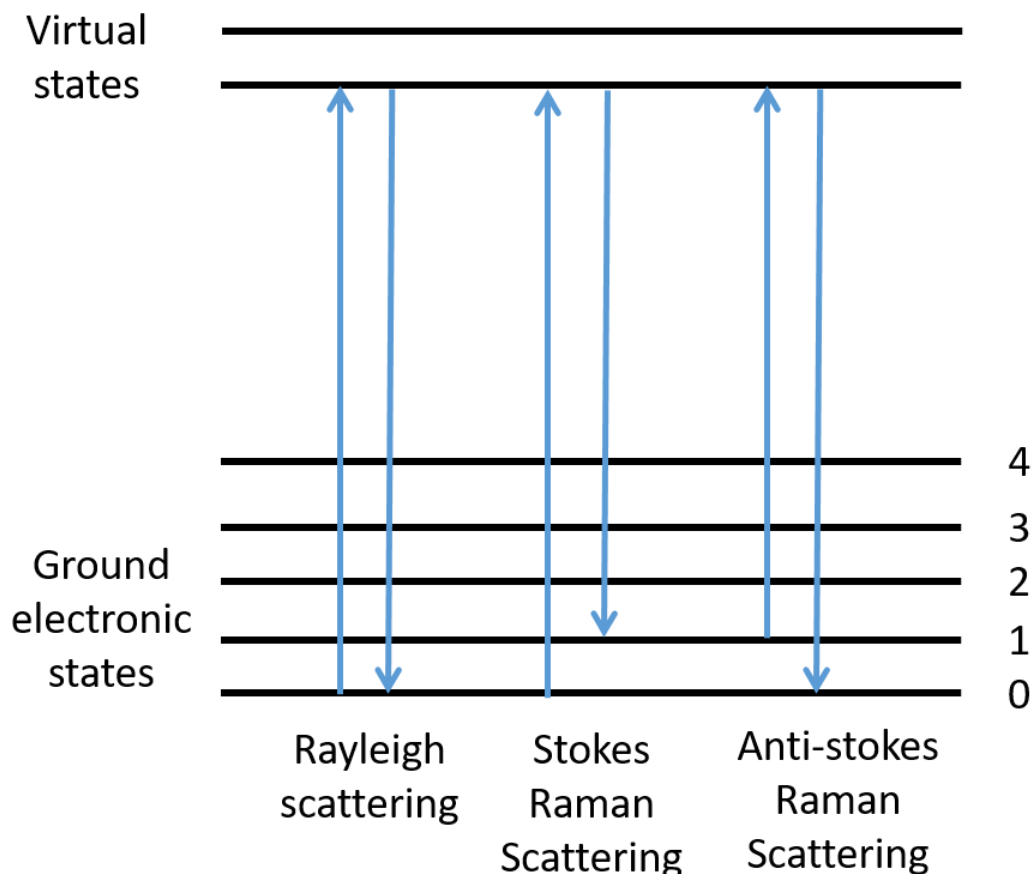


Figure 3.13 Origin of Raleigh scattering and Raman scattering¹⁴.

In this thesis, Raman spectra were recorded on a LabRAM HR Evolution Raman microscope (Horiba, Japan) with an excitation laser wavelength of 785 nm, laser power ranges from 6 to 25 mW and a 600 lines/mm grating. A typical spectrum was collected for 10-180 seconds with 8-16 accumulations to enhance the signal to noised ratio. The detector was a Synapse CCD detector. The Raman shift was calibrated using the Rayleigh line and a Si (100) reference sample.

3.4.5 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was used to characterise material compositions and element states in this thesis. XPS, a surface-sensitive quantitative

spectroscopic technique, widely used in the measurement of elemental composition, empirical formula, chemical state and electronic state of the elements within samples¹⁷²⁻¹⁷³. The technique relies on the measurement of the kinetic energy and number of electrons that ejected from a sample surface (0-10 nm) by an X-ray beam, typical aluminium and magnesium K_{α} X-rays, in ultra-high vacuum (UHV) conditions¹⁷²⁻¹⁷³. An XPS spectrum is given of the number of electrons detected (Intensity) as a function of binding energy and the relationship of binding energy and kinetic energy is:

$$BE = h\nu - KE$$

Where BE is the binding energy, KE is the kinetic energy of an emitted electron, h is Planck's constant, ν is the frequency of incident radiation¹⁷²⁻¹⁷³. The peaks of a spectrum corresponding to the atomic orbital and shell and the binding of the atoms¹⁷²⁻¹⁷³. In general, XPS is sensitive to all elements¹⁷²⁻¹⁷³. Normally, a survey scan is performed first to get an overall composition and closer analysis of elements of interest is taken accordingly¹⁷²⁻¹⁷³.

Elemental analysis was performed using Axis Ultra DLD XPS (Kratos, UK) in this thesis. Data analysis was carried out using CASAXPS software with Kratos sensitivity factors (RSFs) to determine atomic % values from the peak area.

3.4.6 Transmission Electron Microscopy (TEM)

Transmission electron microscopy is a high-resolution microscopy technique. When a high energy beam of electrons is transmitted through a very thin sample, the interactions between electrons and atoms by elastic and inelastic scattering provide

high-resolution images. The specimen needs to be thin, typically 5-100 nm for 100 keV electrons, depending on the density and elemental composition of the material and the required resolution. Therefore, special sample preparation is needed, such as electropolishing and ion-beam etching. **Figure 3.14** illustrates the signals can be generated and detected in TEM. In TEM, bright-field images are the most common images. The thicker sample or the more atoms of a sample scatter or absorb more electrons, thus appear darker. The area that transmits electrons shows brighter. While in dark-field mode, the scattered electrons are used to produce images. Areas that are without scattering, for example, when the primary electron beam passes through the sample without scattering, appear black¹⁷⁴⁻¹⁷⁵.

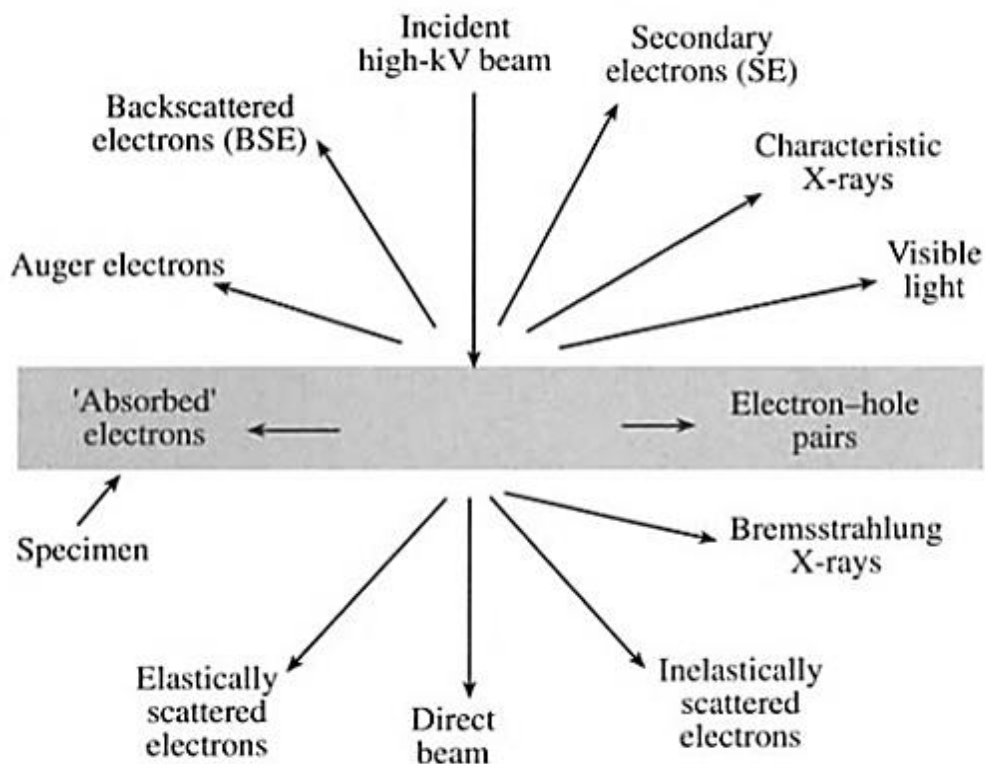


Figure 3.14 Signals generated when a high-energy beam of electrons interacts with a thin sample and most signals can be detected in different TEM¹⁷⁴.

In this thesis, TEM images of fabricated metal-polymer nanocomposites were acquired by using FEG-TEM (JEM-2100F, JEOL). Both bright-field and dark-field images were acquired. The size and distribution of NPs were measured to understand the fabricated structures better. Sample preparation and TEM imaging were accomplished with the help of Dr Christopher Parmenter and Dr Michael Fay (NMRC, University of Nottingham).

4 Gold-polymer Nanocomposite

4.1 Introduction

Recent endeavours have been focused on extending the AM approach to multiple materials, and it has been complemented by efforts to process nanocomposites using TPL. The fabrication of metallic structures has been reported using a range of methods, but each has its drawbacks such as high surface roughness, low quality of metal structures or complex processing steps^{12, 42, 116, 133, 176}. A significant step forward, however, is in the single-step fabrication by two-photon fabrication of nanocomposites, achieved in 2D, by simultaneous photopolymerisation and photoreduction¹² and in a similar fashion by the creation of 3D filigree-like conductive elements that are ‘glued’ together with a polymer resin¹³.

In this chapter, a method for fabricating 3D gold nanocomposite objects are presented. Following the lead of Shukla et al.^{12, 31}, by selecting monomers, initiators and dyes, stable 2D and 3D structures can be formed. In this thesis, radical polymerisation was utilized because of its high reaction rates, ease of processing and wide availability of photoinitiators and monomers^{44, 55}, while taking advantage of previously observed beneficial effects of adding ruthenium complexes on multiphoton reactivity¹⁰, leading to the role of the initiator in overcoming the competition between polymerisation and reduction being explored.

4.2 Gold in IPL-780 resin for Gold-polymer Nanocomposite

Commercial TPP (two-photon polymerisation) resin IPL-780 was used as monomer materials at first. IPL-780 consists of PETA (> 95%) as a monomer and DETC (< 5%) as a photoinitiator according its MSDS¹⁶⁰. A 2D gear structure (**Figure 4.1** (a)) consisting of crossed lines (line gap: 2 μ m) (**Figure 4.1** (b)) was used to test the printability of materials. By adding 1, 2, 3, 4 and 5 wt% of Gold (III) chloride hydrate in IPL-780 resin, no polymerisation was observed even if full laser power of 50 mW was applied. It indicates that insufficient free radicals in IPL-780 resin led to the competition between free radical polymerisation and metal reduction, thus suppressing polymerisation¹². The solution is to add more photoinitiators. When additional photoinitiator was added, polymerisation was observed. When 3 wt% gold chloride hydrate and additional 1 wt% commercial photoinitiator Irgacure 369 were added into IPL-780 resin, polymerisation occurred but failed to print a gear structure as designed. (**Figure 4.1** (c)-(d)) A similar result was found in 5 wt% gold chloride in IPL-780, polymerisation was observed when additional 1 wt% Irgacure 369 was added, but gold particles were strongly aggregated and local burning was generated during fabrication (**Figure 4.1** (e)). After two-photon fabrication, samples on a glass slide were put in propylene glycol monomethyl ether acetate (PGMEA) (Sigma-Aldrich, UK) for 20 min, 2-propanol (Sigma-Aldrich, UK) for 2 min and water for 20 min to remove unreacted materials. This is a sample development step. Most particles observed during fabrication were lost after sample development and polymer structures were too weak to hold gold particles and keep their original shape (**Figure 4.1** (f)). These suggest that adding additional Irgacure 369 photoinitiator in IPL-780 resin is not suitable for fabricating gold-polymer nanocomposites. Photoresist IPL-780 consists of PETA(> 95%, monomer) and DECT (< 5%, photoinitiator). Using

DETC as a photoinitiator and PETA as a monomer to fabricate gold-polymer nanocomposite by simultaneous photopolymerisation and photoreduction was also achieved studied by our group¹⁷⁷. 3D gold-PETA nanocomposite structures were fabricated. However, compared to Irgacure 369, the price of DETC is more than 100 times higher. It was found that when used PETA or TMPTA as a monomer, Irgacure 369 as a photoinitiator and suitable photosensitive dye, gold-containing nanocomposites were successfully fabricated. The details were introduced in section 4.3.

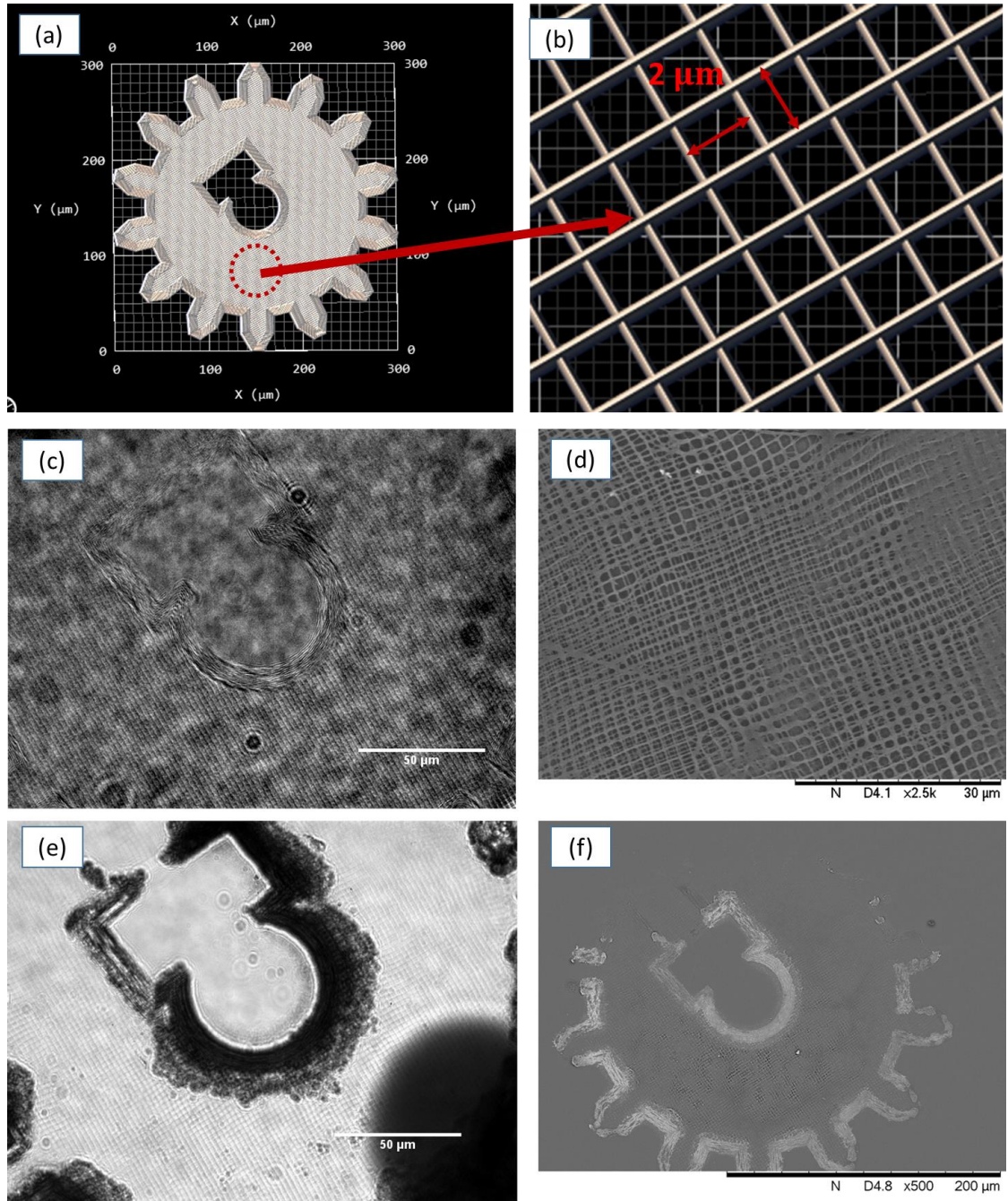


Figure 4.1 (a) a 2D gear structure as designed for printability test; (b) higher magnification of the red circled area. Line gaps are 2 μm ; (c) photo captured during fabrication of 3 wt% gold chloride and 1 wt% Irgacure 369 in IPL-780, gear structure, scan speed 10000 $\mu\text{m/s}$, laser power 35 mW (d) SEM image of the grid lines in gear structure fabricated with 3 wt% gold chloride and 1 wt% Irgacure 369 in IPL-780 (e) photo captured during fabrication of 5 wt% gold chloride and 1 wt%

Irgacure 369 in IPL-780, gear structure, scan speed 10000 $\mu\text{m/s}$, laser power 35 mW (f) SEM image of a gear structure fabricated with 5 wt% gold chloride and 1 wt% Irgacure 369 in IPL-780.

4.3 PETA/TMPTA as Polymer Materials and Irgacure 369 as Photoinitiator for Gold-polymer Nanocomposite

It was found that additional photoinitiator Irgacure 369 in commercial resin IPL-780 was not the best option for fabricating gold-polymer nanocomposites in section 4.2. Tri-acrylate based monomers, PETA and TMPTA were chosen as two monomer candidates for simultaneous photopolymerisation and photoreduction because their three functionalities give high reaction rate⁹⁰. Irgacure 369 was used as a photoinitiator because it works for 780 nm laser two-photon polymerisation (TPP). Ruthenium (II) complex was used as a photosensitive dye because it helps reduce gold ions¹⁰.

4.3.1 Sample Preparation

To prepare the materials of gold-polymer nanocomposites ready for two-photon fabrication, the following steps were taken. Firstly, the gold chloride hydrate and ruthenium (II) complex dye were separately dissolved in ethanol at a maximum concentration of 0.2 g/mL. In section 4.2, 3 wt% gold chloride nanocomposites were failed to fabricate. In this section, fabricating 3 wt% gold-polymer nanocomposite was applied as a target to achieve. Because of the competition in consuming photoinitiators between gold reduction and polymerisation, the same amount of photoinitiator 3 wt% was used. A combination of 3 wt% Irgacure 369, 3 wt% gold (III) chloride hydrate

and 0.1 wt% Ru (II) complex were added in two monomers, PETA and TMPTA, resulting in 6 formulations (**Table 4.1**). The additives were mixed using a magnetic stirrer operating at a speed of 600 rpm for 30 min. Oxygen in formulations may affect the quality of the final structures. A separate set of experiments were performed to assess the effect of purging by passing nitrogen through the mixtures for 15 minutes. One or two drops of each of the resultant combinations were deposited on a glass slide with a pipette, which was then loaded onto the Nanoscribe system for simultaneous photoreduction and photopolymerisation. After processing, samples on glass slides were developed by washing in PGMEA for 20 min, 2-propanol for 2 min and water for 20 min to remove unreduced gold salt and residual monomer. As a final step, the samples were dried in air for 24h before any characterisation.

Table 4.1 Composition of 6 formulations for gold-polymer nanocomposites based on trimethylolpropane triacrylate (TMPTA) and pentaerythritol triacrylate (PETA) monomer systems.

Formulation	Monomer	Gold chloride hydrate wt%	Irgacure 369 wt%	Ru(II) wt%
TMPTA-polymer	TMPTA	0	3	0
TMPTA-Au	TMPTA	3	3	0
TMPTA-Au-Ru	TMPTA	3	3	0.1
PETA-polymer	PETA	0	3	0
PETA-Au	PETA	3	3	0
PETA-Au-Ru	PETA	3	3	0.1

4.3.2 Fabrication of 2D and 3D Polymeric Objects

A series of experiments were performed to ascertain whether 2D and 3D plain polymer structures could be manufactured using the proposed formulations, TMPTA-

polymer and PETA-polymer. A series of structures with an increasing complexity from 2D straight lines (**Figure 4.2(a)**) (line gap: 2 μm), 2D curved structures (**Figure 4.2 (b)**) (curved line gap: 2 μm) to 3D pyramid structures (**Figure 4.2 (c) and (d)**) ($L \times W \times H$ 100 $\times$ 100 $\times$ 46 μm) were fabricated. **Figure 4.3** shows the fabricated TMPTA and PETA polymer structures. It was found that 0.2 wt% Irgacure 369 in TMPTA and PETA is sufficient for polymerisation. Because 3 wt% Irgacure 369 was added in gold-polymer nanocomposite formulations, in order to compare the difference between plain polymer and gold-polymer nanocomposite structures, 3 wt% of Irgacure 369 was used in TMPTA-polymer and PETA-polymer to provide consistency across all formulations. **Figure 4.3** illustrates that sub-micron feature sizes are possible in 2D (**Figure 4.3 (a), (b), (c) and (d)**) and in 3D (**Figure 4.3 (e) and (f)**). The line width of TMPTA and PETA were 635.2 ± 25.0 nm and 398.6 ± 54.1 nm, respectively. The line width difference was caused by the presence of hydroxyl group in PETA, which formed hydrogen bonds and cohesive force¹⁷⁸. The methyl group in TMPTA improved the rigidity of the polymer chain leading to less shrinkage¹⁷⁸. Line gaps, cured line gaps and pyramid dimensions were measured by ImageJ and labelled in the figures. Straight lines and curved lines are printed as designed line gaps and shapes. Shrinkage occurred in 3D pyramid structures but the overall geometry is well presented as designed. TMPTA and PETA are printable for two-photon polymerisation.

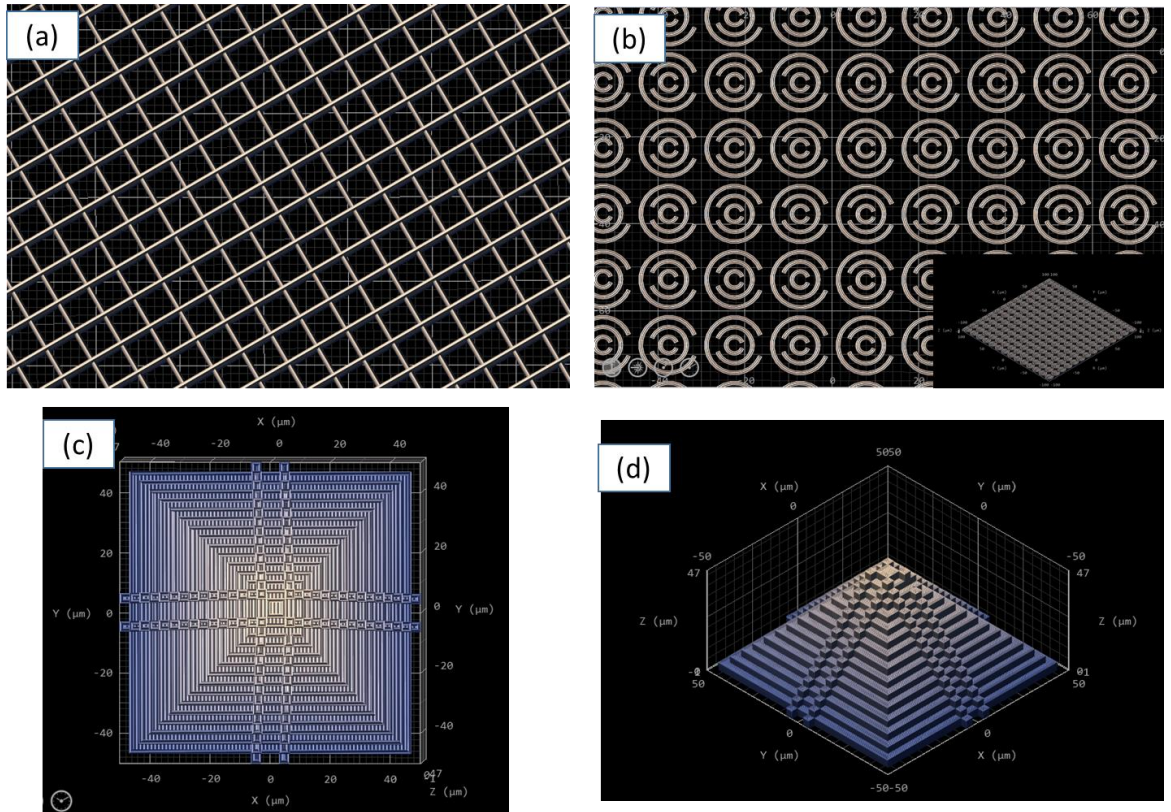


Figure 4.2 A series of fabrications with increasing complexity from (a) 2D straight lines (line gap: $2\mu\text{m}$); (b) 2D curved structures (curved line gap: $2\mu\text{m}$) and (c) and (d) 3D pyramid structures ($L \times W \times H$ $100 \times 100 \times 46\mu\text{m}$)

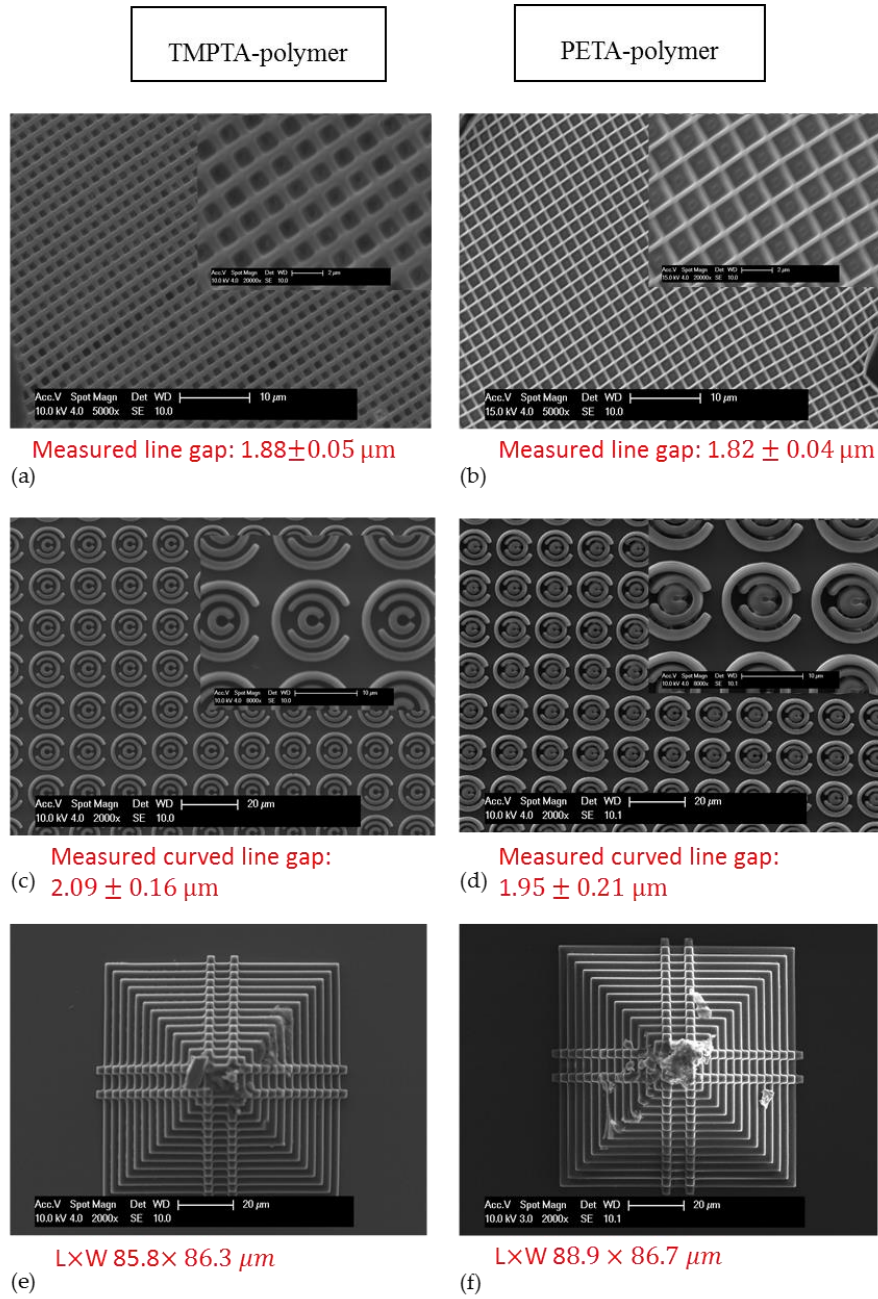


Figure 4.3 SEM images of 2D and 3D fabricated structures using formulations TMPTA-polymer and PETA-polymer. (a), (c) and (e) show the results of fabricating increasingly more complex structures with formulation TMPTA-polymer. (b), (d) and (f) show the results of fabricating increasingly more complex structures with formulation PETA-polymer.

4.3.3 The Effect of Adding Gold Salt

Having established the suitability of the base polymer formulation for two-photon fabrication, gold (III) chloride hydrate (3 wt%) was added, and an assessment of the amount of photoinitiator Irgacure 369 required was performed. By increasing the concentration of the photoinitiator in steps of 1 wt% Irgacure 369 and attempting to fabricate structures, it was determined that 3 wt% was the minimum required concentration of photoinitiator for TMPTA with 3 wt % gold chloride hydrate. Below 3 wt% Irgacure 369, gold particles were generated during fabrication but no polymerisation was observed. It is postulated that the limited number of free radicals lead to competition between free radical polymerisation and metal reduction with the generated free radicals preferentially reducing the gold ions, thus suppressing polymerisation. Similar results were found in Shulka et al.'s work¹¹⁻¹². Gold nanoparticle aggregation was observed during laser exposure when the photoinitiator concentration was below 3 wt%, but the aggregating particles could not maintain a cohesive shape (similar to **Figure 4.1 (e) and (f)**). The polymerisation was only observed when the concentration of Irgacure 369 was at least equal to the concentration of gold chloride hydrate, which was 3 wt%.

When considering the fidelity of the fabrication, it was noted that even though TMPTA achieved polymerisation, the line quality was consistently poor (see **Figure 4.4 (a)**), resulting in build failures as the complexity of the object to be fabricated was increased (**Figure 4.4 (c)**). The line gaps in **Figure 4.4 (a)** are challenging to identify measure (2 μm as designed) and 2D cured structures are incomplete. When using PETA during equivalent experiments, an improvement in overall performance was observed, with consistent 2D structures fabricated (**Figure 4.4 (b) and (d)**). The grid

lines of formulation PETA-Au (**Figure 4.4** (b)) were more uniform compared to formulation TMPTA-Au (**Figure 4.4** (a)), line gaps were $1.88 \pm 0.05\mu\text{m}$, and the line width compared well with a minimum observable size of about 300 nm when using monomer only (formulation PETA-polymer). Inspecting the moieties present in the monomers, it is noted that the difference between PETA and TMPTA lies in the presence of the hydroxyl group in PETA. The hydroxyl group in PETA results in a different distribution of electron density and increases the polarity compared to TMPTA, which suggests a higher reactivity¹⁷⁸. Self-inhibiting happened to TMPTA during the reaction and deformed lines were formed. However, despite these promising results for PETA, the fabrication of 3D structures was a challenge, as deformations appeared as the build was increased in the Z direction (**Figure 4.4** (e)).

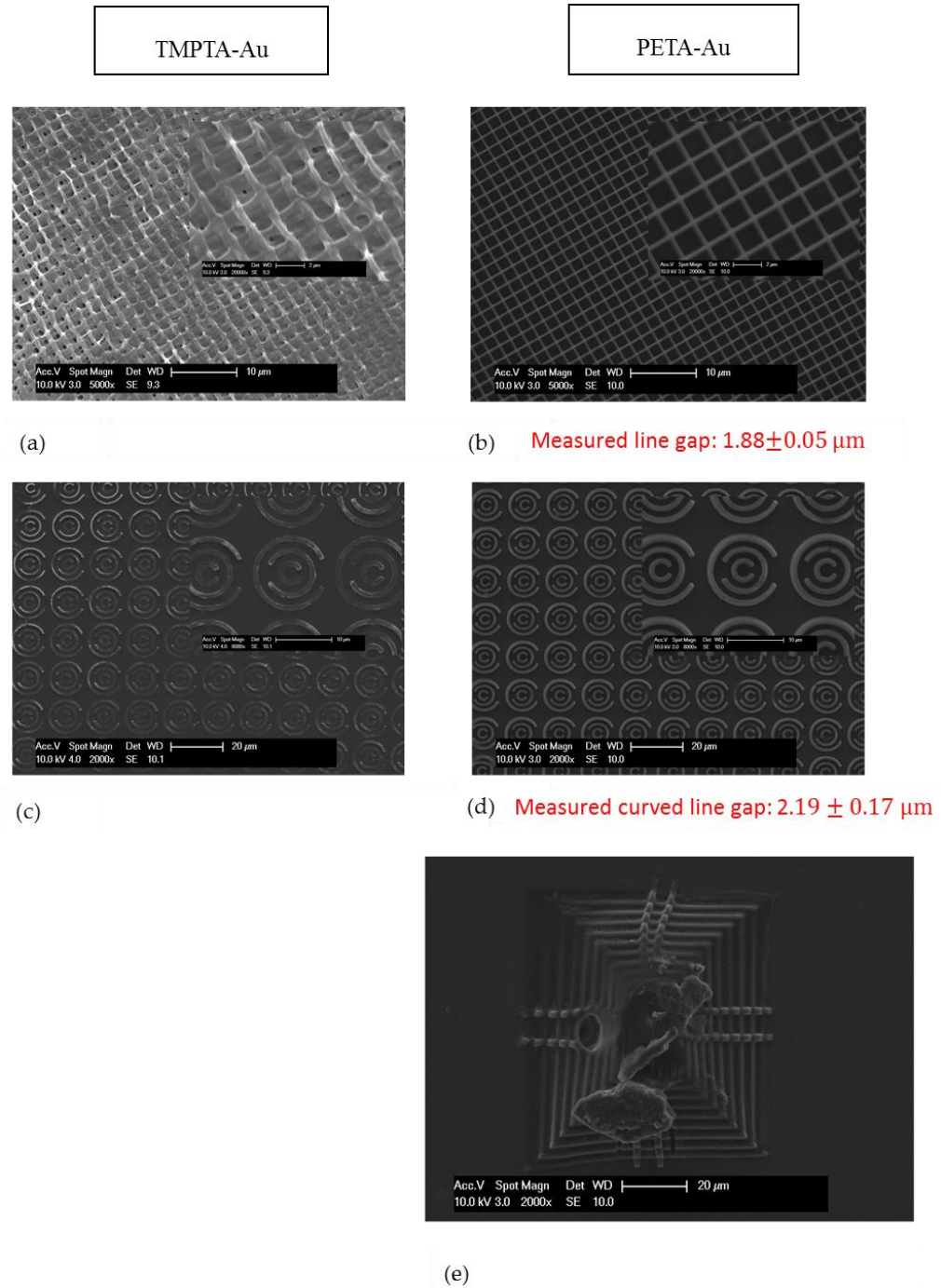


Figure 4.4 SEM images of 2D and 3D fabricated structures using formulations TMPTA-Au and PETA-Au. (a) and (c) show the results of fabricating increasingly more complex structures with formulation TMPTA-Au. (b), (d) and (e) show the results of fabricating increasingly more complex structures with formulation PETA-Au.

4.3.4 The Effect of Adding a Two-photon Sensitive Dye Ru (II)

Ruthenium (II) complexes have been reported previously as an effective addition for promoting gold reduction¹⁰ and thus 0.1 wt% tris(2,2'-bipyridyl) dichlororuthenium (II) hexahydrate was added to the gold (III) chloride hydrate containing formulations (**Table 4.1**). **Figure 4.5** shows SEM images of structures fabricated based on formulations TMPTA-Au-Ru and PETA-Au-Ru.

The addition of the Ru (II) dye to formulation TMPTA-Au-Ru made more uniform grid line and curved line structures (**Figure 4.5** (a)) compared to the formulation without Ru (II) (**Figure 4.4** (a)). For PETA-Au-Ru, 3D pyramid structures were fabricated as designed and more uniform compared to the formulation without Ru (II). More details on linewidth measurement were introduced in section 4.3.6.

Table 4.2 shows the threshold laser power for each formulation. Additional Ru (II) reduced threshold power by 2.5 mW and 4 mW. Similar results were found in the previous

Formulation	Minimum fabrication power (mW)
TMPTA-Au	25.5
TMPTA-Au-Ru	22
PETA-Au	24
PETA-Au-Ru	20

literature¹⁰. $[\text{Ru}(\text{bipy})_3]^{2+}$ has previously been cited as a photosensitive dye, which helps gold reduction^{10, 128}. It consists of a central Ru(II) ion and three bipyridine ligands. Two-photon excitation of Ru(II) complex converts itself to a triplet metal to ligand charge transfer (3MLCT) excited state, which transfers electrons to ligands and then reduces gold ions^{10, 121}. The improvement on the degree of conversion of monomers by adding photosensitive dye Ru (II) was confirmed by Raman

Spectroscopy shown in section 4.3.7. Although fabrication of a 3D structure was possible with PETA, the addition of the Ru (II) complex was not sufficient to allow 2D curve structure and 3D pyramid structure fabrication with the TMPTA based formulation (**Figure 4.5** (e)). It is again because the presence of the hydroxyl groups in PETA increases monomers' reactivity, provides more uniform polymer structures and makes better geometrical uniformity¹⁷⁸.

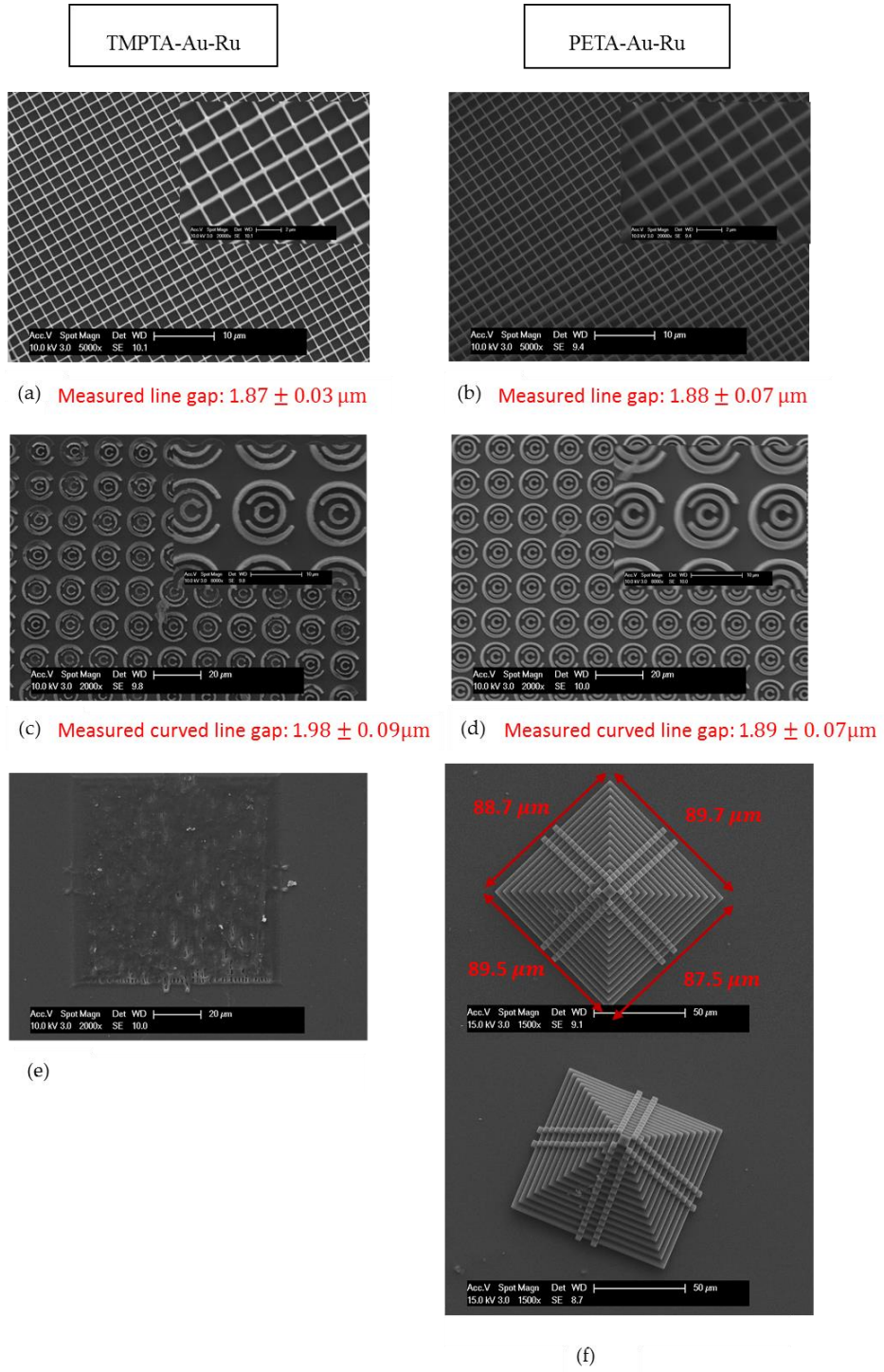


Figure 4.5 SEM images of 2D and 3D fabricated structures using formulations G3 and G6. (a), (c) and (e) show the results of fabricating increasingly more complex structures with formulation TMPTA-Au-Ru (b), (d) and (f) show the results of fabricating increasingly more complex structures with formulation PETA-Au-Ru. (f) shows both plan view and at a tilt angle of 30° .

Table 4.2 The minimum fabrication power (mW) for each formulation.

Formulation	Minimum fabrication power (mW)
TMPTA-Au	25.5
TMPTA-Au-Ru	22
PETA-Au	24
PETA-Au-Ru	20

4.3.5 UV-vis Spectra of Raw Materials

Figure 4.6 shows the optical absorption spectra of PETA, TMPTA, gold chloride hydrate, Irgacure 369 and ruthenium dye. All these materials were dissolved in isopropanol separately. No absorption band was detected at the laser wavelength of 780 nm, which indicated that the polymerisation and reduction were led by a two-photon absorption process. Irgacure 369 has two absorption peaks at 230 nm and 325 nm. The absorption peak at 230 nm is attributed to the typical π - π^* transition, while the peak at 325 nm corresponds to the electronic transition from the ground state to the intramolecular charge transfer (ICT) state^{83, 179}. In the case when a 780 nm NIR fibre laser was used, depending on the concentration of Irgacure 369 in the resin, TPA can occur in which two 390 nm photons were absorbed simultaneously if the laser intensity reached a certain threshold value⁴⁴. $[\text{Ru}(\text{bipy})_3]^{2+}$ shows three absorption peaks. 250 and 280 nm are related to π - π^* transition and 450 nm is the absorption peak of 3MLCT, which is the Ru to bipy ligands charge transfer excitation¹⁸⁰.

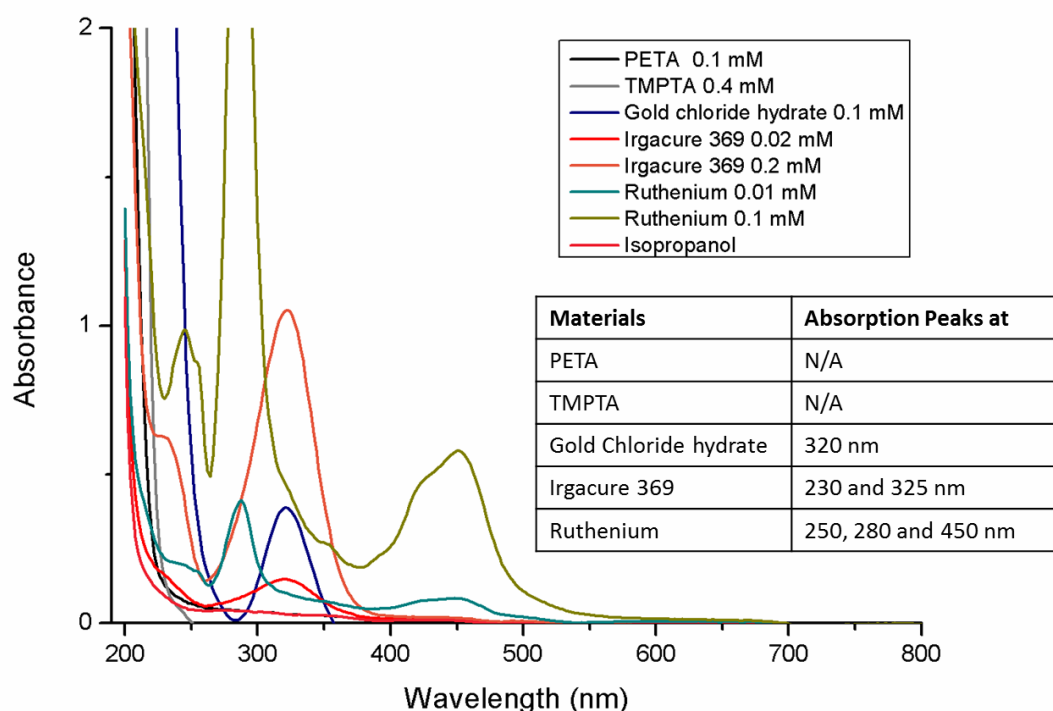


Figure 4.6 Normalised UV-vis absorption spectra of pure isopropanol, PETA is isopropanol, TMPTA in isopropanol, gold chloride hydrate in isopropanol, Irgacure 369 and ruthenium dye in isopropanol with different concentrations.

4.3.6 Line Width Measurement

To examine further the processing differences for each gold-containing formulation (TMPTA-Au, TMPTA-Au-Ru, PETA-Au and PETA-Au-Ru), single lines were written using laser powers ranging from 10 to 50 mW in increments of 5 mW (**Figure 4.7**). Line width was measured from SEM and shown in **Figure 4.8**. Degassing had a great effect on the line width of the formulations using TMPTA as a monomer. Without degassing, the presence of oxygen is likely to consume a proportion of free radicals resulting in a reduction in the number of radicals available for polymerization

propagation. Therefore, TMPTA-Au without degassing shows thinner lines than TMPTA-Au with degassing. Adding Ru (II) dye decreased the minimum laser power for line measurement (from 10 to 50 mW, the minimum laser power that lines were clear enough to be observed and measured) from 35 mW (TMPTA-Au without degassing) to 25 mW (TMPTA-Au-Ru without degassing) and from 35 mW (TMPTA-Au with degassing) to 30 mW (TMPTA-Au-Ru with degassing). The result further emphasizes the role that additional Ru (II) dye has a positive effect on eliminating the competition between photopolymerisation and photoreduction. When used PETA as a monomer, PETA-Au-Ru without degassing shows the smallest line width (149.0 ± 4.0 nm, 20 mW), which was the highest resolution achieved. Compared to TMPTA, lower minimum laser power for line measured were needed, which means that PETA based materials can be easier to be fabricated with higher polymerisation efficiency. The methyl group in TMPTA led to less shrinkage than PETA. Therefore, the line width of TMPTA formulations was higher than PETA formulations¹⁷⁸. It was found that the presence of oxygen mainly decreased line width and the presence of Ru (II) dye mainly decreased minimum laser power for the line measurements.

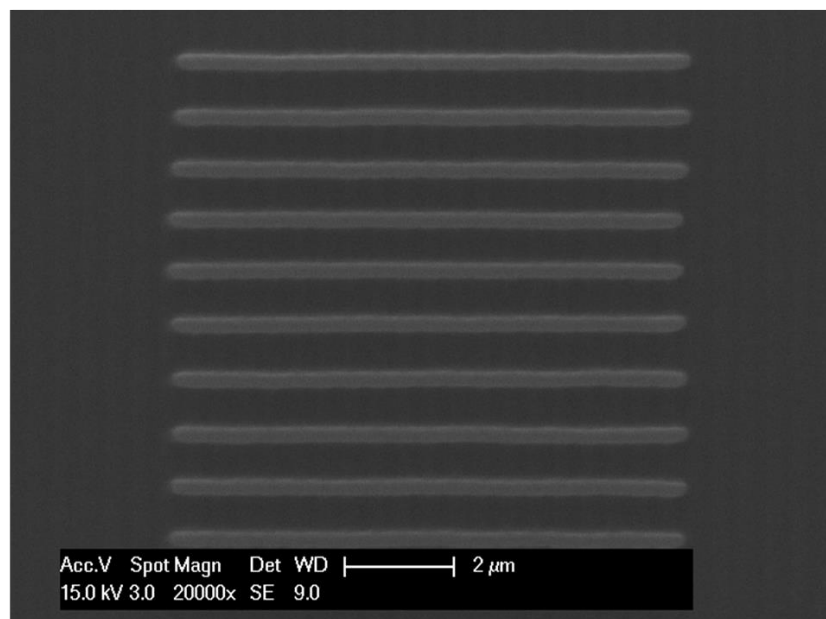


Figure 4.7 a typical set of fabricated lines (formulation PETA-Au-Ru without degassing, 35 mW).

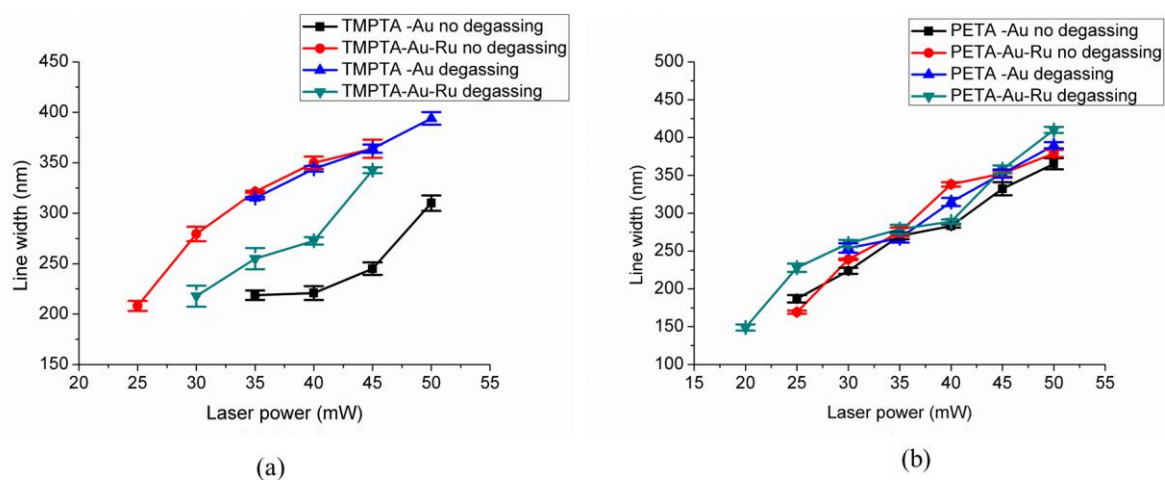


Figure 4.8 (a) Line width as a function of laser power for formulation TMPTA-Au and TMPTA-Au-Ru, with & without degassing and (b) line width as a function of laser power for formulation PETA-Au and PETA-Au-Ru, with & without degassing.

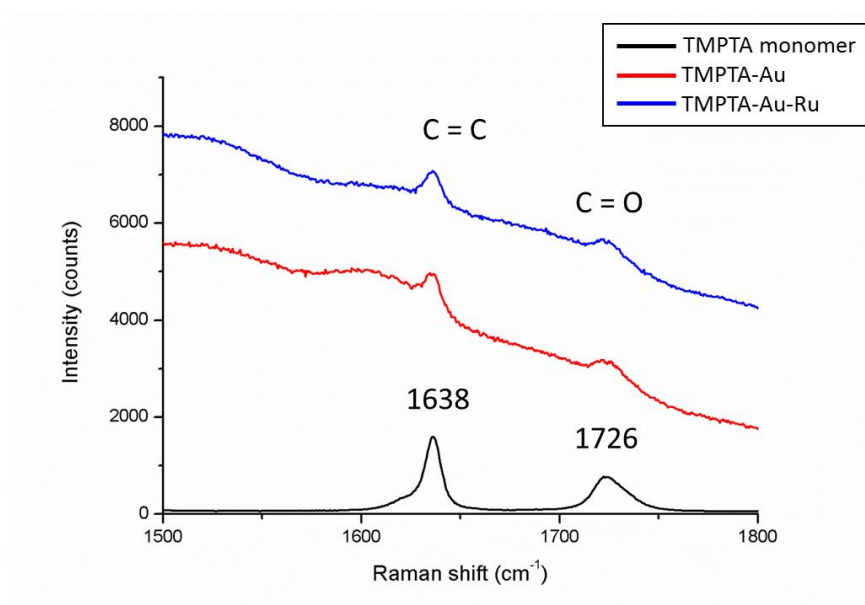
4.3.7 Degree of conversion (DC) measured by using Raman Spectroscopy

Raman spectra of samples TMPTA-Au, TMPTA-Au-Ru, PETA-Au and PETA-Au-Ru and of the monomers were obtained and the degree of conversion (DC) for the samples was calculated using the ratios of areas of the peaks associated with displacement of the C=C and C=O bonds in the polymer materials (**Figure 4.9**)¹⁸¹. Two distinctive peaks were observed at 1638 and 1726 cm⁻¹, which represent the C=C and C=O groups respectively. The C=C bonds were reduced to C–C bonds during polymerisation resulting in a reduction of intensity at 1638 cm⁻¹, while the intensity of C=O is unaffected due to the non-participation of the bond in the reactions. The degree of conversion, Δ , can thus be calculated from:

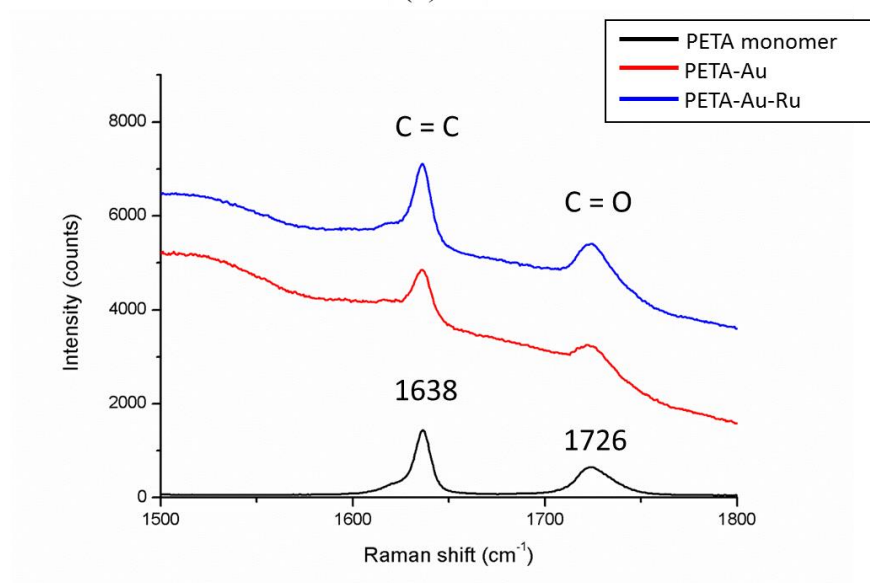
$$\Delta = 1 - \frac{A_{\text{C=C}}/A_{\text{C=O}}}{A'_{\text{C=C}}/A'_{\text{C=O}}} \quad \text{Equation 4.1}$$

where $A_{\text{C=C}}$, $A_{\text{C=O}}$, $A'_{\text{C=C}}$ and $A'_{\text{C=O}}$ are the peak intensities in the Raman spectra related to the C=C and C=O groups in the polymerised structures and the non-polymerised monomers. It relies on the assumption that disproportionated C=C bonds are not produced, but it is likely that they are present and as a consequence, the calculation of the degree of conversion represents an estimate of the lower bound¹⁸¹. Using Equation 4.1, the estimated degrees of conversion for each of the samples produced from the formulations were calculated and are shown in **Table 4.3**. It indicated a greater degree of conversion for PETA compared to TMPTA, correlating with observations of more uniform and stable structures for PETA monomer. The presence of Ru (II) also promoted the conversion that reduced the competition between photopolymerisation and photoreduction¹⁰. Ru (II) complex reduced gold

ions and the free radicals generated from Irgacure 369 initiated the polymerisation processes.



(a)



(b)

Figure 4.9 Raman spectra of polymerised structures using formulations TMPTA-Au and TMPTA-Au-Ru and unpolymerised TMPTA monomer (b) Raman spectra of polymerised structures using formulations PETA-Au and PETA-Au-Ru and unpolymerised PETA monomer.

Table 4.3 Calculated DC values formulation TMPTA-Au, TMPTA-Au-Ru, PETA-Au and PETA-Au-Ru

Formulation	Degree of conversion, $\Delta\%$
TMPTA-Au	41.6 ± 5.2
TMPTA-Au-Ru	44.5 ± 6.5
PETA-Au	49.6 ± 4.8
PETA-Au-Ru	58.8 ± 8.0

4.3.8 Characterisation of the Presence of Gold within Gold-polymer Nanocomposites

In order to confirm the presence of gold within the 3D structure (formulation PETA-Au), a build was halted midway during the fabrication of the pyramid structure. SE and BSE SEM and images from EDX of the semi-fabricated structures were then obtained (Figure 4.10 (a)). Gold particles were observed from the BSE images (Figure 4.10 (b)). The average particle size measured from the image by Image J was 123.8 ± 100.7 nm (Figure 4.10 (c)). Gold was detected using EDX from the flat surface (Figure 4.10 (d)). The spectra of particles at locations 1, 2 and 3 showed two clear Au peaks at 2.2 and 9.7 eV (shown for location 3 in Figure 4.10 (e)). A Cl peak was determined at around 2.8 eV. A qualitative comparison was then performed between the expected area ratio ($\sim 1:4$, Gold to Chlorine) and the observed area ratio of the main peaks. The observed area ratio of the main peaks for each element was found to be 5.3:1 (Gold to Chlorine), pointing towards the formation of elemental gold. A similar inspection of a 3D object fabricated using formulation PETA-Au-Ru (Figure 4.11) shows the presence of elemental gold through a large Au peak at 2.2 eV with no

significant Cl peak.). Gold particles were observed from the BSE images (**Figure 4.10** (b)). The average particle size measured from the image by Image J was 123.8 ± 100.7 nm (**Figure 4.10** (c))). Gold was detected using EDX from the flat surface (**Figure 4.10** (d)). The spectra of particles at locations 1, 2 and 3 showed two clear Au peaks at 2.2 and 9.7 eV (shown for location 3 in **Figure 4.10** (e)). A Cl peak was determined at around 2.8 eV. A qualitative comparison was then performed between the expected area ratio (~1:4, Gold to Chlorine) and the observed area ratio of the main peaks. The observed area ratio of the main peaks for each element was found to be 5.3:1 (Gold to Chlorine), pointing towards the formation of elemental gold. A similar inspection of a 3D object fabricated using formulation PETA-Au-Ru (**Figure 4.11**) shows the presence of elemental gold through a large Au peak at 2.2 eV with no significant Cl peak.

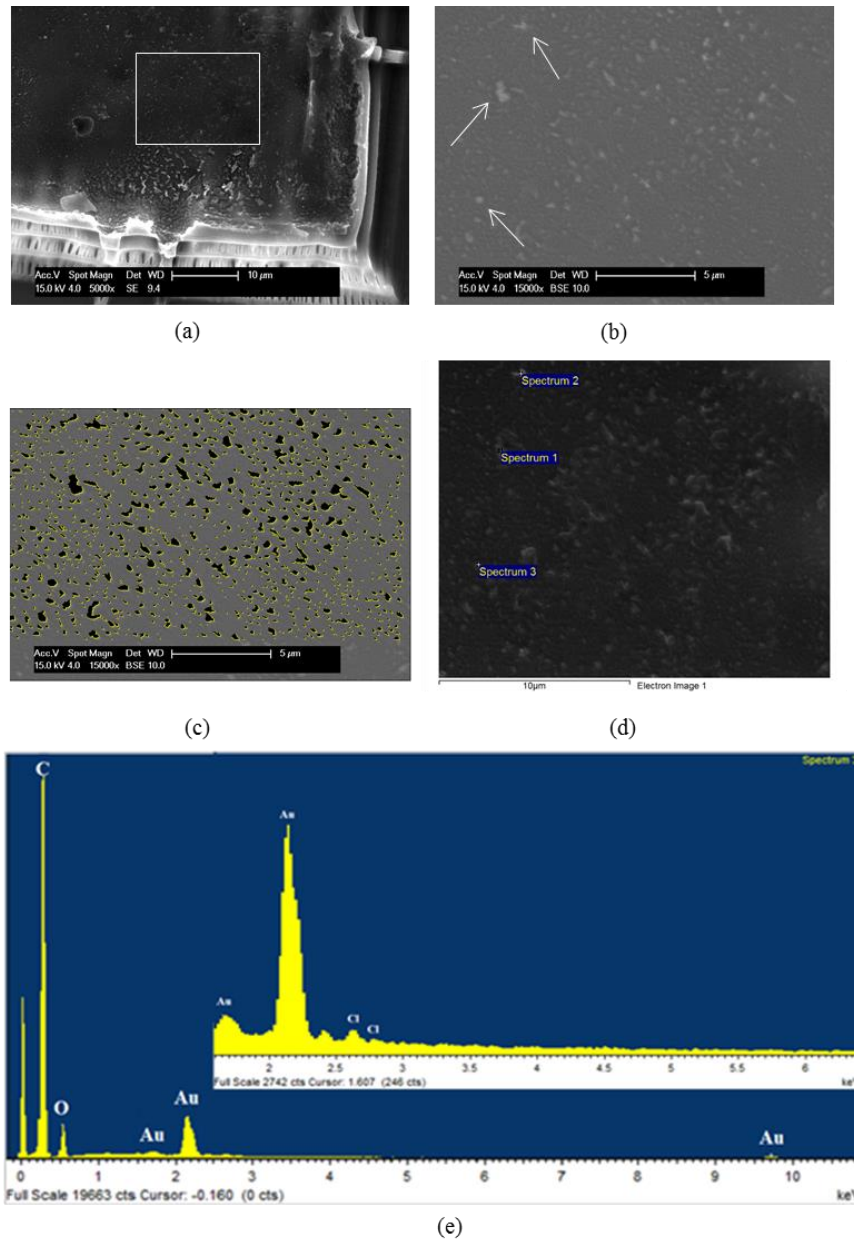
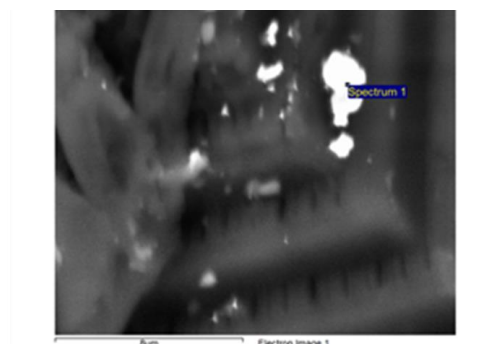
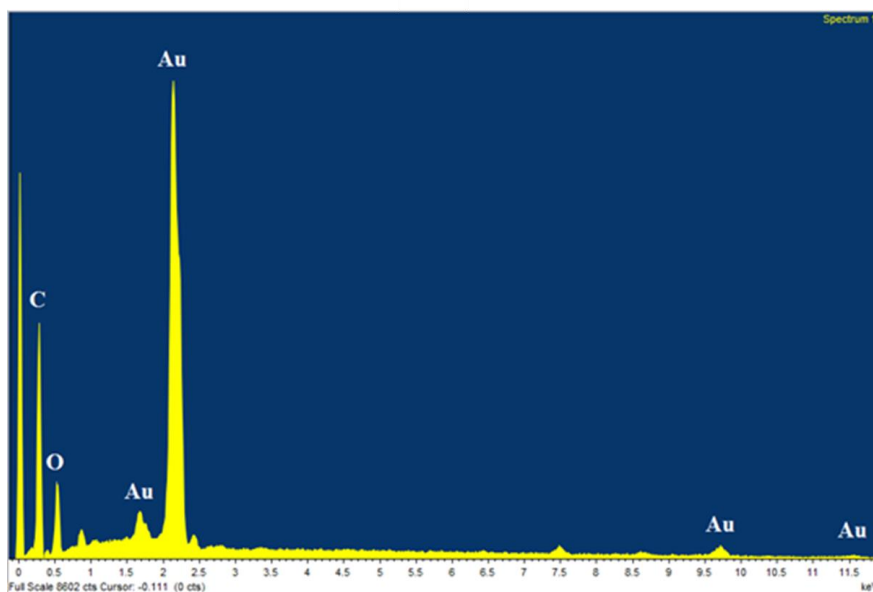


Figure 4.10 (a) Scanning electron microscope (SEM) image of a part completed 3D fabrication using formulation PETA-Au; (b) A backscattered electron (BSE) image of the fabricated structure from (a) showing the location of suspected gold particles at higher magnification; (c) ImageJ gold particle analysis; (d) SEM image of Energy-dispersive X-ray spectroscopy (EDX) of the area, and (e) EDX spectrum of the particles at Location 3.



(a)



(b)

Figure 4.11 (a) A backscattered electron (BSE) image showing the presence of suspected gold particles at the surface of a structure fabricated using formulation PETA-Au-Ru; (b) An Energy-dispersive X-ray spectroscopy (EDX) spectrum of the particle located at Position 1 in (a), indicating the presence of elemental gold.

Furthermore, XPS analysis showed the presence of a small amount of gold (<0.1 atomic %) on the sample surface ($\overline{[001]}$). XPS is a surface-sensitive technique which excites photoelectrons that have relatively short attenuation lengths of 3–5 nm in polymers. Therefore the information depth for XPS analysis is about 10 nm for a typical 1000 eV photoelectron excited by the standard Al K alpha X-ray source

(1486.6 eV). A large area of analysis approximately $300 \times 700 \mu\text{m}$ was used, so some signal was observed from the surrounding substrate. Therefore, the true concentration of gold element should be higher than 0.1 atomic%. The full-scan spectra that include background elements were shown in Appendix A Figure A1. In order to analyse the elemental state of gold, high sensitivity/low-resolution spectra at pass energy 80 eV were used to obtain the Au 4f energy region in an attempt to ascertain if gold was present in the structures. The Au 4f peak for bulk gold is normally observed at 84 eV; ¹⁸²⁻¹⁸³ a broad feature was observed at higher binding energy, which may be associated with the unreacted starting material gold chlorides, and a smaller feature was observed at $83.6 \pm 0.2 \text{ eV}$ which is likely to be the Au 4f $7/2$ peak usually associated with the Au metallic state for the NPs. From these techniques, therefore, it can be concluded that gold ions were reduced to metallic gold particles on structure surface and simultaneous photopolymerisation and photoreduction to fabricate gold-polymer nanocomposites was achieved.). XPS is a surface-sensitive technique which excites photoelectrons that have relatively short attenuation lengths of 3–5 nm in polymers. Therefore, the information depth for XPS analysis is about 10 nm for a typical 1000 eV photoelectron excited by the standard Al K alpha X-ray source (1486.6 eV). A large area of analysis approximately $300 \times 700 \mu\text{m}$ was used, so some signal was observed from the surrounding substrate. Therefore, the true concentration of gold element should be higher than 0.1 atomic%. The full-scan spectra that include background elements were shown in Appendix A Figure A1. In order to analyse the elemental state of gold, high sensitivity/low-resolution spectra at pass energy 80 eV were used to obtain the Au 4f energy region in an attempt to ascertain if gold was present in the structures. The Au 4f peak for bulk gold is normally observed at 84 eV; ¹⁸²⁻¹⁸³ a broad feature was observed at higher binding energy, which may be associated

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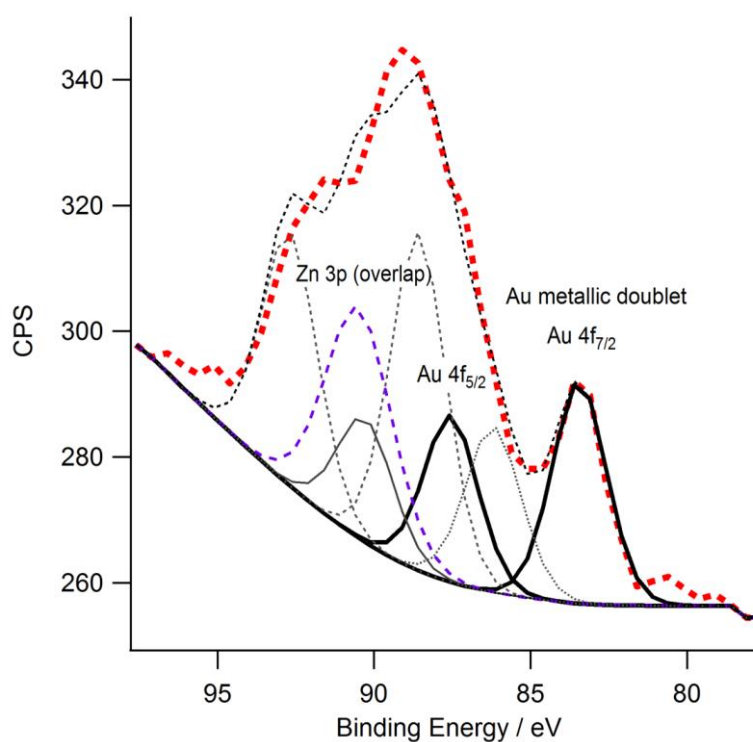


Figure 4.12 An X-ray photoelectron spectroscopy spectrum determined for a partially completed 3D build of formulation PETA-Au. The peak at 83.6 ± 0.2 eV was identified as signalling the presence of gold NPs proximal to the exposed surface. The remainder of the peaks is associated with gold in other, unreduced, states and with Zn from the surrounding substrate glass.

4.4 Conclusions

- Adding additional Irgacure 369 photoinitiator in commercial IPL-780 resin is not suitable for fabricating gold-polymer nanocomposites. The competition between photopolymerisation and photoreduction makes it difficult to form uniform composite structures. Gold ions consume free radicals so that polymer structures are too weak to form structures as designed.
- Both TMPTA and PETA are suitable monomers for two-photon polymerisation (TPP) when Irgacure 369 is used as a photoinitiator. Polymer 2D straight lines, 2D cured lines and 3D pyramid structures were printed as designed. PETA is a more efficient monomer compared to TMPTA. Shrinkage after printing processes and sample development stage should be considered when designing a structure.
- For the first time, 3D gold-polymer composite structures were fabricated, and simultaneous photoreduction (from gold ions to metallic gold) and photopolymerisation (from monomers to polymers) were confirmed by Raman spectroscopy and XPS.
- Ruthenium (II) complexes are useful material for promoting gold reduction¹⁰. In this thesis, ruthenium (II) dye was found useful to reduce the competition between photoreduction and photopolymerisation. It also reduced laser power for fabricating composite structures. Additional ruthenium (II) dye was the key component to fabricate 3D complex structures.
- This work started with some preliminary investigation to fabricate 3D composite structures, confirm the presence of gold particles on structure surface and analyse the chemical state of generated gold particles. Fabricating 3D gold-polymer nanocomposite structures provides a promising application

in metamaterials. According to the literature, the surface plasmon resonance of gold particles is size related¹⁵⁷⁻¹⁵⁸. Particle sizes from 100 -400 nm have broader peaks and particle sizes below 2 nm do not have surface plasmon resonance. The average size measured from SEM sample surface was 123.8 ± 100.7 nm. Smaller sizes in tens of nanometre size could not be seen from the SEM used so higher magnification SEM or TEM imaging is suggested in future work. More analyses on gold particles are needed in the future, such as size & shape measurement on gold NPs within composite structures. In microelectronic applications, continuous metal structures are important to form conductive structures³⁹. Therefore, analysing the real concentration of gold nanoparticles and the minimum gold concentration for conductive composites are suggested to be the next step in future work.

5 Silver-polymer Nanocomposite

5.1 Introduction

The combination of photoreduction and photopolymerisation brings the promise to produce metal nanocomposites with high resolution and complexity. Liu et al.¹⁸⁴ and Hu et al.¹⁷⁷ fabricated 3D gold-polymer composite structures using simultaneous photopolymerisation and photoreduction. In addition to gold, silver NPs are another attractive type of metallic NPs due to their good conductivity, chemical stability, catalytic behaviour, optical properties (e.g. SPR) and antimicrobial properties^{19, 185}. No researches have been done on simultaneous photopolymerisation and photoreduction of silver-polymer nanocomposites yet. In this section, 3D silver-polymer nanocomposites were presented by simultaneous photopolymerisation and photoreduction. A phase-transfer method¹⁸⁶ that transferred silver ions from water to an organic medium was introduced to improve the compatibility of silver salt in a triacrylate-based monomer.

5.2 Water-Soluble Materials for Silver-polymer Nanocomposites

From the literature, silver nitrate is one of the most common silver sources used in TPR^{9, 34-35, 37-38, 40, 45, 112-113, 115, 120, 122, 124}. Silver nitrate is inorganic salt and is soluble in water, but it is insoluble or slightly soluble in most organic solvents¹⁵⁹. Therefore,

a suitable selection of monomers, photoinitiators, solvents and photosensitive dyes is a crucial step for the fabrication of stable silver-polymer objects. Due to the high solubility of silver nitrate in water (256 g/100 mL, 25 °C¹⁵⁹), water-soluble photoinitiators and monomers for two-photon fabrication were first considered.

P2CK and E2CK are benzylidene ketone-based hydrophilic two-photon initiators. Carboxylic acid sodium salts were introduced at the end of amino groups to improve the solubility in water^{83, 87}. The large cross-section and wide processing window provide the possibility for the precise microfabrication of hydrogels such as PEGDA (water-soluble oligomer)⁸⁴. Silver nitrate and P2CK are both soluble in water. However, when aqueous solutions of silver nitrate and P2CK were mixed, small orange particles were precipitated, as shown in **Figure 5.1**. E2CK showed a similar result with an aqueous silver nitrate solution. The precipitation may be due to the combination of carboxylic acid ions in P2CK or E2CK and silver ions and the poor solubility of carboxylic acid silver salt in water.

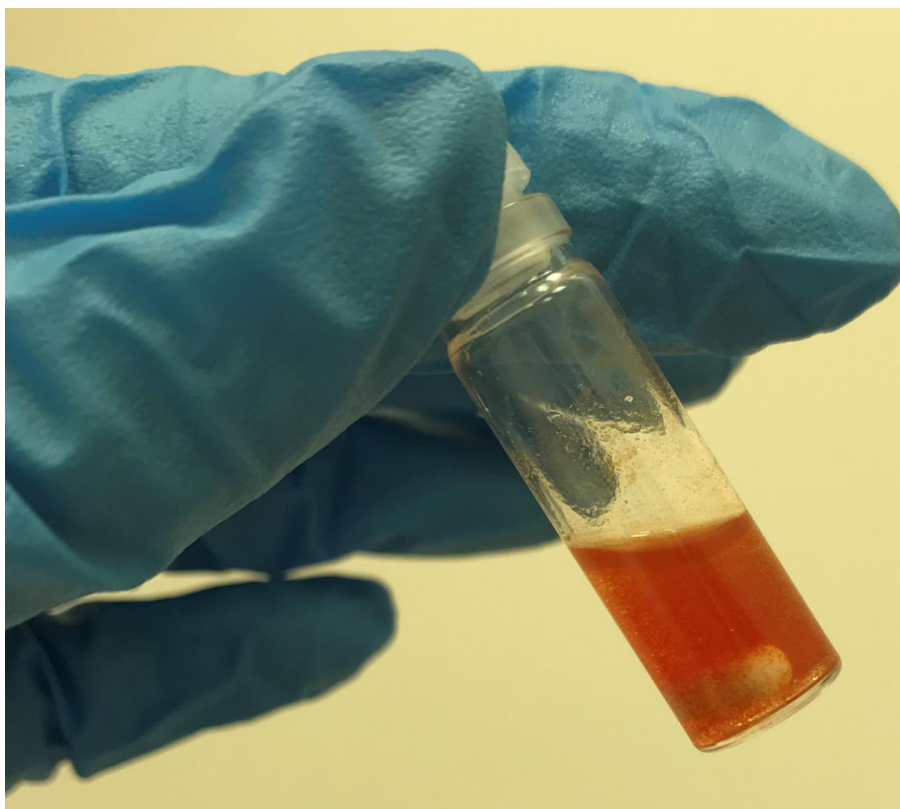


Figure 5.1 *Water-soluble photoinitiator P2CK and silver nitrate in water – orange particle precipitation in water.*

Irgacure 2959 is a commercial water-soluble photoinitiator used in TPP, especially in PEGDA. Nguyen et al.¹⁸⁷ reported that PEGDA was cross-linked using Irgacure 2959 by TPP and Blasco et al.¹³ presented using acrylate-functionalized poly(ethylene glycol) derivative (PEG-triacry) as an oligomer, Irgacure 2959 as a photoinitiator and gold chloride as a metal source to fabricate gold-containing bridge-like structure via simultaneous photopolymerisation and photoreduction. Research shows that benzoyl radicals generated from Irgacure 2959 have higher reactivity than alkyl radicals in polymerisation processes⁸⁵. The generated alkyl radicals are found useful to deliver electrons to metal ions and to reduce metal ions⁸⁶. In this thesis, PEGDA (1000 M_w) containing silver nitrate aqueous solutions with different concentrations of Irgacure

2959 were assessed to fabricated silver-polymer nanocomposites. A small amount of PETA or TMPTA was added to introduce more functional groups to increase the reaction rate and act as a crosslinking agent⁹⁰. **Table 5.1** shows the formulations with different concentrations of Irgacure 2959.

Table 5.1 Composition of 6 formulations for silver-polymer composites based on 1 wt% PETA or 1% TMPTA in PEGDA monomer systems with different photoinitiator concentrations.

	Irgacure 2959 wt% (1 wt% in water)	AgNO ₃ wt%	PEGDA:PETA (99:1 by weight)	PEGDA:TMPTA (99:1 by weight)
PEG-PETA-99:1-2595-1	1	10	89	N/A
PEG-PETA-99:1-2595-3	3	10	87	N/A
PEG-PETA-99:1-2595-5	5	10	85	N/A
PEG-TMPTA-99:1-2595-1	1	10	N/A	89
PEG-TMPTA-99:1-2595-3	3	10	N/A	87
PEG-TMPTA-99:1-2595-5	5	10	N/A	85

Figure 5.2 shows the SEM images of fabricated gear structures (designs are shown in **Figure 4.1** (a)-(b)) using 6 formulations in **Table 5.1**. Under the same processing conditions (scan speed 10000 $\mu\text{m/s}$ and laser power 50 mW), samples with the same amount of PETA and TMPTA did not show obvious differences. Higher amounts of photoinitiator of Irgacure 2959 did not improve the overall performance on structural geometry. The polymerisation was only observed when the laser power reached 35 mW and the samples contained at least 5 wt% Irgacure 2959. A minimum laser power of 40 mW was required to initiate polymerisation when the samples contained 1 or 3 wt% Irgacure 2959. The aggregation of silver particles and local heating were observed during laser fabrication. The composition between photopolymerisation and photoreduction led to weak polymerisation process so that the polymer structures were

not enough to hold silver particles. Therefore, silver particles just aggregated and agglomerated on the glass substrate. Polymer lines were not clear and difficult to distinguish from SEM images. The fabrication of 3D silver-polymer structures was a challenge, as there were not enough supportive polymer structures to hold silver particles in the Z direction.

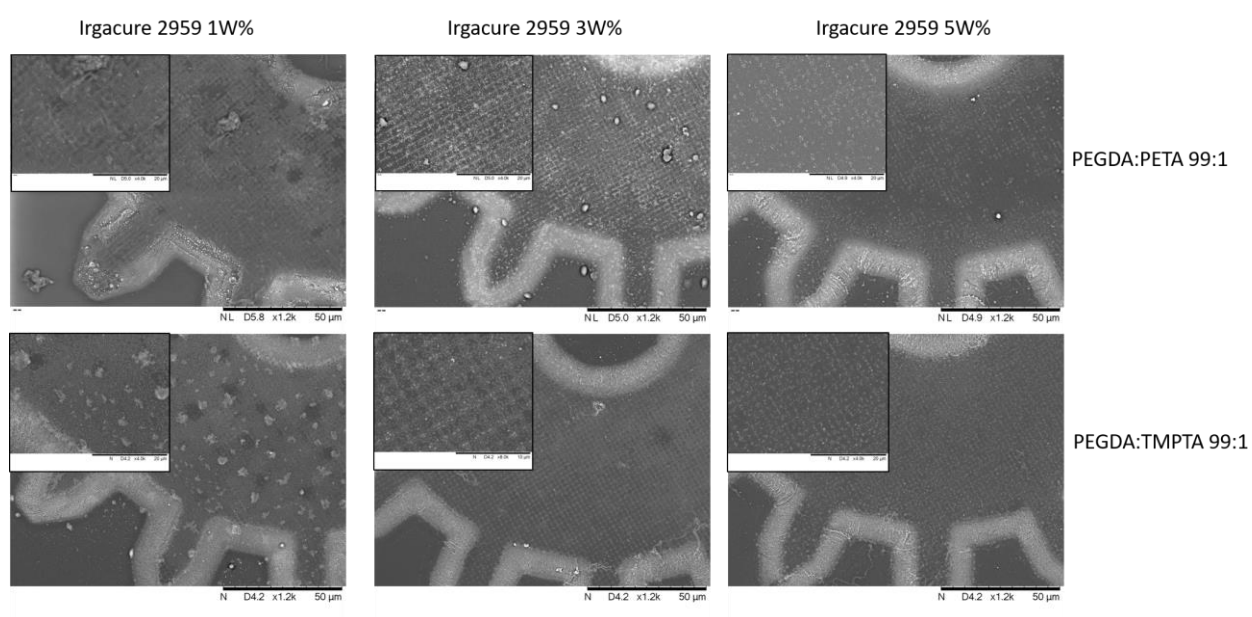


Figure 5.2 SEM images of fabricated structures using 1 wt% PETA and 1 wt% TMPTA in PEGDA as monomer systems, respectively, and different Irgacure 2959 concentrations. (6 formulations in Table 5.1)

By adding a higher amount of PETA or TMPTA (**Table 5.2**), the polymerisation rate can be improved due to higher functionality and polymer structures may be stronger due to higher crosslink density⁹⁰. **Figure 5.3** shows fabricated gear structures with different amount of PETA or TMPTA under the same processing conditions (10000μm/s, laser power 50 mW). Compared to 1 wt% PETA or TMPTA in PEGDA, 3 wt% PETA or TMPTA in PEGDA gave more structure details and clearer grid lines

in gear structures. Adding 5 wt% PETA or TMPTA in PEGDA made denser structures and particles were held by polymers. Nevertheless, the fabricated structures were just 2D and lost many structural details. Presumably, this was due to the low efficiency of Irgacure 2959 in our two-photon fabrication system and low polymerisation rate of PEGDA in TPP. From the literature, TPP rate of PEGDA containing 2 wt% Irgacure 2959 upon 780 nm laser was prohibitively slow¹⁸⁷. Irgacure 2959 has a peak absorption at around 285 nm and low at 390 nm, which means that Irgacure 2959 is not likely the best choice as a photoinitiator in TPA with a 780nm laser⁸⁴. The absorption poorly matched with laser wavelength limited the initiation rate of polymerisation¹⁸⁸. In addition, lower functionality of PEGDA compared to higher functionality such as triacrylate monomers generally gives a lower reaction rate in TPP⁹⁰. In conclusion, it is difficult to obtain suitable formulations using water-soluble photoinitiators and monomers to fabricate silver-polymer nanocomposites by TPL system used in this thesis with Nanoscribe system. To overcome the problems, solutions are: 1) exploring more water-soluble photoinitiators that are compatible with silver salt and monomers, 2) using a suitable laser beam for Irgacure 2959 photoinitiator, or 3) using Irgacure 369 photoinitiators and PETA monomers, improving the solubility of silver salt and mixing these components in a solvent. Option 3 is the most straightforward solution and the details were introduced in section 5.3.

Table 5.2 Composition of 3 formulations for silver-polymer composites based on 1, 3 and 5 wt% PETA or TMPTA in PEGDA monomer systems.

	Irgacure 2959 wt%	AgNO ₃ wt%	PEGDA:PETA
PEG-PETA-99:1-2959-3	3	10	99:1

PEG-PETA-97:3-2959-3	3	10	97:3
PEG-PETA-95:5-2959-3	3	10	95:5
PEG-TMPTA-99:1-2959-3	3	10	99:1
PEG-TMTPA-97:3-2959-3	3	10	97:3
PEG-TMPTA95:5-2959-3	3	10	95:5

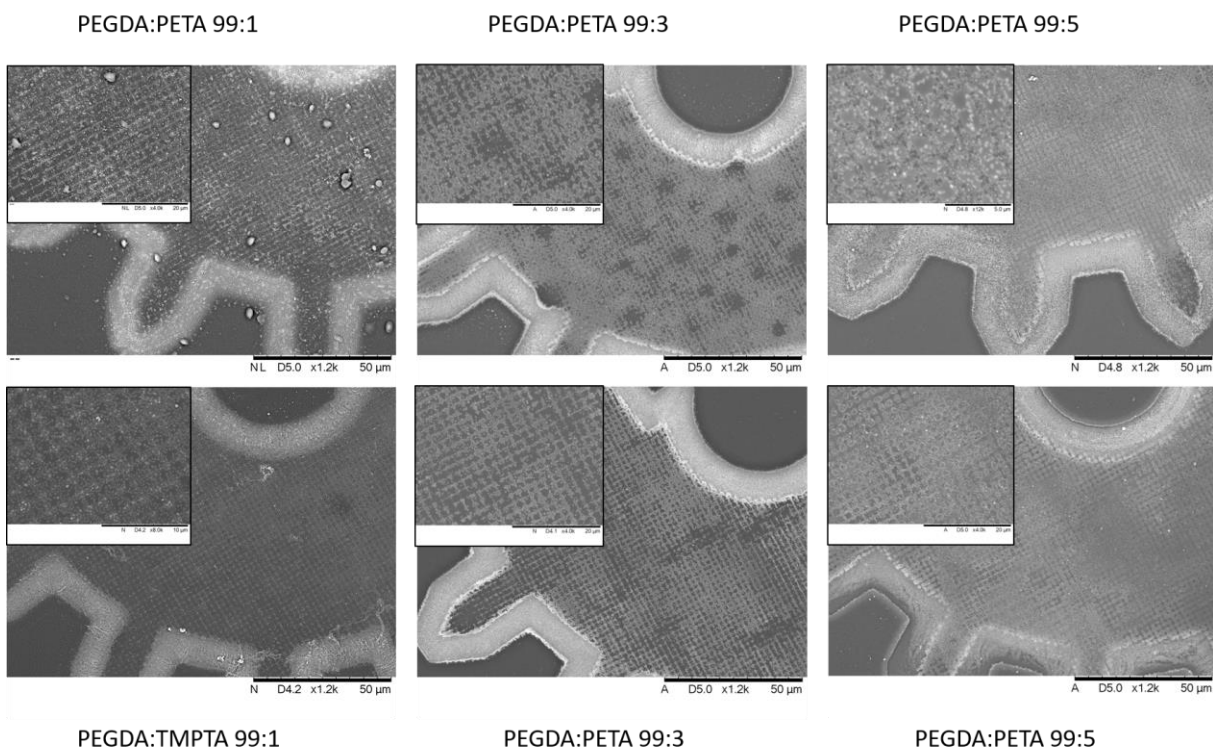


Figure 5.3 SEM images of fabricated structures using 1,3 and 5 wt% PETA and 1, 3 and 5 wt% TMPTA in PEGDA as a monomer, respectively. (6 formulations in Table 5.2).

5.3 Phase-transfer Protocol for Silver-polymer Nanocomposites by Two-photon Fabrication

It was challenging to find a suitable water-soluble monomer and photoinitiator for the fabrication of silver-polymer nanocomposites by simultaneous photopolymerisation

and photoreduction. Finding a suitable solvent for silver nitrate, monomers and photoinitiator with high polymerisation efficiency was also a challenge. PETA and Irgacure 369 are applicable for two-photon fabrication and successfully used in gold-polymer fabrication. Therefore, in order to deal with the solubility problems of silver nitrate, PETA and Irgacure 369, a phase-transfer protocol that transfers silver ions from the water phase to organic toluene phase, was introduced¹⁸⁶. Coumarin 30 photosensitive dye has been reported that it promotes the silver reduction⁹, so it was added in the formulations for fabricating silver-polymer nanocomposites. Successful fabrication of silver-polymer nanostructures was subsequently achieved.

5.3.1 Sample Preparation

To prepare the materials of silver-polymer nanocomposites for two-photon fabrication, the following steps were taken. Firstly, the silver ions were transferred from water to toluene. 1 mL of 0.5 M aqueous silver nitrate solution was mixed with 1 mL of ethanol containing DDA (Dodecylamine) with the mole ratio of DDA: silver nitrate of 10:1. After 5 min of stirring, 1 mL of toluene was added and the mixer was stirred for 5 min. The silver ions in toluene were separated from the aqueous phase and the aqueous phase was bleached (no white drops in transparent toluene phase). The concentration of silver in toluene would be 0.5 M. The aqueous phase remained to be analysed by inductively coupled plasma atomic emission spectrophotometry to calculate the transfer efficiency (shown in section 5.3.2). Then, 1, 3 and 5 wt% Irgacure 369 were added to PETA separately. 0.5 M silver ions in toluene with the molar ratio of silver ions: PETA 1:5 and 0.1 wt % Coumarin 30 photosensitive dye were added to the photoresist, resulting in 6 formulations (**Table 5.3**). The additives were mixed using a magnetic stirrer operating at a speed of 600 rpm for 30 min. After processing, the

sample on the glass slide was developed by washing in PGMEA, 2-propanol and water to remove the unreduced silver salt and residual monomer. As a final step, the samples were dried in air for 24h before any characterisation.

Table 5.3 Composition of 6 formulations for silver-polymer nanocomposites in PETA monomer system.

Formulation	PETA wt%	Irgacure 369 wt%	Coumarin 30 (dye) wt%	PETA : Ag ⁺ (mole ratio)
1%-polymer	99	1		
1%-composite	99	1		5:1
1+0.1%-composite	98.9	1	0.1	5:1
3%-polymer	97	3		
3%-composite	97	3		5:1
3+0.1%-composite	96.9	3	0.1	5:1
5%-polymer	95	5		
5%-composite	95	5		5:1
5+0.1%-composite	94.9	5	0.1	5:1

5.3.2 Phase Transfer of Silver Ions from Water to Toluene Phase

In the phase transfer process, a silver DDA complex (Ag-DDA) was formed and it can be then extracted by toluene because the ethanol acted as an intermediate solvent ensuring the maximum contact between silver ions and DDA. The non-polar tail of DDA helps the compounds to dissolve in non-polar toluene solvent¹⁶¹. **Figure 5.4** shows the phase separation of silver in the toluene phase and the aqueous phase.

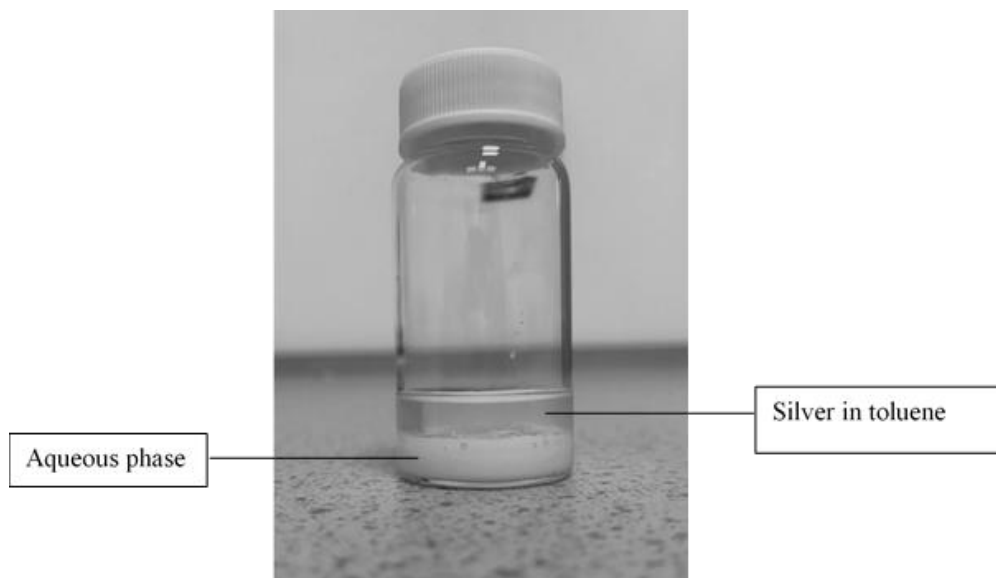


Figure 5.4 Photograph of successful transfer of silver ions from the aqueous phase to toluene.

The transfer efficiency (TE) was analysed by ICP-AES and calculated using the equation:

$$\text{TE (\%)} = 100 ([M^{n+}]_i - [M^{n+}]_f) / [M^{n+}]_i \quad \text{Equation 5.1}$$

where $[M^{n+}]_i$ and $[M^{n+}]_f$ were the silver concentrations in the aqueous phase after and before the silver transfer, respectively. The concentrations of silver ions were measured at two emission wavelengths (328.068 nm and 338.289 nm).

Table 5.4 The concentrations of silver ions before and after phase transfer (in ppm).

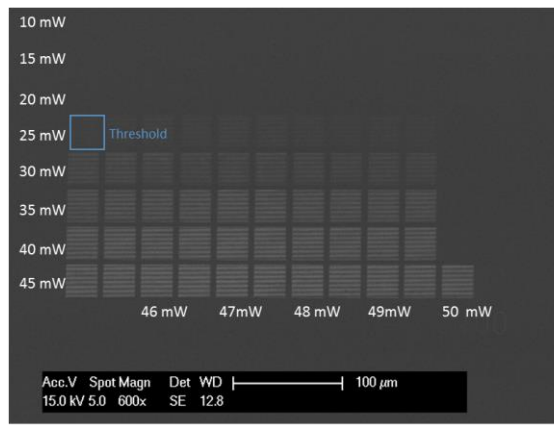
	Concentrations at 328.068 nm	Concentrations at 338.289 nm	Average Silver concentration
Before phase transfer	55.600 ± 0.470	54.420 ± 0.990	55.010 ± 0.930
After phase transfer	-0.368 ± 0.001	-0.332 ± 0.001	-0.350 ± 0.020

The concentration of silver ions after phase transfer was -0.350 ppm within the experimental error of ± 0.4 ppm. Therefore, the silver ions were completely transferred from the water phase to the toluene phase.

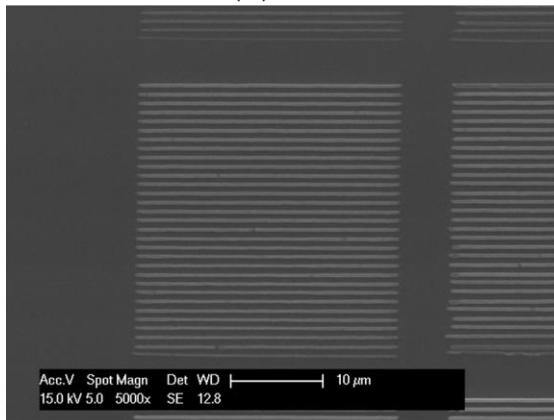
5.3.3 The Effect of Irgacure 369 Concentration and Presence of Coumarin 30 Dye in Silver-polymer Nanocomposites on Line Width

Single line structures (**Figure 5.5**) were written and the line width was measured by SEM XL30 (Philips, Netherlands) with different concentrations of Irgacure 369 (1, 3 and 5 wt%), with or without coumarin 30 dye and different laser power (0 - 50 mW in increments of 0.5 mW). The minimum laser power (threshold laser power) for writing a single clear line was obtained and compared in **Figure 5.6**. The addition of coumarin 30 dye decreased the threshold laser power especially for the formulations with 1% Irgacure 369 (from 25.0 ± 0.6 mW to 20.2 ± 0.7 mW). Similar results have been found in Ishikawa et al.'s work⁹. The result indicates that additional coumarin 30 dye helps silver reduction and reduces required laser power. Coumarin 30 is an organic donor-acceptor dye containing an electron-releasing substituent, diethylamino group, and an electron-withdrawing substituent, methylbenzimidazolyl group¹⁸⁹. These functional groups allow intramolecular charge transfer and optical absorption tuning. Under excitation, electrons were transferred from the donor to the acceptor and to the silver ions that promote to the photosensitised reduction. Without coumarin

dye 30, samples with a higher concentration of photoinitiator showed the lower threshold of laser power. Compared 5%-composite to 1%-composite, the threshold laser reduced around 32%. It is attributed to a higher probability of radical formation with more photoinitiator, thus reducing the threshold energy accordingly¹⁷⁷. The threshold laser power for different structures may be different. Sometimes it may be lower for more complex 3D structures due to the heat generated during the writing processes.



(a)



(b)

Figure 5.5 An example of SEM images showing fabricated line structures using different laser power (formulation 1%-composite) (a) line structures fabricated using laser power from 10-50 mW; (b) lines fabricated using 45 mW.

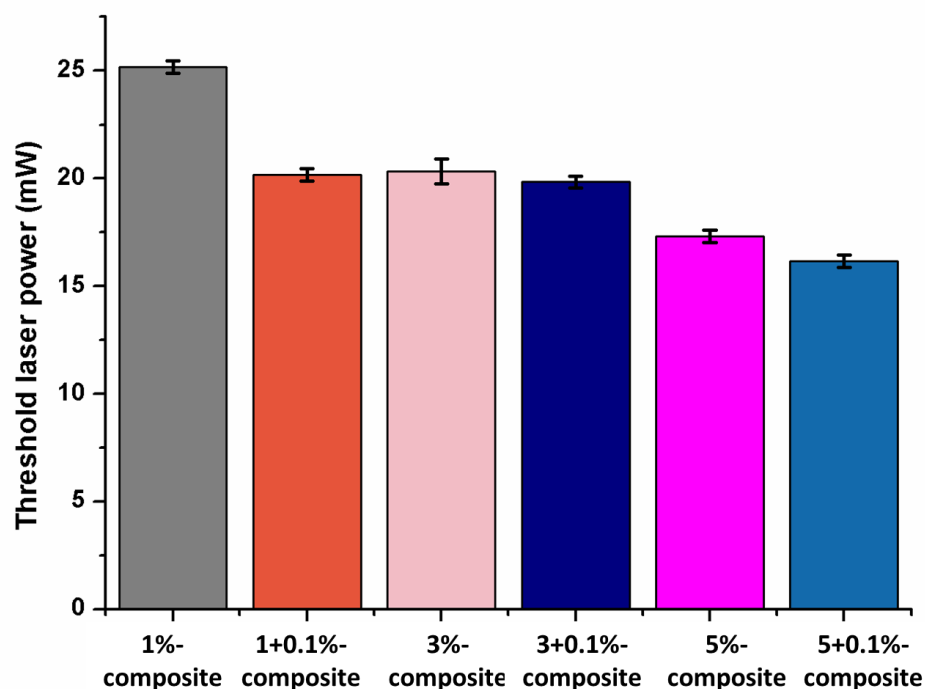


Figure 5.6 The threshold laser power (mW) for each formulation.

Line width was measured by SEM with different concentrations of Irgacure 369 (**Figure 5.7**). Even though 0.2 wt % Irgacure 369 in PETA is sufficient for polymerisation, in order to compare to silver-polymer composites, polymers without silver materials also contained 1, 3 and 5 wt% Irgacure 369. **Figure 5.7** (a) illustrates that line width of both polymer and silver-polymer composites increase with the increasing Irgacure 369 concentration prepared under the same processing conditions (scan speed 10000 $\mu\text{m/s}$ and laser power 30 mW). Line width increased from 319.4 ± 11.1 nm, 343.2 ± 15.9 nm to 385.6 ± 19.2 nm. Compare silver-polymer composites to polymers, adding silver increased the line width. The line width of 5%-polymer was 385.6 ± 19.2 nm while the line width of 5%-composite was 605.0 ± 15.7 nm. With extra

coumarin 30 dye, the line width dropped compared to the composites without dye and gave higher resolution. When 0.1 wt% coumarin 30 dye was added, the line width of 5+0.1%-composite was decreased to 547.0 ± 11.4 nm. **Figure 5.7** (b) shows the relationship between the line width and the concentrations of Irgacure 369 and different laser power. Generally, a higher concentration of Irgacure 369 increased the line width. It was the result of more radicals that drove polymerisation and improved the degree of polymer conversion. Also, wider lines came with higher laser power. The line structures were likely to be burnt at high laser power when 3 wt% and 5 wt% Irgacure 369 were involved and it led to a smaller processing window than the formulation with 1 wt% Irgacure 369.

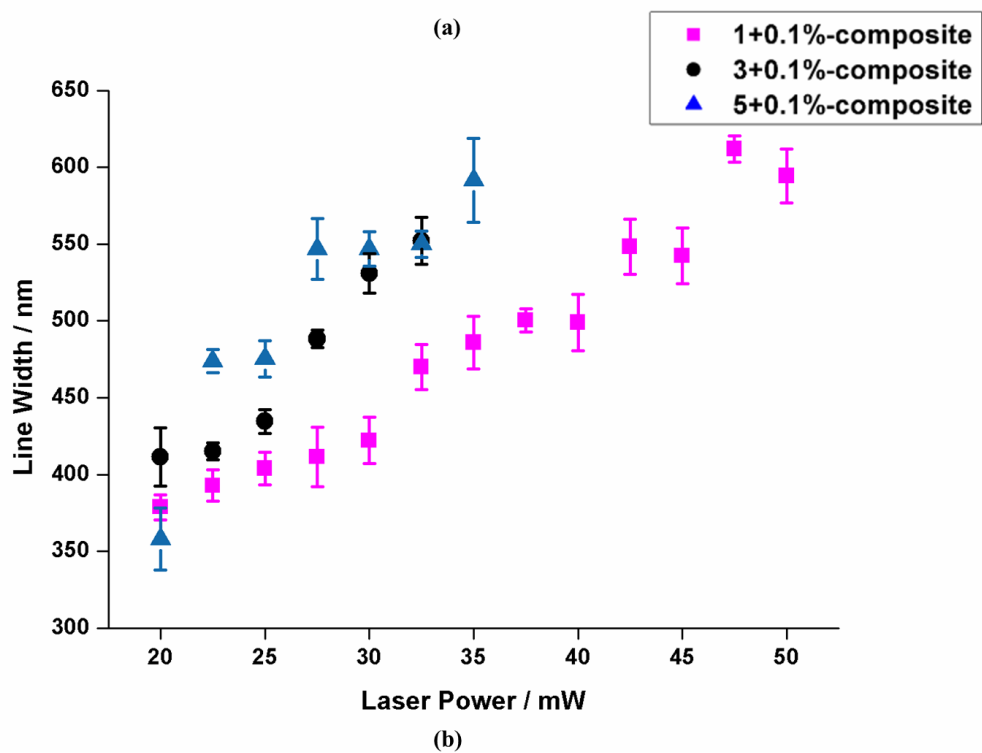
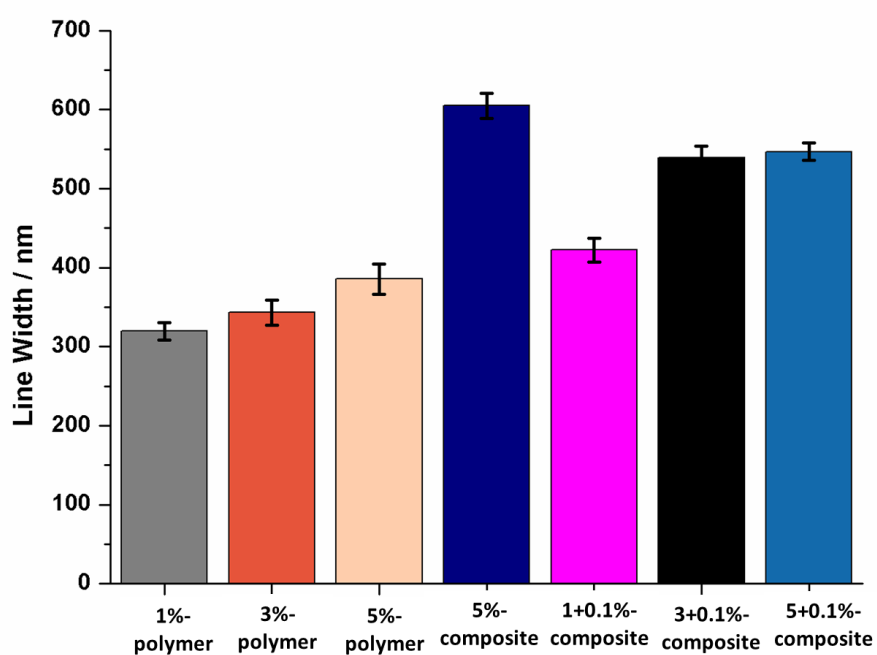


Figure 5.7 The relationship between (a) the line width and photoinitiator concentration and the presence of coumarin 30 dye and (b) the line width and laser power.

To confirm the success of the photopolymerisation and understand the relationship between polymerisation process and photoinitiator concentration, processing conditions and the presence of the dye, block samples of $80 \times 80 \times 30 \text{ }\mu\text{m}$ (**Figure 5.8**) were fabricated and analysed by Raman spectroscopy. The Raman spectra of monomers, polymers and silver-polymer composites are shown in **Figure 5.9**. The DC can be calculated using the area ratios of the peaks representing C=C bond at 1638 cm^{-1} and C=O bond at 1726 cm^{-1} in the polymers and monomers. The C=C bonds consumed during polymerisation whilst the C=O bond are unaffected. Therefore, the degree of conversion can be calculated from Equation 4.1.

$$\Delta = 1 - \frac{A_{\text{C=C}}/A_{\text{C=O}}}{A'_{\text{C=C}}/A'_{\text{C=O}}} \quad \text{Equation 4.1}$$

where $A_{\text{C=C}}$, $A_{\text{C=O}}$, $A'_{\text{C=C}}$ and $A'_{\text{C=O}}$ are the peak intensities in the Raman spectra related to the C=C and C=O groups in the polymerised structures and monomers.

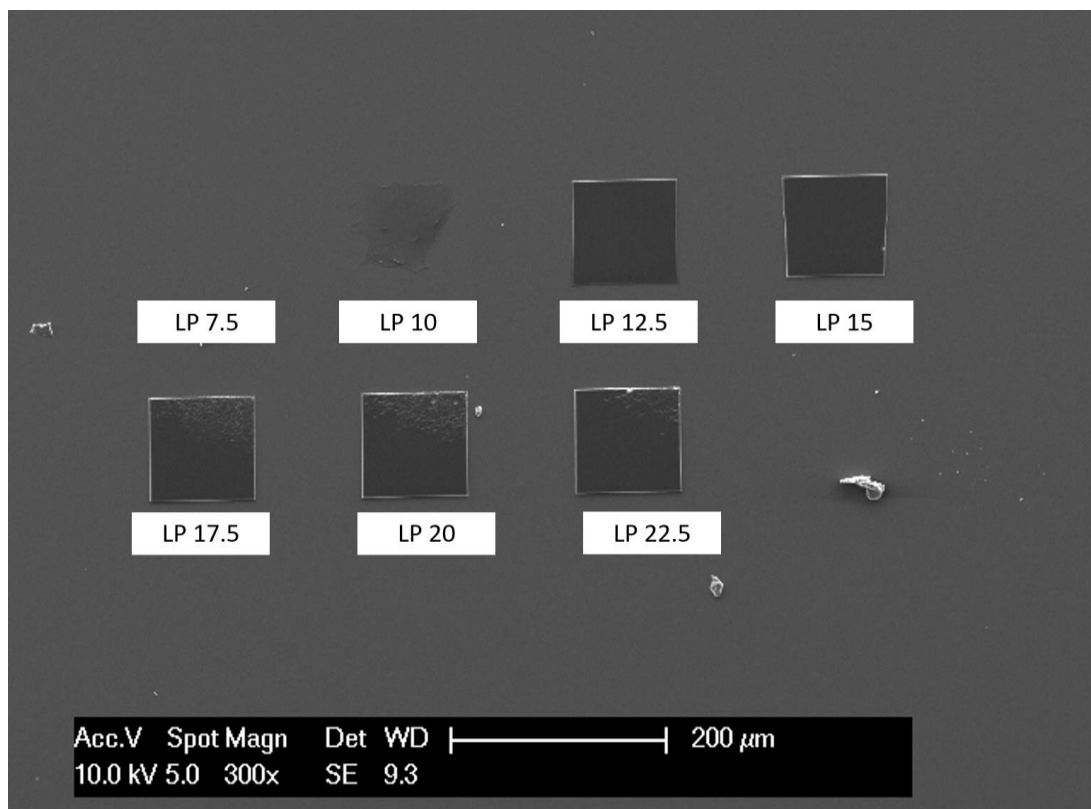
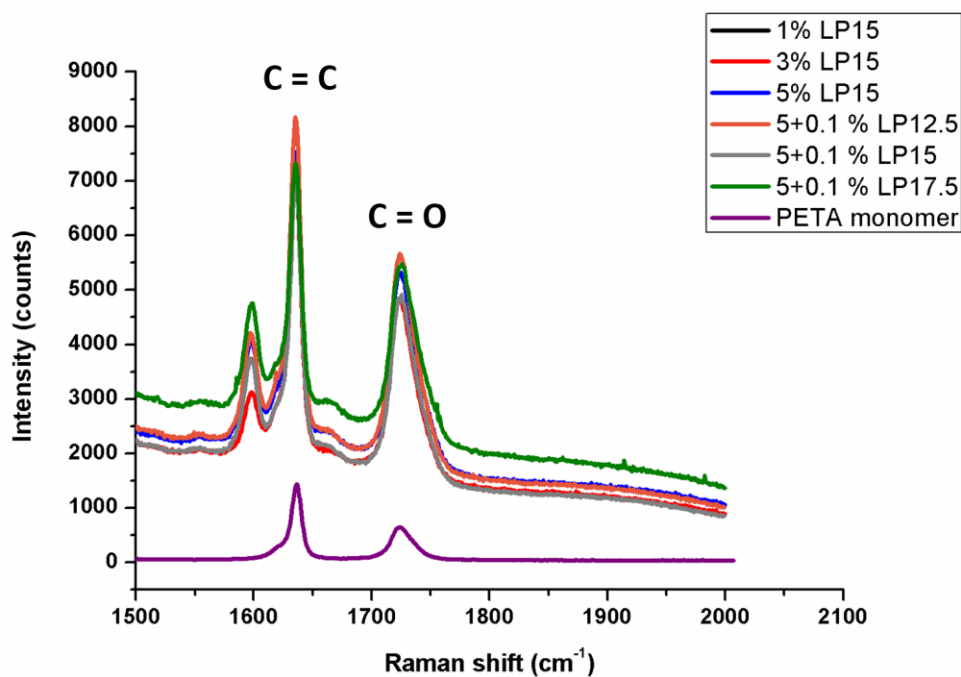
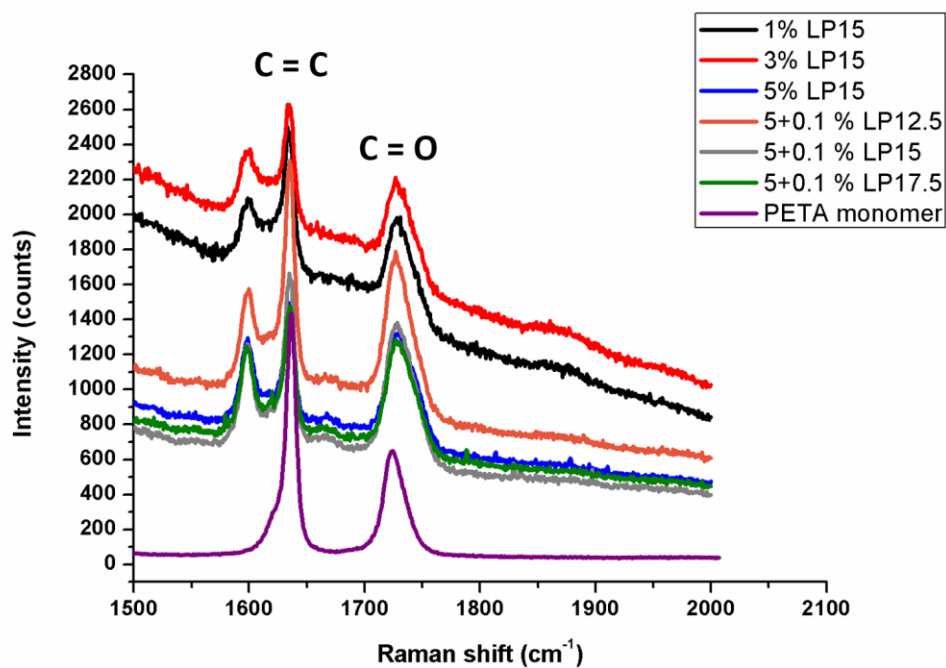


Figure 5.8 An example of SEM image showing block samples of $80 \times 80 \times 30 \mu\text{m}$ fabricated using formulation 5+0.1%-composite with different laser power / mW.

(LP 7.5 represents laser power 7.5 mW)



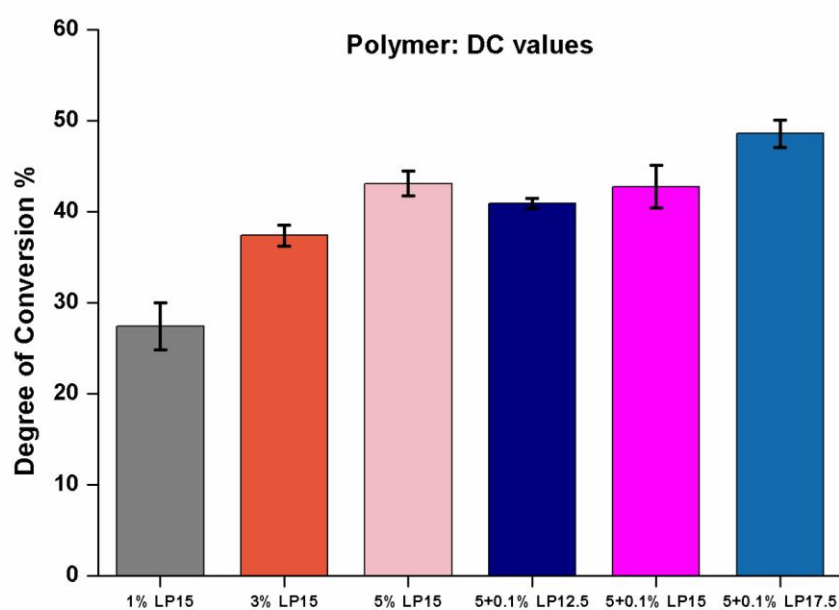
(a)



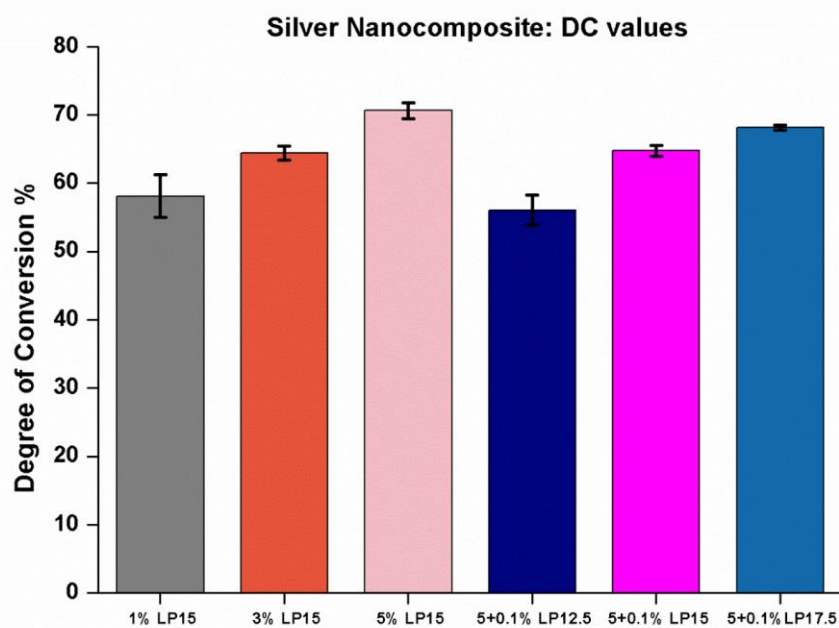
(b)

Figure 5.9 The Raman spectra of (a) monomer and polymers and (b) monomer and silver-polymer composites using different laser power, different photoinitiator concentrations and with/without coumarin 30 dye. (5 + 0.1 % LP 12.5 represents 5 wt% Irgacure 369, 0.1 wt% coumarin 30, and laser power 12.5 mW)

Using Equation 4.1, the degrees of conversion for polymer and silver-polymer composite produced from different formulations were calculated and compared in **Figure 5.10**. For both polymeric and composite materials, the DC values increased with increasing photoinitiator concentrations when used the same processing laser power. The DC value of 1%-polymer was $27.4 \pm 2.6\%$. The DC value of 5%-polymer was increased to $43.1 \pm 1.4\%$. The DC value of 1%-composite was $58.1 \pm 3.5\%$. The DC value of 5%-composite was improved to $70.6 \pm 1.2\%$. Higher processing laser power improved the C=C conversion. For example, for formulation 5+0.1%-composite, the DC values increased from $56.1 \pm 2.2\%$ to $68.2 \pm 0.4\%$ with increasing laser power from 12.5 to 17.5 mW. The addition of coumarin 30 dye did not have an obvious effect on the degree of conversion for polymers. However, the DC values for the composites were reduced when samples were produced at the same laser power. For example, when laser power was 15 mW, the DC value of 5+0.1%-composite was about 6 % lower than the DC value of 5%-composite. It indicated that coumarin 30 did not affect the polymerisation process.



(a)



(b)

Figure 5.10 DC values of (a) polymer and (b) silver-polymer composites fabricated at a range of laser powers, concentrations and with/without coumarin 30 dye.

The optical absorption spectra of pure isopropanol, PETA, Irgacure 369, coumarin 30 and transferred silver ions (all dissolved in isopropanol separately) at different concentrations are shown in **Figure 5.11**. No absorption at 780 nm indicates the polymerisation and reduction were driven by the TPA process. Two absorption peaks at 230 nm and 325 nm of Irgacure 369 represents the typical π - π^* transition and the electronic transition from the ground state to the ICT state, respectively. Coumarin 30 dye has stronger absorption than Irgacure 369 at 390 nm. In the case a 780 nm NIR fibre laser was used, depending on the concentration of Irgacure 369 in the resin, TPA can occur in which two 390 nm photons were absorbed simultaneously if the laser intensity reached a certain threshold value. It is then supposed that the presence of coumarin 30 would transfer electrons to the silver ions that promote to the photosensitised reduction and/or transfer electrons to the photoinitiator that generated radicals. For the TPR with a dye, two photons were absorbed simultaneously and then the electrons transferred from the lowest unoccupied molecule orbital level to the metal ions and generate metal atoms. The generated metal atoms could contribute to nucleation or charge recombination^{111, 113}. Generally, the dye is not consumed and acts as a catalyst to enhance the formation of metal atoms⁴⁶.

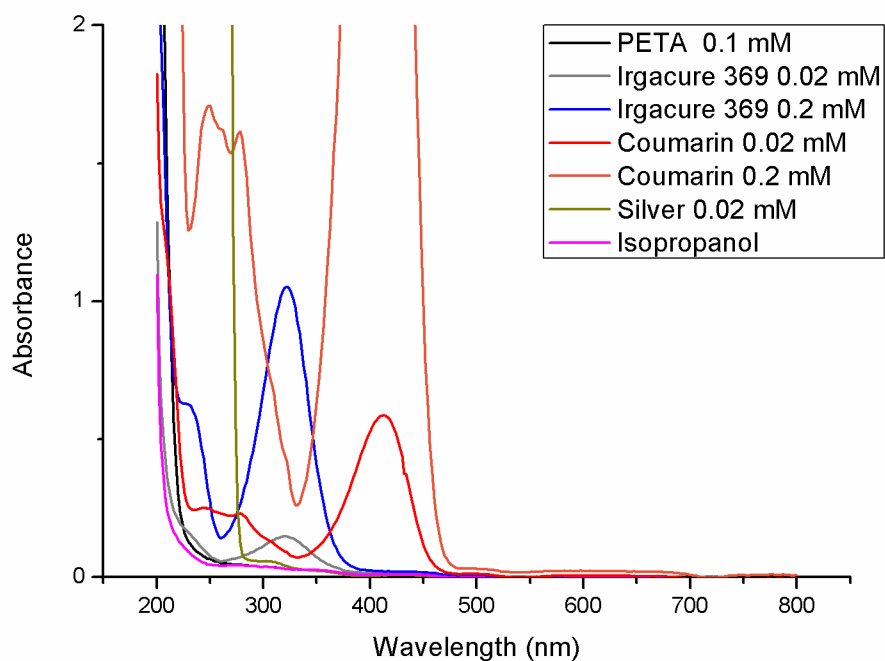


Figure 5.11 UV-vis spectra of silver precursor PETA, Coumarin 30 and Irgacure 369.

5.3.4 Fabrication of 2D & 3D Silver Composite Structures

Apart from 2D line structures, a series of silver-containing complex 2D & 3D structures shown in **Figure 5.12** were fabricated by simultaneous TPP and TPR. 5 wt% of photoinitiator allowed for fabricating structures with details and successful fabricated 3D complex structures. Delicate 3D models with high spatial resolution can be fabricated and provide promising applications such as plasmonic metamaterials and chiral metamaterials.

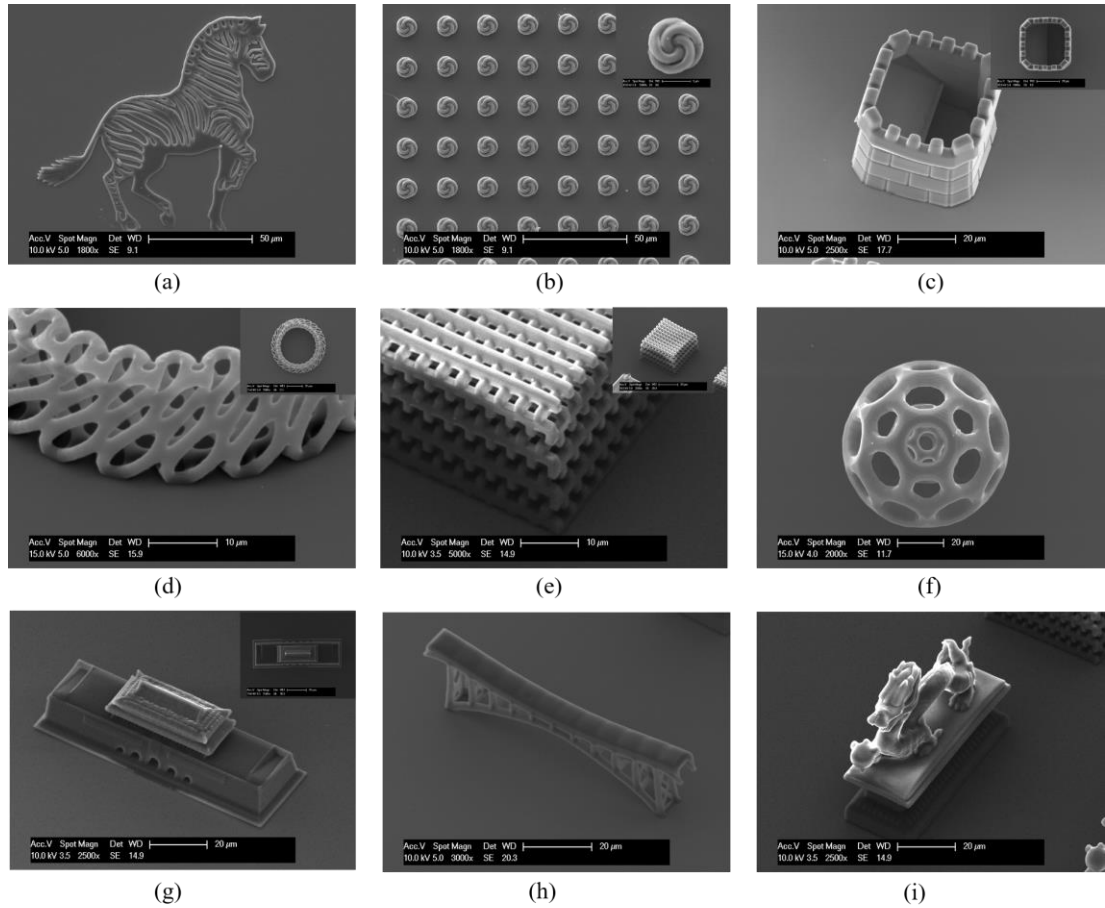


Figure 5.12 SEM images of 2D and 3D silver-polymer nanostructures (a)-(c) using formulation 5%-composite including 2D zebra, 3D knot array structure and 3D dice tower and (d)-(i) using formulation 5+0.1%-composite including 3D bracelet, photonic woodpile structure, 3D ball structure, 3D Tiananmen Square, 3D bridge structure and 3D Chinese dragon..

Figure 5.13 compares 3D Eiffel Tower structures fabricated using formulation 1%-composite and 5%-composite. The structures with 1 wt% photoinitiator lost structural details and it was too weak to keep the structure in 3D. When 5 wt% Irgacure 369 was added, the structures showed improved structural details and they were strong enough to withstand the sample development process.

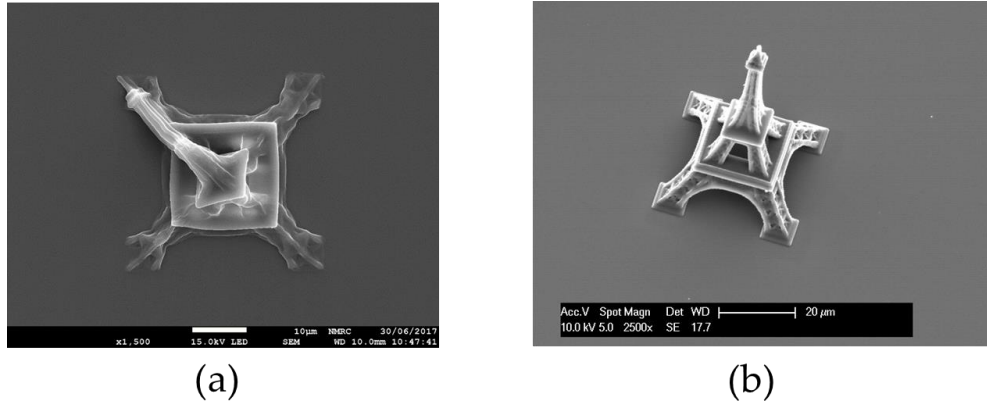


Figure 5.13 SEM images of fabricated Eiffel Tower structures using (a) formulation 1%-composite and (b) formulation 5%-composite.

Coumarin 30 dye did not show much effect on 3D structure fabrication with 5 wt % Irgacure 369. The dice tower structures fabricated with formulation 5%-composite and 5+0.1% composite are shown in **Figure 5.14** (a) and (b). However, when coumarin 30 was added, there was a significant scattering of the laser observed (shown in **Figure 5.14** (d)) during two-photon processing which may indicate better light interaction. Even though the coumarin 30 dye did not show much effect on overall structural performance, it affected the line width and processing laser power as discussed before. The presence of coumarin 30 dye also affected the formation of silver NPs and it was discussed in section 5.3.5.

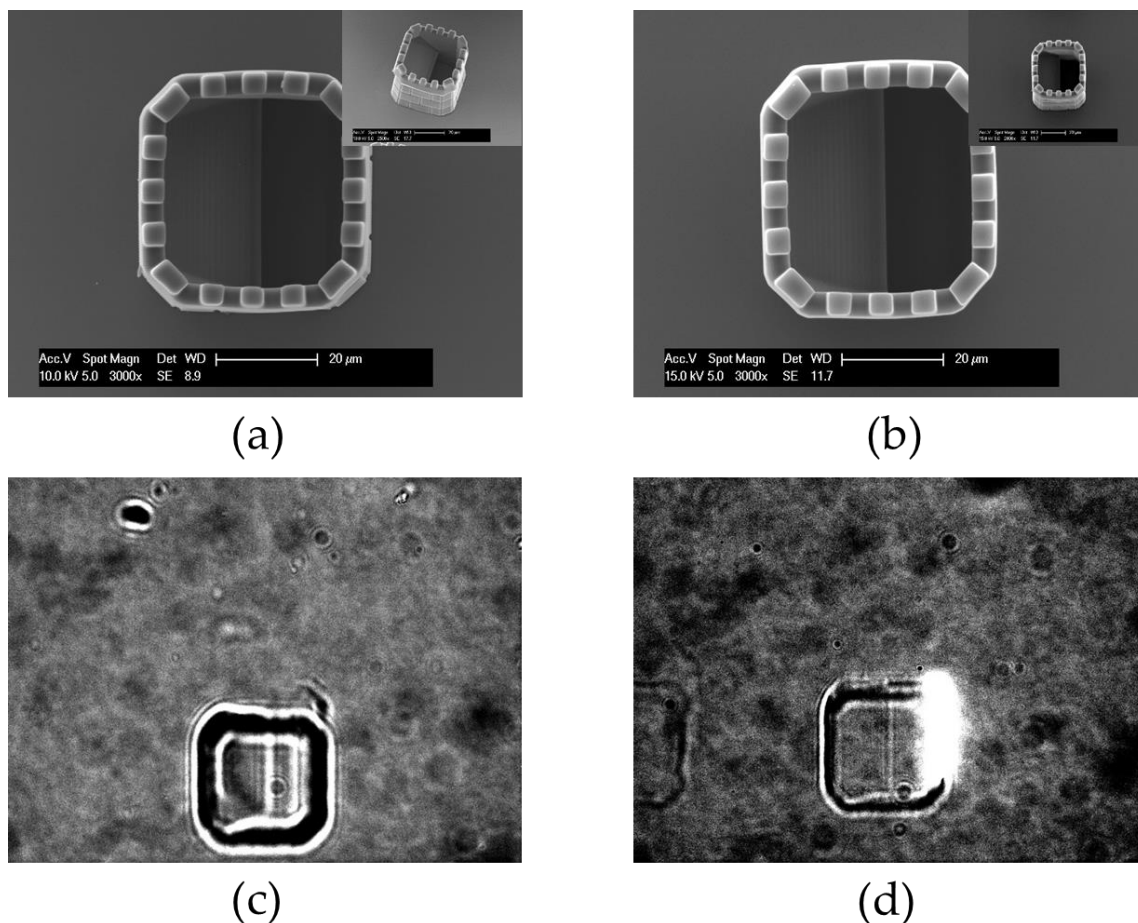


Figure 5.14 SEM images of dice tower structures using (a) formulation 5%-compoiste and (b) formulation 5+0.1%-composite. Photo captured during fabrication using (c) formulation 5%-composite and (d) formulation 5+0.1%-composite..

5.3.5 Characterisation of the Presence of Silver within Silver-polymer Nanocomposites

To confirm the presence of silver within the 3D structures, SEM image and EDX scanning of the woodpile structures fabricated using formulation 5+0.1%-composite (**Figure 5.12** (e)) were acquired by XL30 SEM (**Figure 5.15**). Silver particles were observed from the structure surface (**Figure 5.15** (a)) and the silver element was

detected using EDX (**Figure 5.15 (b)**). The spectra of the particle showed a clear Ag peak at 3.0 eV.

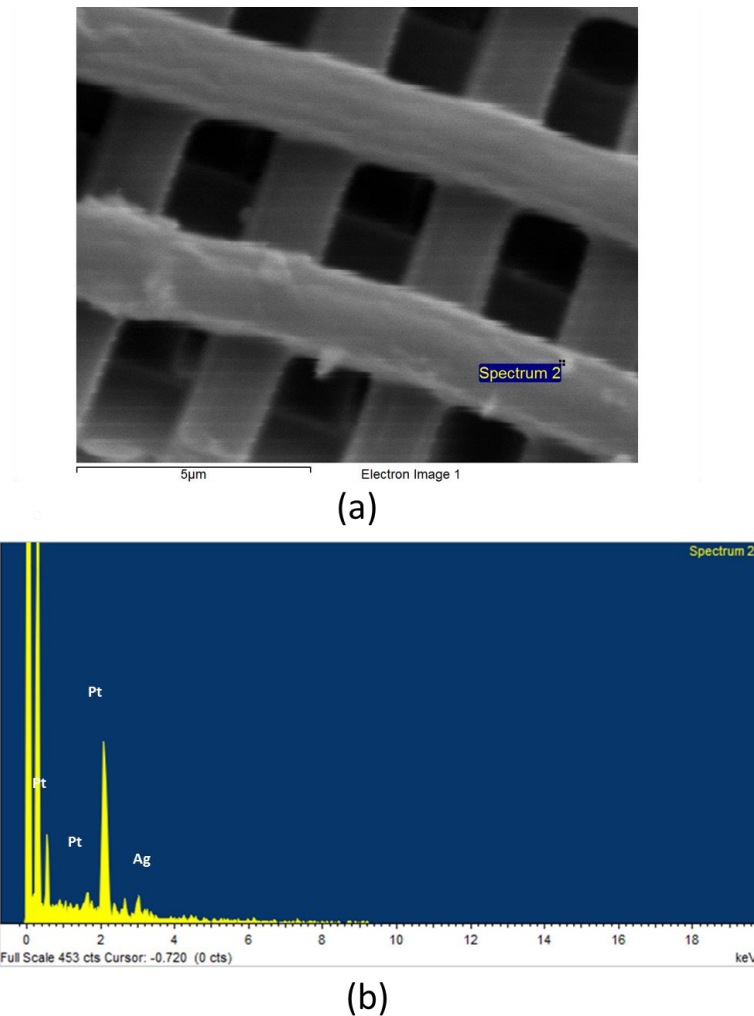


Figure 5.15 (a) SEM image of woodpile structures fabricated using formulation 5+0.1%-composite; (b) EDX spectrum of the particles at Location 2.

7100F FEG-SEM was then combined with EDX was employed to better observe the presence of silver particles within the fabricated structures owing to its higher resolution. **Figure 5.16** demonstrates the FEG-SEM images of fabricated structures with formulation 1+0.1%-composite. **Figure 5.16** (a) and (b) are the LED (lower electron detector) and BED (backscattered electron detector) images of the same

sample position. The BED images presented a large atomic-number-based contrast difference between the polymer matrix and silver particles so that silver particles could be observed and measured. Some large particles (maximum 63.40 nm from the image) were aggregated on the structure surface while smaller (minimum 11.65 nm from the image) particles were also observed. Silver particles were also observed on other fabricated structure surfaces shown in **Figure 5.16** (c)-(f). Generally, the silver particles were isolated on the surface and could be observed.

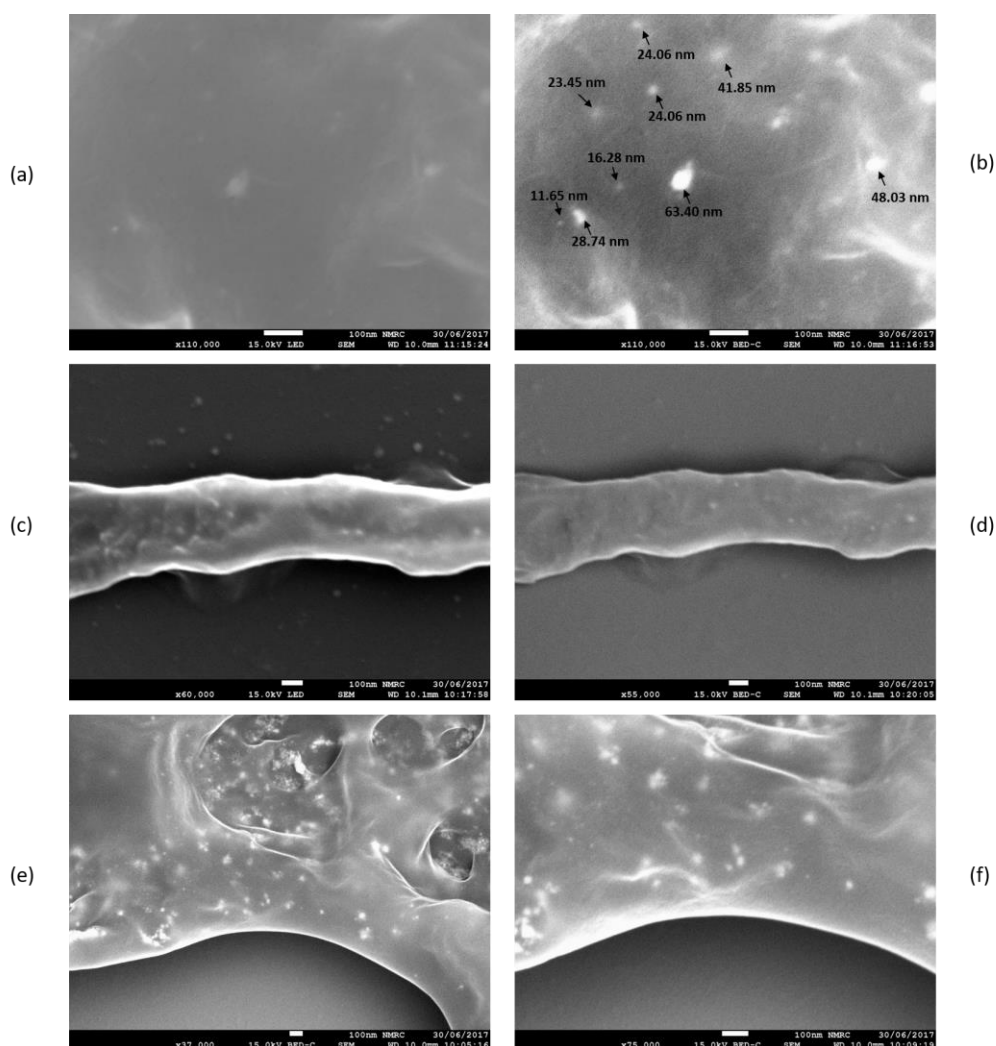


Figure 5.16 (a) and (c): FEG-SEM images of silver-polymer nanocomposites fabricated using formulation 1+0.1%-composite. (b), (d), (e) and (f): the backscattered electron (BSE) images showing the presence of silver particles.

Figure 5.17 shows the FEG-SEM images of fabricated structures using formulation 5%-composite ((a) - (b)) and formulation 5+0.1%-composite ((c)-(f)). The silver peak at 3.0 eV was detected by EDX mapping (**Figure 5.17** (g)). For the 3D objects fabricated using the formulation 5%-composite, the particles found on the surface are similar to the particles found in formulation 1+0.1%-composite, which were aggregated in relatively large particle size but some smaller particles were also visible. On the contrary, the same objects fabricated using 5+0.1%-composite presented more uniform particles in size and distribution. The result supports the idea that additional coumarin 30 helped the reduction of silver ions and formed more silver seeds resulting in a better distribution of silver particles. The electrons of benzoyl and benzyl radicals and the electrons from coumarin 30 dye were injected into silver ions so that more silver seeds were formed when additional coumarin 30 and more photoinitiators were added¹⁹⁰. Thus, more uniformly dispersed silver particles were obtained by strong electrical repulsion forces¹⁹⁰.

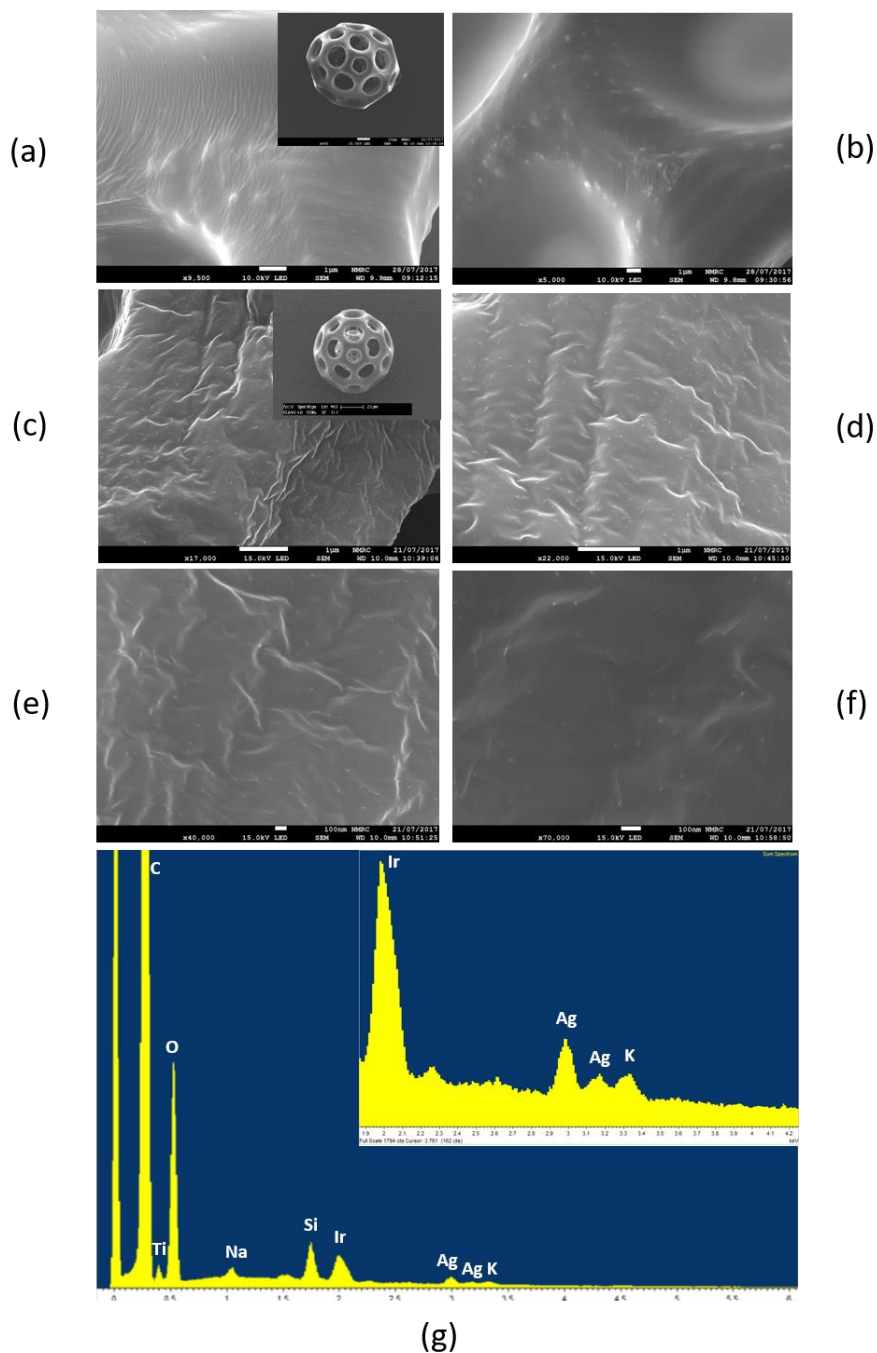


Figure 5.17 (a)-(b) FEG-SEM images of 5%-composite that show the presence of silver NPs with increasing magnifications; (c)-(d) FEG-SEM images of 5+0.1%-composite that show the presence of silver NPs with increasing magnifications; (e)-(f) BSE image showing the presence of silver particles on 5+0.1%-composite surface with increasing magnifications.; (g) An EDX spectrum of the particles shows the presence of silver element on 5+0.1%-composite.

In order to measure the particle size accurately and better understand the silver particles inside the structures, TEM images were acquired. To acquire the electron transparency samples for TEM image, FIB-SEM was used to thin structures and the process is shown in **Figure 5.18**. Two-photon fabricated structure (a knot structure in **Figure 5.12**) was firstly glued to a nano-manipulator needle by Pt deposition. The knot structure was lifted out by adjusting the needle height and then mounted onto a TEM grid by Pt deposition. The Pt between knot structure and the nano-manipulator probe was removed by FIB (Focused ion beam). Finally, the knot structure was thinned by FIB from both sides, leaving behind a thin electron-transparent lamella as shown in **Figure 5.19** (a)-(b). Before TEM imaging, the EDX spectrum was acquired and the peak at 3.0 eV confirmed the presence of silver. (**Figure 5.19** (c)-(d))

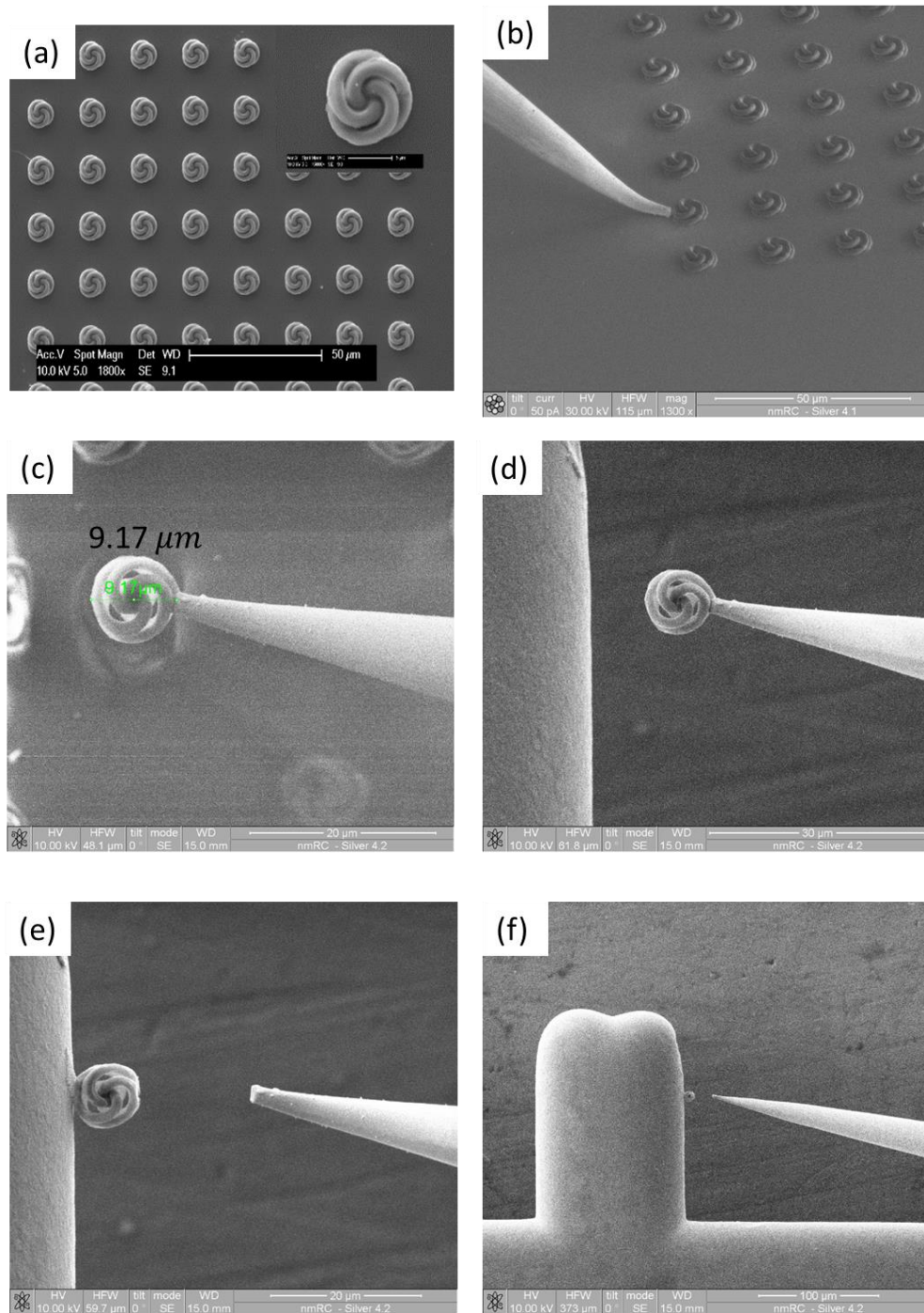


Figure 5.18 SEM images illustrates the proces of TEM sample preparation. (a) SEM imgaes of knot structures fabricated using 5+0.1%-composite; (b)-(d) a knot structure was picked up by a nano-manipulator needle; (e)-(f) the knot structure was mounted onto a TEM grid.

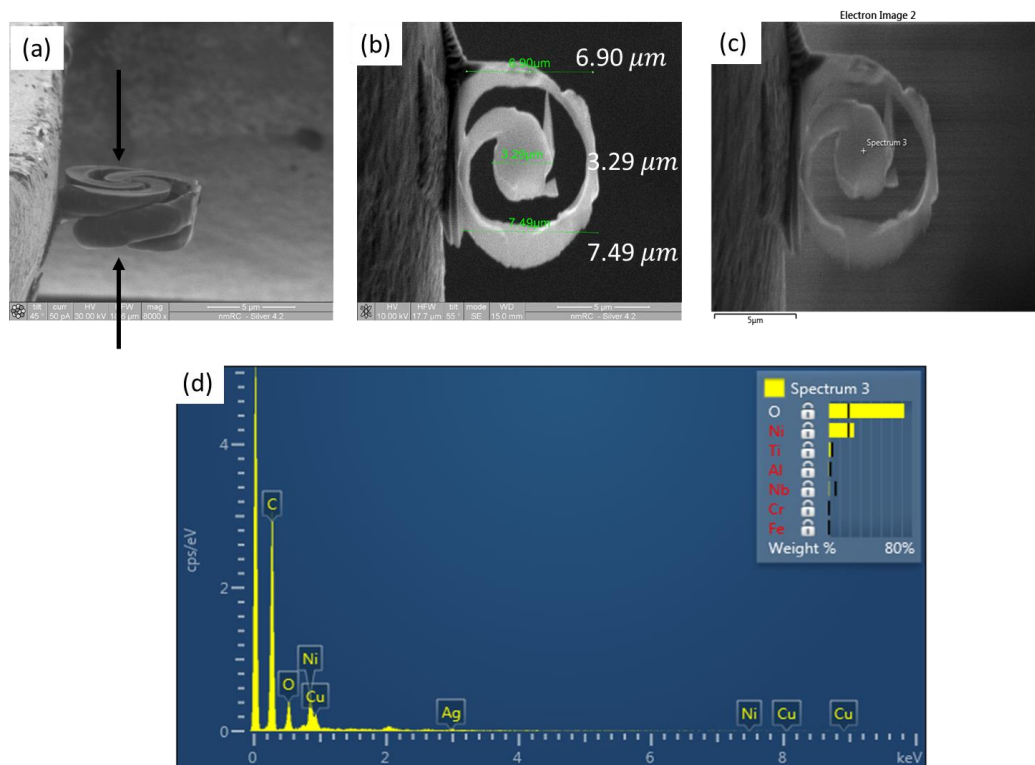


Figure 5.19 (a)-(c) The knot structure mounted on the TEM grid was thinned by FIB both sides leaving behind a thin electron-transparent lamella; (d) the EDX spectrum of location 3 in (c).

Silver NPs were noted within the polymer matrix by both bright-field TEM and DF-STEM (Dark Field Scanning Transmission Electron Microscopy) analysis. As shown in **Figure 5.20**, silver particles were not uniformly distributed within the thinned knot structured fabricated using formulation 5%-composite. Silver particles were only observed in a few areas and varied in size. Spherical particles were predominantly observed. The most uniform distribution area was recorded (**Figure 5.20** (d)) and the mean particle size and distribution were evaluated by Image J (**Figure 5.21**). The average size was 4.97 ± 0.94 nm. EDX analysis confirmed that they were all silver-containing particles.

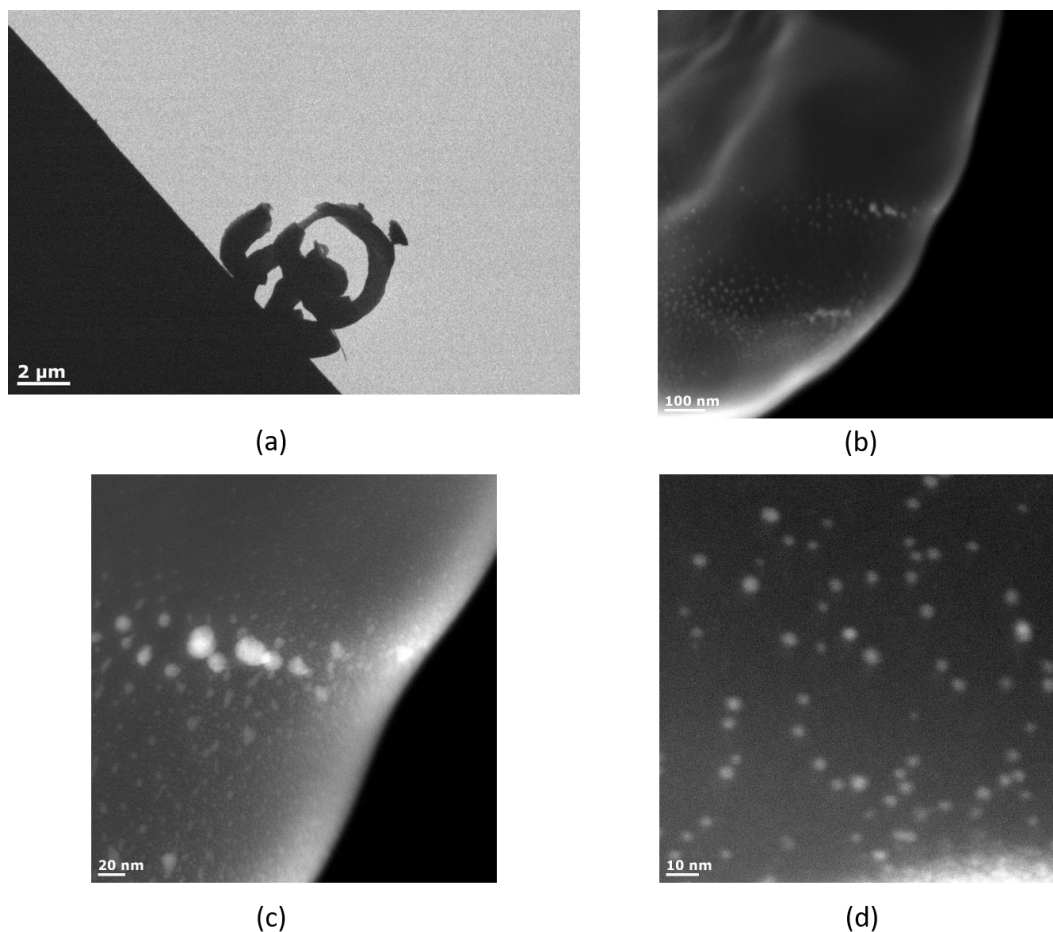


Figure 5.20 A series of DF-STEM images showing the presence of silver particles in the thinned knot structures fabricated using formulation 5%-composite. DF-STEM images were obtained in the dark field, where species in high atomic contrast present as bright features (silver particles). (a) The knot structure thinned by FIB; (b)-(c) Different magnification of DF-STEM images show the presence of silver NPs; (d) The most uniform distribution of silver NPs area selected from the thinned knot structure.

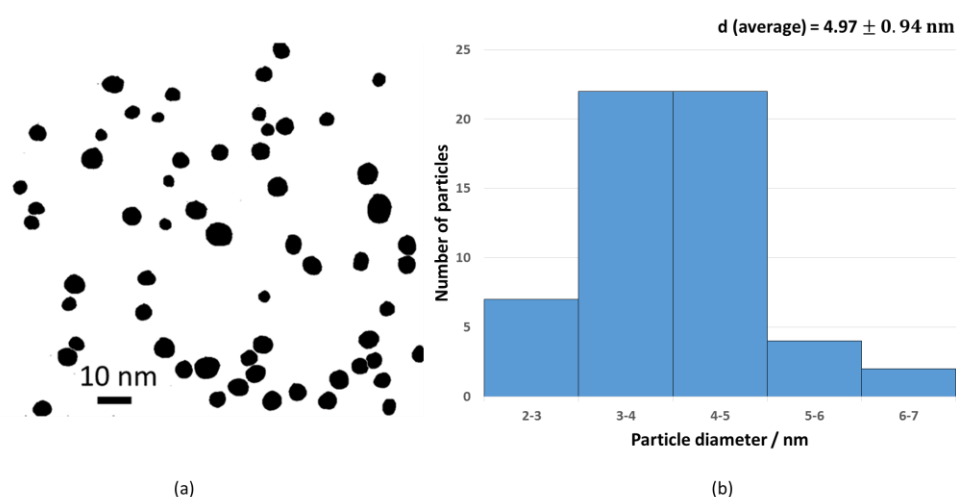


Figure 5.21 (a) The particle sizes observed in Figure 5.20 (d) were analysed and measured by Image J; (b) Particle distribution. The average sizes of particles are $4.97 \pm 0.94 \text{ nm}$.

From FEG-SEM images (**Figure 5.17**), Silver NPs were more uniform and easier to be found in the structure fabricated using formulation 5+0.1%-composite compared to formulation 5%-composite. Both bright-field TEM (**Figure 5.22**) and DF-STEM (**Figure 5.23**) images present that silver NPs were embedded in the polymer matrix. The particles were analysed by EDX to confirm the presence of silver. A group of DF-STEM images at different tilt angles were taken to attest that the particles were distributed throughout the thinned lamella. (Appendix B) Some large NPs around 10-20 nm were also observed on the outer surface. The average size is $5.80 \pm 1.50 \text{ nm}$ and the particle distribution is presented in **Figure 5.24**. Even though the average particle size measured from formulation 5+0.1%-composite is greater than formulation 5%-composite, the silver particles fabricated using formulation 5+0.1%-composite were more uniformly distributed within the whole structures rather than a few areas. Thus, the results provide the evidence that coumarin 30 dye helped

photoreduction of silver ions. Additional electrons from coumarin 30 dye were injected into silver ions and reduced silver NPs were dispersed better because of stronger electrical repulsion forces¹⁹⁰.

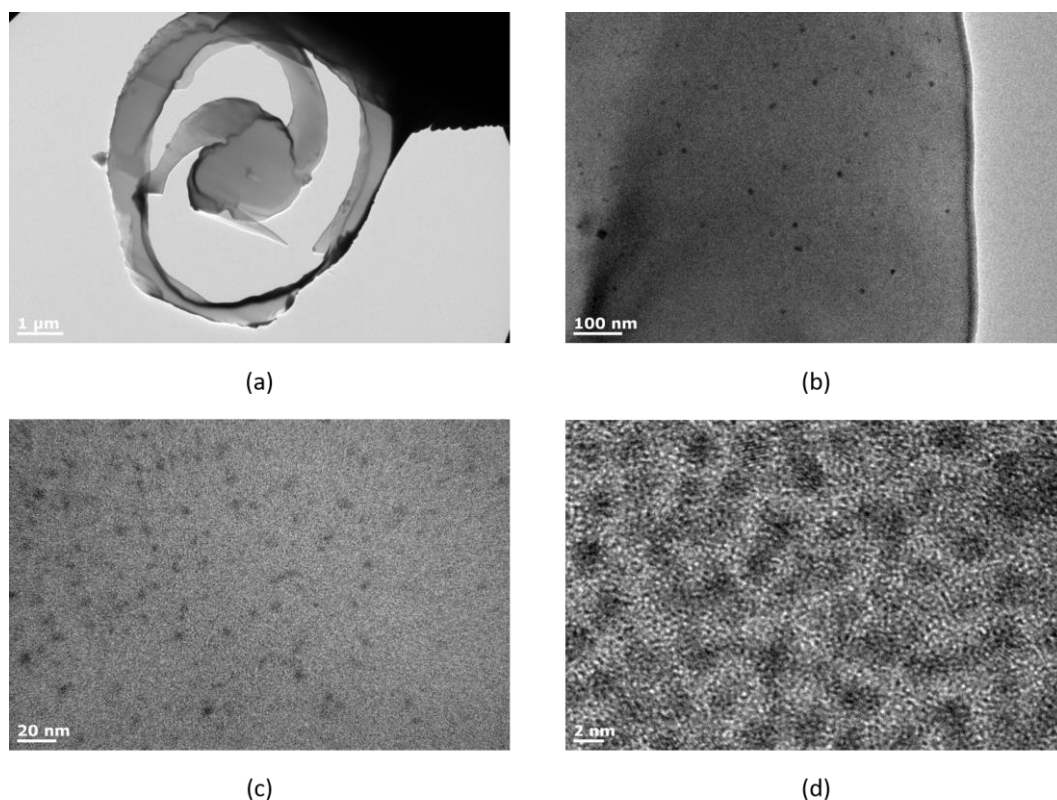


Figure 5.22 A series of TEM images showing the presence of silver particles in the thinned knot structures fabricated using formulation 5+0.1%-composite. Compare to DF-STEM images, TEM images were obtained in bright field, where species in high atomic contract present as dark features (silver particles). (a) The knot structure thinned by FIB; (b)-(d) Different magnification of TEM images show the presence of silver NPs.

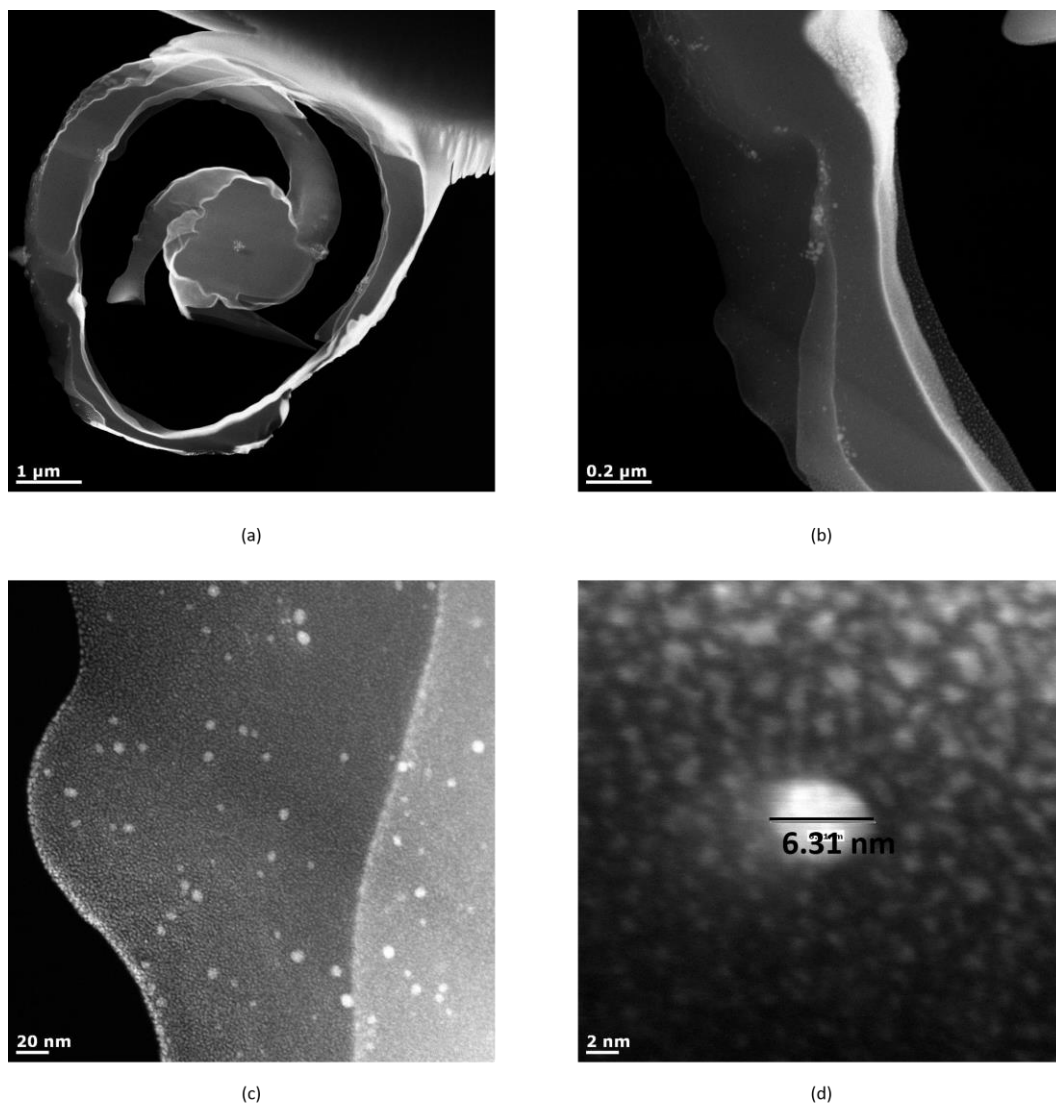


Figure 5.23 A series of DF-STEM images showing the presence of silver particles in the thinned knot structures fabricated using formulation 5+0.5%-composite. (a) The knot structure thinned by FIB; (b)-(d) Different magnification of TEM images show the presence of silver.

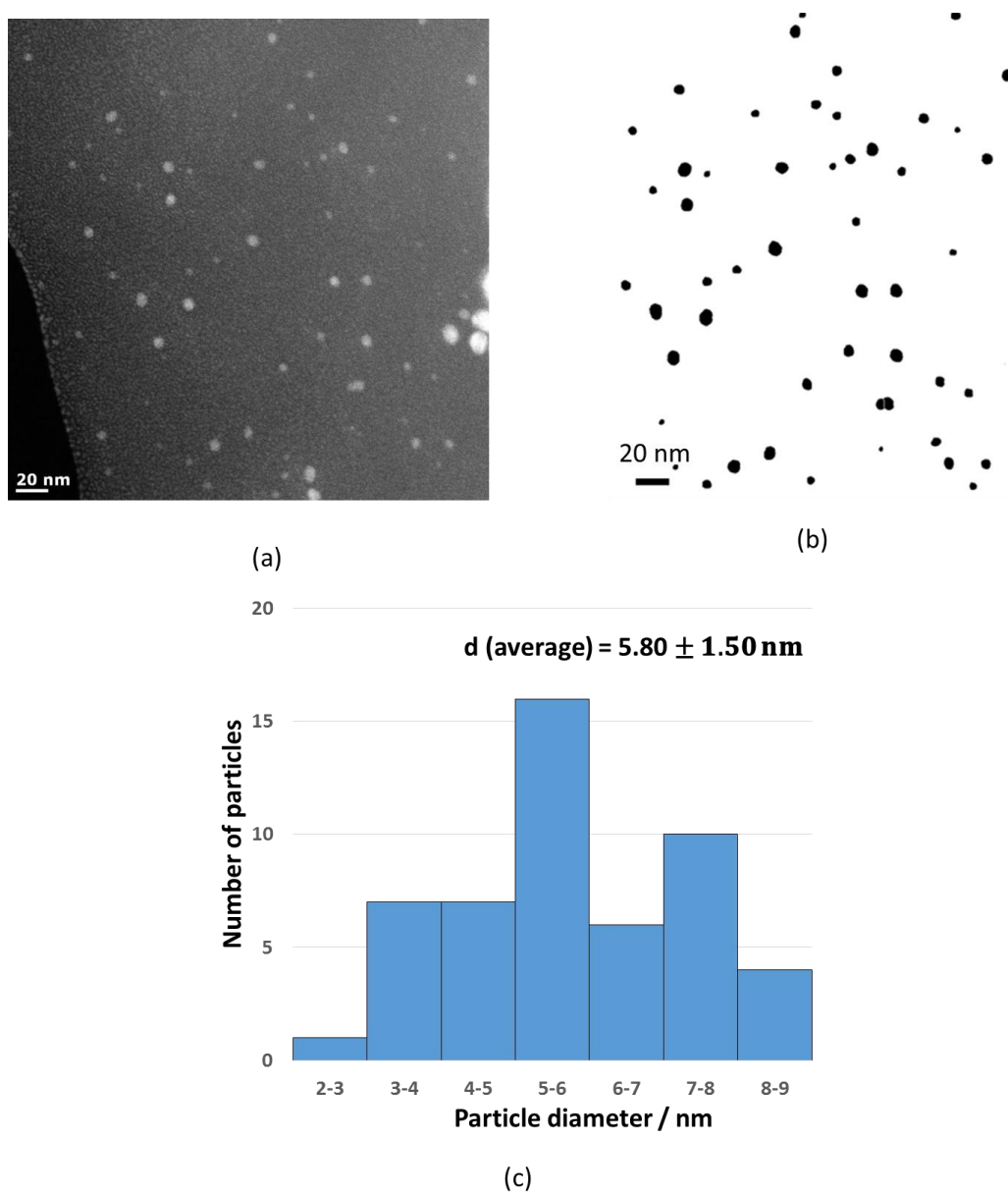


Figure 5.24 (a) DF-STEM image presenting silver particles in thinned knot structures fabricated using formulation 5+0.1%-composite. (b) The particles were analysed and measured by Image J; (b) Particle distribution and fitted normal distribution (orange curve). The average sizes of particles are $5.80 \pm 1.50 \text{ nm}$.

The XPS spectra and the Auger MNN spectra of silver precursor (dried silver ions in toluene) (**Figure 5.25** (a)-(b)) and fabricated silver-polymer composites using formulation 5+0.1% (**Figure 5.25** (c)-(d)) verify the reduction of silver ions. All

binding energies were calibrated according to the C 1s peak centred at 284.8 eV. Because the binding energy of Ag 3d_{5/2} and Ag 3d_{3/2} for silver metallic state Ag⁰ and silver ions are similar, the Auger parameter (AP) was used to identify the silver elemental states further¹⁹¹. During X-ray emission, the released energy between different energy levels results in an emitted photon, but the energy may also be transferred and emits another electron from the atom, which is Auger electrons¹⁹². The Auger parameter can be calculated as:

$$AP = BE (3d_{5/2}) + KE (AgM_4N_{45}N_{45}) \quad \text{Equation 5.2}$$

where BE is bending energy and KE is the Auger kinetic energy.

The calculated AP values are listed in **Table 5.5**. The peaks appearing at 368.4 and 374.4 eV with a separation of 6 eV in **Figure 5.25** (a) correspond to the Ag 3d_{5/2} and Ag 3d_{3/2} respectively and the peaks appearing at 349.4 and 355.1 eV in **Figure 5.25** (b) represent the AgM₅N₄₅N₄₅ and AgM₄N₄₅N₄₅ respectively. According to the literature values, the fitted peaks of Ag precursor and calculated AP value suggests that the silver in the precursor is silver ions¹⁹³.

For the silver-polymer nanocomposites fabricated using formulation 5+0.1%, the fitted high-resolution spectra for Ag 3d suggest that silver is presented in more than one state (The full-scan spectra were shown in Appendix A Figure A2). The peaks at 368.5 and 374.2 eV and the AP value of 726.7 confirm the existence of silver in the metallic state Ag⁰^{191, 193-194}. Another double peak of Ag 3d at 367.7 and 373.6 eV is in good agreement with the literature values for Ag₂O¹⁹⁴⁻¹⁹⁶. The results confirm that

silver ions were reduced to the silver metallic state Ag^0 and the presence of Ag_2O may be due to the residue of silver ions or the oxidation of metallic silver.

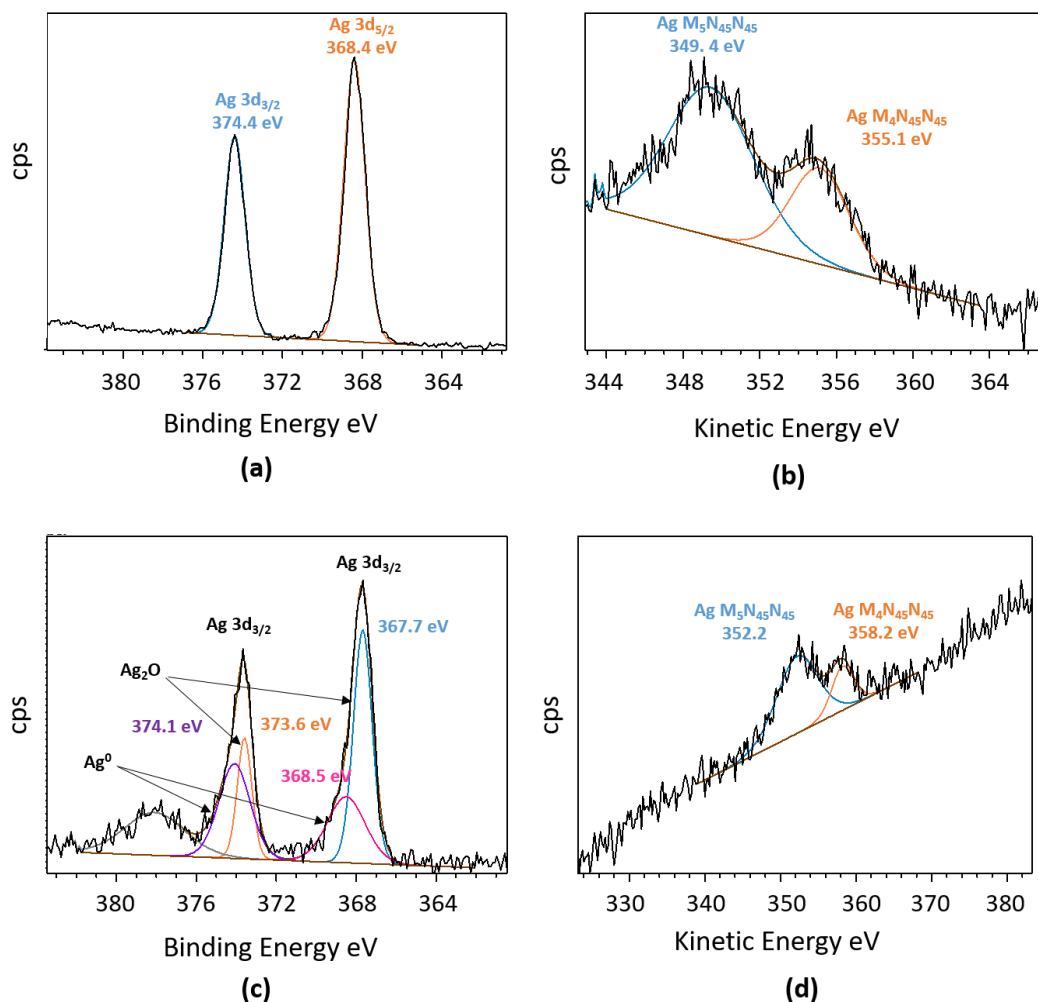


Figure 5.25 The XPS spectra and the Auger MNN spectra of (a)-(b) silver precursor (dried silver ions in toluene) and (c)-(d) fabricated silver-polymer composite using formulation 5+0.1%-composite verify the reduction of silver ions.

Table 5.5 *The bending energy of silver and Auger parameter obtained from XPS spectra and corresponding reference values from literature.*

	Binding energy (eV) Ag 3d _{5/2}	Binding energy (eV) Ag 3d _{3/2}	Auger parameter AP-3d _{5/2} , M ₄ N ₄₅ N ₄₅
Ag precursor	368.4	374.4	723.5
AgNO ₃ reference ¹⁹³	368.8		723.8
5+0.1%-composite	368.5	374.1	726.7
	367.7	373.6	
Ag ⁰ reference ^{191, 193-194}	368.3	374.3	726.3
Ag ₂ O reference ¹⁹⁴⁻¹⁹⁶	367.6	373.6	

5.4 Conclusions

- Finding and optimising a suitable formulation that consists of water-soluble photoinitiators and monomers for the fabrication of simultaneous photopolymerisation and photoreduction were challenging. The solutions are either exploring new high-efficiency water-soluble photoinitiators, using an alternative TPL system suitable for the existing photoinitiators, or modifying formulations with known materials suitable for the process. In this thesis, modifying formulations has been achieved through the phase-transfer protocol.
- For the first time, simultaneous photopolymerisation and photoreduction were used to fabricate silver-polymer nanocomposites. The phase-transfer protocol was used in TPL for the first time. The protocol solved the solubility problem that most non-water-soluble photoinitiators and monomers for TPP are difficult to mix with inorganic metal salts.
- The sizes of silver NPs were related to the concentrations of photoinitiators. Higher concentrations of photoinitiators led to smaller particle sizes. The

reason may be because more free radicals increased reduction rate and generated more silver seeds with smaller sizes rather than fewer aggregations of silver particles with bigger dimensions.

- The distribution of silver NPs was found to be related to the addition of coumarin 30 dye. Additional coumarin 30 dye provided the best line resolution of 547.0 ± 11.4 nm and gave more uniform particle distribution compared to the composite fabricated without dye. The average silver NPs size was 5.80 ± 1.50 nm. In addition, the DDA used in the phase transfer method may also help the dispersion of silver NPs because of DDA's long carbon chain.
- The fabricated structures such as knot array structure and photonic woodpile structure provide potential in metamaterial applications. The ability to control silver particle size and distribution is important for the applications in optical metamaterials applications and a primary investigation of size control has been done in this thesis. Apart from material formulations, different processing parameters such as laser power and scanning speed may affect silver NPs. A study on the relationship between processing parameters and reduced silver NPs is suggested in future work.

6 Copper-polymer Nanocomposite

6.1 Introduction

This PhD research initially focused on noble metals including gold and silver, whereas not any studies on copper NPs in the two-photon fabrication area have been done yet. Copper is the most abundantly used and inexpensive metal source that exhibits electronic, catalytic, photonic, chemical and biological properties similar to noble metals^{162, 197-200}. Several methods for preparing copper NPs through photochemical reduction have been reported under UV irradiation^{162, 190, 201-202}. Neither research has been reported on two-photon reduction (TPR) of copper ions nor on composite fabrication by TPL. In this section, 3D copper-polymer nanocomposites were fabricated by simultaneous photopolymerisation and photoreduction.

6.2 Selection of Materials for Copper-polymer Nanocomposite

Literature has shown that copper ions with a photoinitiator were successfully photoreduced to copper NPs under UV irradiation^{162, 190, 202}. Thus, simultaneous photopolymerisation and photoreduction using ethanol solution of CuCl₂ as a copper source, Irgacure 369 as a photoinitiator and PETA a monomer were assessed. When a photoresist consists of 1 wt % CuCl₂, 1 wt% Irgacure 369 and PETA in ethanol for two-photon fabrication, full laser power of 50 mW and a scan speed of 10000 µm/s were required to observe structure formation (**Figure 6.1**). However, the geometry of printed samples was not as the designed gear structure (**Figure 4.1** (a)-(b)). The structure was not improved with additional photoinitiator of Irgacure 369. When 3 wt % of CuCl₂ was added, full laser power (50 mW) and a much slower scan speed of 1000 µm/s were required to obtain structures. Due to the positive results that use the

phase transfer method to fabricate silver-polymer nanocomposites and DDA may act as a dispersion agent for metal particles, a similar process route was used to fabricate copper-polymer nanocomposites. The results were presented and discussed in section 6.3.

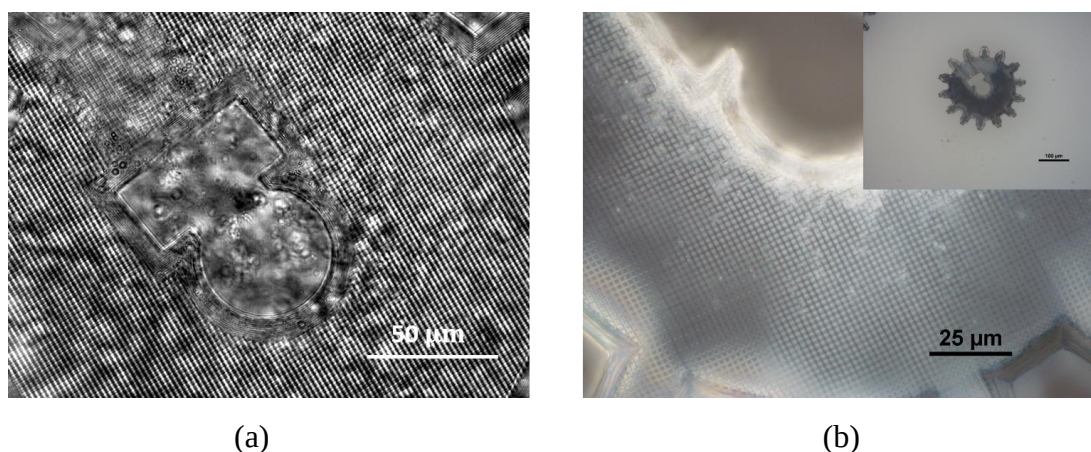


Figure 6.1 (a) photo captured during two-photon fabrication using 1 wt % CuCl_2 , 1 wt% Irgacure 369 and PETA in ethanol with full laser power of 50 mW and a scan speed of 10000 $\mu\text{m/s}$; (b) optical microscope images of fabricated structures after sample development.

6.3 Phase-transfer Protocol for Copper-polymer Nanocomposites by Two-photon Fabrication

6.3.1 Sample Preparation

To prepare the materials of copper-polymer nanocomposites ready for two-photon fabrication, the following steps were taken. Firstly, the copper ions were transferred from water to toluene. 1 ml of 0.3 M aqueous copper (II) sulphate pentahydrate solutions¹⁸⁶ were mixed with 1 ml of ethanol that containing DDA with the mole ratio

of DDA : copper (II) sulfate pentahydrate (10:1). After 5 min of stirring, 1 ml of toluene was added and the mixer was stirred for 5 min. The copper ions in toluene were separated from the aqueous phase and the aqueous phase was bleached (**Figure 6.2**). Next, 5 wt% of photoinitiator Irgacure 369 was added in PETA. 0.3 M silver ions in toluene with the mole ratio of silver ions : PETA 1:5 and 0.1 wt % Coumarin 30 were added to the photoresist. (Formulation in **Table 6.1**) The additives were mixed using a magnetic stirrer operating at a speed of 600 rpm for 30 min. After two-photon fabrication, the glass slide was put in PGMEA for 20 min, 2-propanol for 2 min and water for 20 min to remove unreacted materials.



Figure 6.2 Photograph of successful transfer of copper ions from aqueous phase to toluene.

Table 6.1 Formulation for copper-polymer nanocomposites in PETA monomer system

Formulation	PETA wt%	Irgacure 369 wt%	Coumarin 30 wt%	PETA : Cu ²⁺
PETA-Cu-Ru	94.9	5	0.1	5:1

6.3.2 Fabrication of 2D & 3D Copper Composite Structures

2D and 3D structures were fabricated using formulation PETA-Cu-Ru through simultaneous photopolymerisation and photoreduction. The SEM images are shown in **Figure 6.3**. However, some large copper particles were generated on the structure surfaces and remained even after the sample development step by solvents. **Figure 6.4** illustrates the SIMS (Secondary Ion Mass Spectrometry) image of a $500 \times 1000 \times 5 \mu\text{m}$ rectangle structure consisting of fifty $100 \times 100 \times 5 \mu\text{m}$ square structures. The generated copper particles are located on the surface of the structures. From the mapping image, aggregated copper particles from tens of micrometres to around 100 micrometres were found. Some smaller particles less than $10 \mu\text{m}$ were also observed.

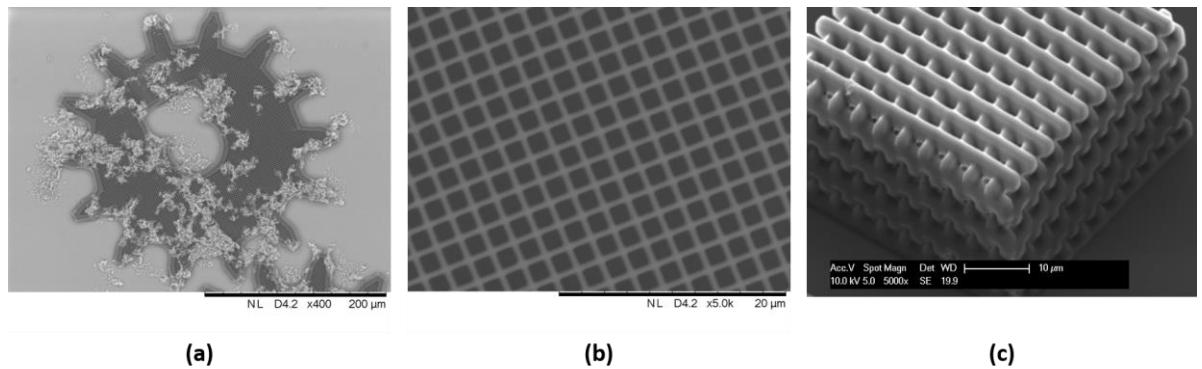


Figure 6.3 (a)-(b) 2D and (c) 3D copper-polymer structures fabricated using formulation PETA-Cu-Ru through simultaneous photopolymerisation and photoreduction.

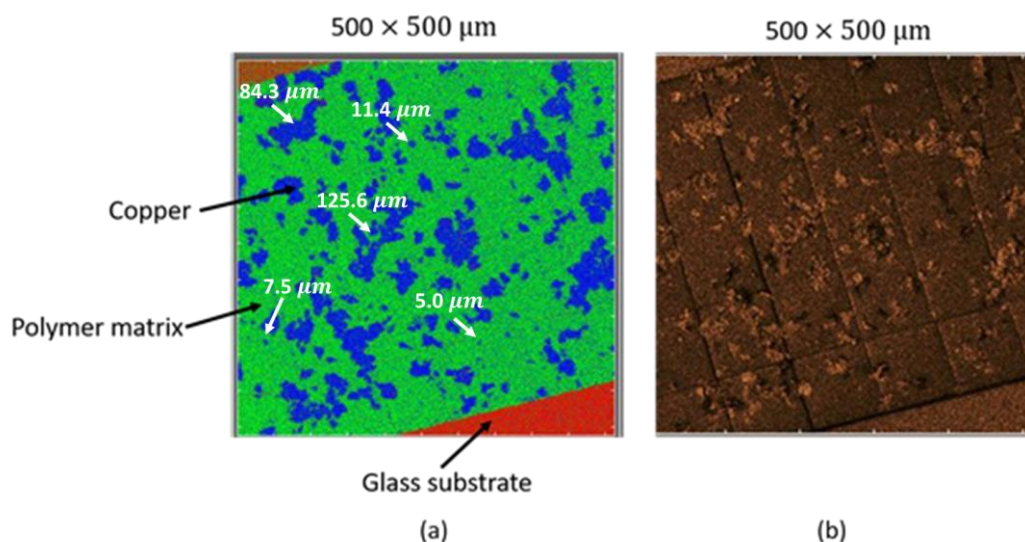


Figure 6.4 (a) SIMS image of a $500 \times 1000 \times 5 \mu\text{m}$ rectangle structure consisting of fifty $100 \times 100 \times 5 \mu\text{m}$ square structures illustrates the presence and location of copper particles embedded within the polymer matrix; (b) The optical image of the rectangle structure.

6.3.3 Characterisation of the Presence of Copper within Copper-polymer Nanocomposites

Apart from the large copper particles generated on the structure surface from 5-100 μm , some smaller particles around 1 μm randomly embedded on the surface were also observed from the SEM images (**Figure 6.5**). To make a comparison, EDX was used to characterise the chemical composition of those particles with different sizes. A Cu peak at 0.9 eV and S peak at 2.3 eV were detected for both particles but with different atomic ratio (**Figure 6.6** (c)). For the large aggregated particle generated on the surface (**Figure 6.6** (b)), the atomic ratio of Cu : S is 2.6:1. While the atomic ratio of

4:1 for the smaller particles that embedded on the structure surface (**Figure 6.6** (a) spectrum 1) points towards the reduction of copper ions.

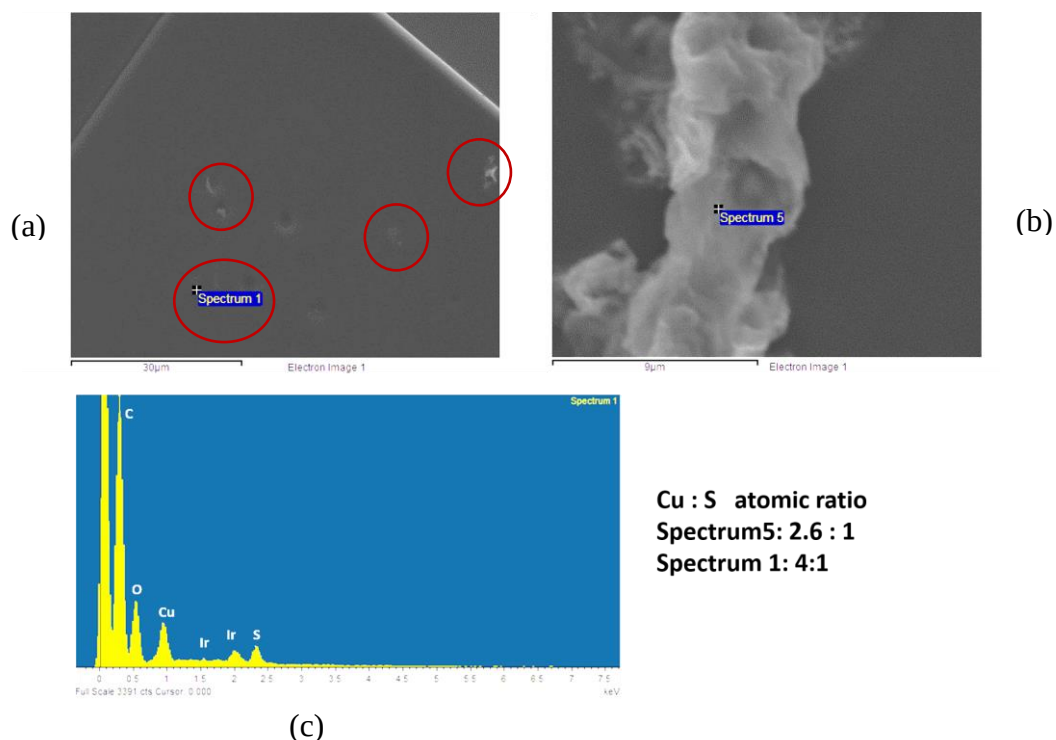


Figure 6.5 The (a) smaller copper particle around $1\mu\text{m}$ found within structure surface and (b) larger copper particles generated on structure surface were characterised by EDX; (c) the EDX spectrum of location 1 in (a). The Cu : S atomic ratio was measured and compared.

The chemical state of the copper element was further analysed by XPS. The XPS spectra of the copper precursor (dried copper ions in toluene) and the fabricated copper-polymer composite were acquired. The full-scan spectra of all elements, including background elements were shown in Appendix A Figure A3. All binding energies were calibrated according to the C 1s peak centered at 284.8 eV. The spectral

shape of copper precursor after phase transfer process (**Figure 6.6** (a)) is very similar to the spectrum of copper (II) sulphate pentahydrate (**Figure 6.6** (c)) but with 1.9 eV chemical shift which may indicate the formation of a DDA-copper complex. The shake-up satellite peaks (Figure 6.6 (a) and (c), circled peaks by the blue dashed lines), which are the characteristic of the d^9 configuration in the ground state of a material such as Cu^{2+} , indicates the presence of Cu^{2+} ²⁰³⁻²⁰⁴. The shake-up satellite peaks are caused by the discrete energy losses that the excited electrons in the valence band to a higher energy state ²⁰⁵⁻²⁰⁶. The satellite peaks are useful characteristic for copper and nickel oxides ²⁰⁷. The high resolution of XPS scan for the fabricated copper-polymer composite shows two copper states indicating the changes of chemical state after two-photon fabrication. Due to the binding energy values, calculated auger parameters and no shake-up satellites, two Cu 2p_{3/2} peaks at 932.3 and 932.6 eV are suggestive of Cu_2O and metallic copper, respectively ^{203, 208-209}. The measured values, calculated values and the values from the literature are listed in **Table 6.2**. The presence of Cu_2O on the surface may be due to partial oxidation of the metallic copper or the by-product of the reduction process.

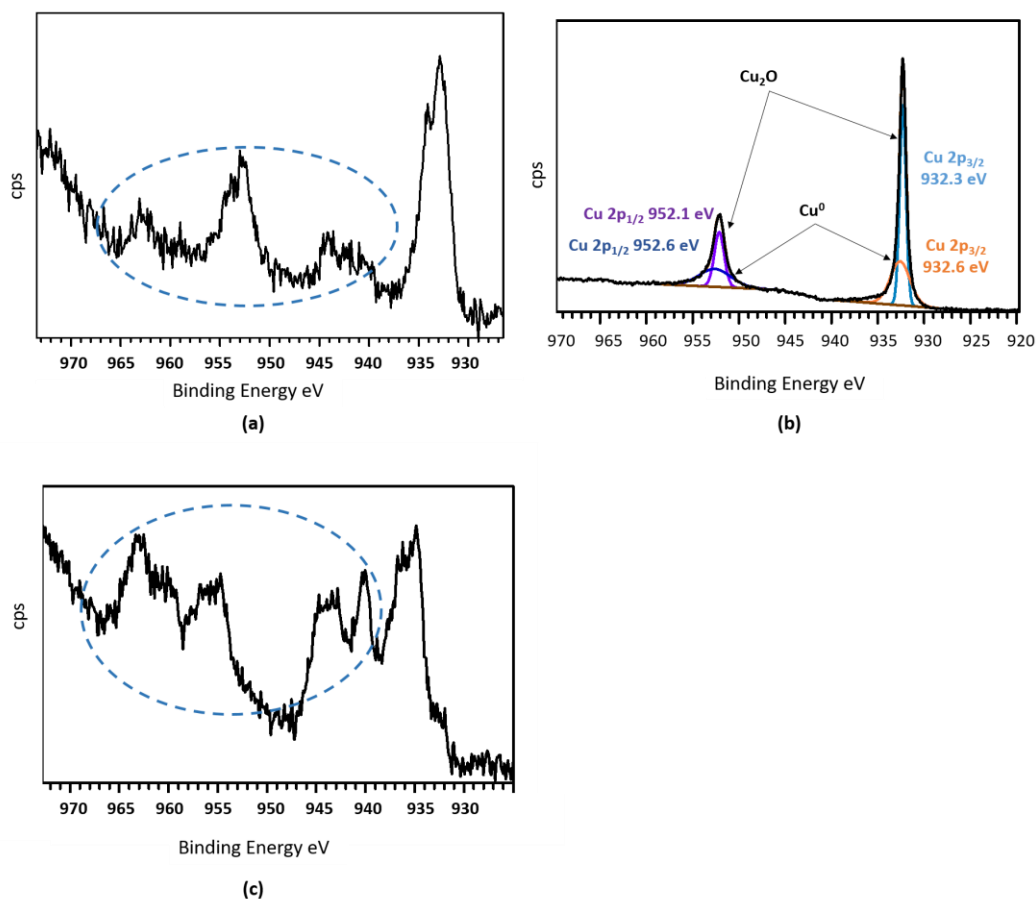


Figure 6.6 The XPS spectra of (a) copper precursor (dried silver ions in toluene) and (b) fabricated copper-polymer composite verify the reduction of copper ions; (c)

The XPS spectra of copper (II) sulphate pentahydrate.

Table 6.2 The binding energy of copper and Auger parameter obtained from XPS spectra and the corresponding reference values from the literature.

	Binding energy (eV) Cu 3d _{3/2}	Auger parameter AP-3d _{3/2} , L ₃ M ₄₅ M ₄₅
Cu-polymer composite	932.6	1851.3
	932.3	1849.0
Cu ⁰ reference ^{203, 208-209}	932.6	1851.2
Cu ₂ O reference ^{203, 208-209}	932.4	1849.2

6.4 Conclusions

- This chapter reported a primary study on the fabrication of copper-polymer nanocomposites through simultaneous TPP and TPR.
- Compare to gold and silver reduction, copper ions required more energy to be reduced. When used Irgacure 390 as a photoinitiator and PETA as a monomer in ethanol, structure formation was only observed when full laser power of 50 mW was applied for 1% copper composite and a much slower scan speed of 1000 $\mu\text{m/s}$ was used for 5 % copper composite. It is because copper ions owe lower reducibility compared to gold and silver. The reduction potential of Cu^{2+} to Cu is +0.34 V, which is lower than Au^{+} to Au, +1.69 V and Ag^{+} to Ag, 0.80V²¹⁰.
- A similar phase transfer method to prepare silver-polymer nanocomposites was used to fabricate copper-polymer nanocomposites. Both 2D and 3D structures were built and the presence of reduced copper particles was confirmed. The phase-transfer protocol could be applied in the synthesis of a variety of metal-polymer composites through simultaneous photopolymerisation and photoreduction including Mn, Fe, Co, Ni, Zn, Ru, Rh and Pd metals¹⁸⁶.

7 General Discussion

The aim of this research is to investigate the possibility of using simultaneous photopolymerisation and photoreduction to produce 3D metal-polymer nanocomposites which could be potentially applied in microelectronics, metamaterials and SERS. In this thesis, gold-, silver- and copper-polymer 3D nanocomposites structures were successfully fabricated through simultaneous photopolymerisation and photoreduction by TPL. Different formulations and processing parameters were assessed to print the structures as designed. The missing gaps between the printed method and printed structures, chemical mechanism, optimisation of processing parameters and characterisations on fabricated structures were filled through this study.

7.1 Gold-polymer Nanocomposite

3D gold NPs containing nanocomposites were fabricated using PETA as a monomer, commercial photoinitiator Irgacure 369 as a photoinitiator and gold chloride hydrate as a metal source. Compared to Shukla et al.'s work¹¹⁻¹², more complex 2D structures were generated, and 3D structures were fabricated for the first time. The reason for more complex structures is probably due to the polymerisation used in this study is free radical polymerisation. In Shukla's work, epoxy type resin, SU-8 was used as a monomer for cationic polymerisation. According to literature, the polymerisation rate of cationic is higher than radical with the same amount of functional groups²¹¹. The polymerisation rate of diacrylate monomers is one order magnitude higher than difunctional epoxides because of diacrylate monomers' higher propagation rate constant²¹¹. The key feature of cationic is more challenging to terminate

polymerisation than free radical and the termination occurs by chain transfer to inactive materials or impurities such as water²¹². A post-curing process is needed for SU-8 epoxy resin¹². In Blasco's work, free-radical polymerisation using Irgacure 2959 as a photoinitiator, PEG-triacry with acrylic acid as an oligomer and gold chloride hydrate as a metal source was performed to fabricate filigree-like structures. However, reduced gold particles were trapped and aggregated in PEG-triacry oligomer and difficult to form complex structures and keep structure details. It may be because oligomer has longer chain than monomers such PETA. The gaps between crosslinked chains were bigger so that gold particles were aggregated in the gaps. Compared to the literature¹¹, the line width of the gold-polymer nanocomposites in this study was dropped from 750 nm in Shukla's work to 150 nm. The line resolution was further reduced to 78 nm when used DETC as a photoinitiator, PETA as a monomer and gold chloride hydrate as a metal source²¹³.

7.2 Silver- and Copper-polymer Nanocomposites

Silver- and copper-polymer nanocomposites were fabricated through simultaneous photopolymerisation and photoreduction for the first time. Silver metallic structures have been produced through direct deposition of silver ions in previous literature^{9, 34-35, 37-38, 40, 45, 112-113, 115, 120, 122, 124}. No complex 3D structures such as photonic woodpile structures have been directly written through TPL before. For direct deposition of silver solution, the minimum line width and silver dot size fabricated through direct reduction of silver ions using coumarin photon sensitive dye were 400 nm and 550 nm respectively⁹. Smaller silver dots of 22 nm were later directly reduced by a shorter laser beam (580 nm)³⁵. 2D C-shape array with a line width of 220 nm using 532 nm wavelength laser and NDSS as a surfactant⁴⁵. For the direction of silver ions in a

polymer matrix, a line width of 1 μm was written in PVP films⁴⁰. Through simultaneous photopolymerisation and photoreduction combined with the metal ion phase transfer method, a line width of 547.0 ± 11.4 nm, which is wider than directly deposited silver lines but thinner than the silver lines in the PVP films, was obtained. Uniformly distributed silver NPs with an average size of 5.80 ± 1.50 nm was achieved. A primary investigation on copper-polymerisation composites was conducted in this research and the results suggest the broader applications of the phase-transfer method¹⁸⁶ in two-photon fabrication.

7.3 Potential Applications

This research pushed fabrication on metal-polymer nanocomposites through simultaneous photopolymerisation and photoreduction on step further – from method concept to more comprehensive understanding and controllability on the method. The achievements provide more potentials in real applications such as metamaterials and microelectronics.

In metamaterials applications, metals such as silver, gold and copper, which exhibit surface plasmon resonance (SPR) effects, are generating interest in optoelectronics and photonics²¹⁴. At the plasmon resonance frequency, the incident electromagnetic field enhancement can be used for optical manipulating such as resonant light scattering, light bending, superlensing and surface-enhanced Raman scattering (SERS)¹¹⁰. For the real optical devices, controllability on nanostructure and the sizes and shapes of NPs are essential. For example, the gold helix photonic metamaterials as broadband circular polarizer fabricated through the inversion method (section 2.4.3), chiral structures in 3D were required¹⁴². However, the technique is complex

and challenging to achieve more complicated designs. High-resolution ($15 \times 20 \mu\text{m}^2$, 100 nm line width) 2D silver-PVA composites for plasmonics with the average nanoparticle size of 8.4 ± 1.5 nm were fabricated through electron-beam lithography²¹⁴. However, the method has been limited to 2D and structural complexity.

This work started with an investigation on 3D gold-composite structures. Suitable formulations were developed to fabricate 3D structures. The presence of gold NPs was verified. However, only SEM images were obtained to characterise the aggregated gold particles on the structure. The average size was 123.8 ± 100.7 nm. Even if the build was halted midway during the fabrication of the pyramid structure, suggesting the presence of gold particles throughout the printed structures, the characterisation of NPs inside the structures is suggested in future work. The particle surface geometry, including sizes, shapes and distributions, affect the SPR effect²¹⁴⁻²¹⁵. Therefore, a study on gold NPs control is useful. Primary research on the influence factors on silver NPs' size and distribution was carried out in this thesis. Formulations, including photoinitiator concentrations and the presence of photosensitive dye, were found relevant to particle sizes and formulations. A comprehensive study on silver sizes, shapes and distributions are required in the future for specific applications. The metamaterials made of copper suffer from fabrication complexity¹⁹. The ability to fabricate copper-polymer 3D nanostructures was assessed in this thesis, which provides a promising application in copper metamaterials. The abilities to control structure and fabricate complex 3D structures such as photonic woodpile structures suggest that fabricating metal-polymer composites through simultaneous photopolymerisation and photoreduction is worthwhile for research and development in metamaterials applications.

In microelectronic applications, continuous metal structures and metallic loading are key factors to form conductive structures³⁹. In this thesis, gold, silver and copper metals were used to fabricate 2D and 3D structures, which are useful for microelectronic devices such as spring inductor¹³¹, but the conductivities of fabricated structures were not evaluated. Whether the metallic loading was enough to generate conductive materials were not assessed. Therefore, the real concentration of metal in the composites and the minimum metal concentration for conductive composites is suggested to be studied in the future. In this thesis, metal: monomer molar ratio of 1:5 was used for gold-, silver- and copper-polymer nanocomposites. If a higher concentration of metal source is required, new photoinitiators with higher efficiency for two-photon fabrication are necessary. Another challenge for real application is the writing speed of two-photon lithography. Several approaches have been reported to improve the speed of TPP, such as multi-focus²¹⁶⁻²¹⁷, multi-beam interference²¹⁸⁻²¹⁹ and focal field engineering²²⁰⁻²²¹. In Yang's work, the scan speed was improved from 1000-20000 $\mu\text{m/s}$, which are the normal TPP scan speed, to 6 $\mu\text{m/s}$ via 3D focal field engineering²²⁰. However, the methods developed are limited to structure design or lack of more material tests. Therefore, the improvement in scan speed of two-photon fabrication is required.

In summary, this work demonstrated that fabricating 2D and 3D metal-polymer nanocomposites through simultaneous photopolymerisation and photoreduction in a single step is achievable. The fabricated structures were more complicated and more controllable than previously reported work, which suggests the method and developed

formulations could be used to produce high complexity devices potentially used in metamaterials and microelectronic.

8 Conclusion and Future Work

8.1 Conclusions

This thesis investigated the manufacture of metal-polymer nanocomposites by simultaneous two-photon polymerisation reduction. With the experimental results and discussion, the key findings are as following:

- It is the first time that 3D gold-polymer nanocomposites have been fabricated by simultaneous free-radical photopolymerisation and photoreduction. A formulation with gold chloride hydrate as a metal source, PETA as a monomer, Irgacure 369 as a photoinitiator and additional ruthenium (II) complexes as a photosensitive dye was developed and used to fabricate 3D pyramid structures. The line width was sub-wavelength resolution down to 150 nm. Adding additional photoinitiator and photosensitive dye was useful to reduce the competition between photopolymerisation and photoreduction. The presence of ruthenium (II) dye in formulations was crucial for fabricating 3D complex structures. The presence of gold metallic particles was confirmed and the average particle size on the structure surface was 123.8 ± 100.7 nm.
- For the first time, simultaneous photopolymerisation and photoreduction were used to fabricate 2D and 3D silver-polymer nanocomposites. The phase-transfer protocol was found useful to solve the solubility problems of metal sources, monomers and photoinitiators. Higher concentrations of photoinitiators led to smaller silver particle sizes. The distribution of silver NPs was found relevant to the addition of coumarin 30 dye. Additional coumarin 30 dye made the line resolution of 547.0 ± 11.4 nm and the average silver NPs size of 5.80 ± 1.50 nm.

- A primary study on the fabrication of copper-polymer nanocomposites through two-photon manufacturing was constructed. The phase-transfer method was found useful for fabricating metal-polymer through simultaneous two-photon polymerisation and metal reduction.
- The relationship between processing conditions and final printed structures were evaluated in this work. The minimum laser power for fabrications was found related to formulations, including photoinitiator concentrations and the presence of photosensitive dye. The line width resolution could be controlled by formulations, processing laser power and the presence of oxygen. The metal particle sizes were observed relevant to photoinitiator concentrations, photosensitive dye and sample preparation method such as the phase-transfer method.
- The fabricated 2D and 3D metal-polymer nanocomposites through simultaneous photopolymerisation and photoreduction in a single step suggest promising potentials to produce metamaterials and microelectronic devices.

8.2 Future Work

The thesis enabled the first production of 3D gold-, silver- and copper-polymer nanocomposites by single-step two-photon lithography. A fundamental understanding of the fabrication was constructed. Several suggestions for future work are listed as follows:

- Further systematic studies are required for the fabrication of copper-polymer nanocomposites to find out the effects of materials, concentrations and processing conditions on printed structures.

- The particle size and distribution of generated metal NPs were characterised and analysed. A comprehensive study on how to control the particle size and distribution is necessary. The study will be especially useful when the nanocomposites are used in certain applications.
- For the phase-transfer protocol, the concentration of metal ions affected the final results of transferring of metal ions from the water phase to the organic solvent phase. The effect of metal ions' concentration on fabricated nanocomposites needs to be evaluated.
- Some photosensitive dyes were found useful in TPR. The optimum concentration and the effect on particle formation need to be further assessed. The mechanism needs to be investigated and fully understand.
- The mechanical and optical properties were not tested in this thesis. For specific applications such as photonics, metamaterials, plasmonics, electronics, catalysis, bio-sensing and so on, the mechanical, optical and other required properties would be very important. By controlling the nanoparticle sizes and the distributions of NPs and unique design of fabricated structures, the possibility of a particular type of application could be investigated.
- For the longer-term view of the technology, developing real applicable devices in metamaterials and microelectronics is predicted. An improvement in scan speed of two-photon fabrication is required. The cost of materials and two-photon lithography need to be considered. The balance between structure quality, efficiency and cost need to be evaluated in the future.

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Appendix A

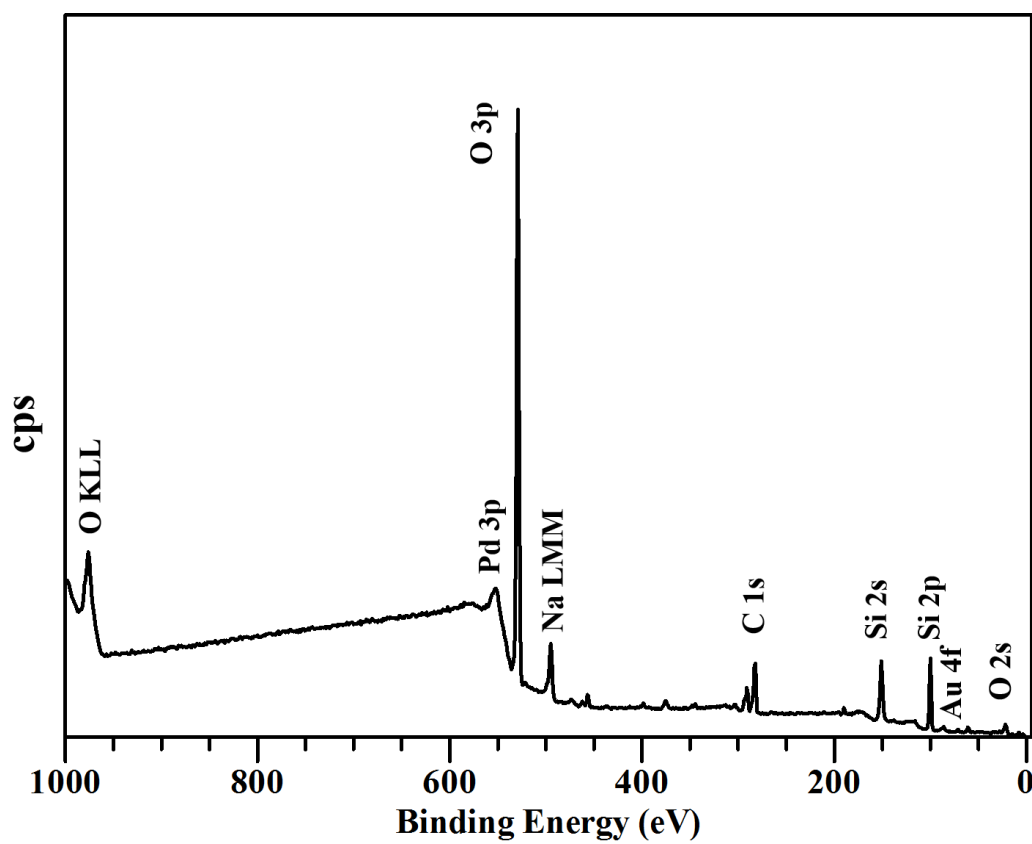


Figure A1 An XPS full-scan spectrum for a partially completed 3D gold-polymer.composite build of formulation G5.

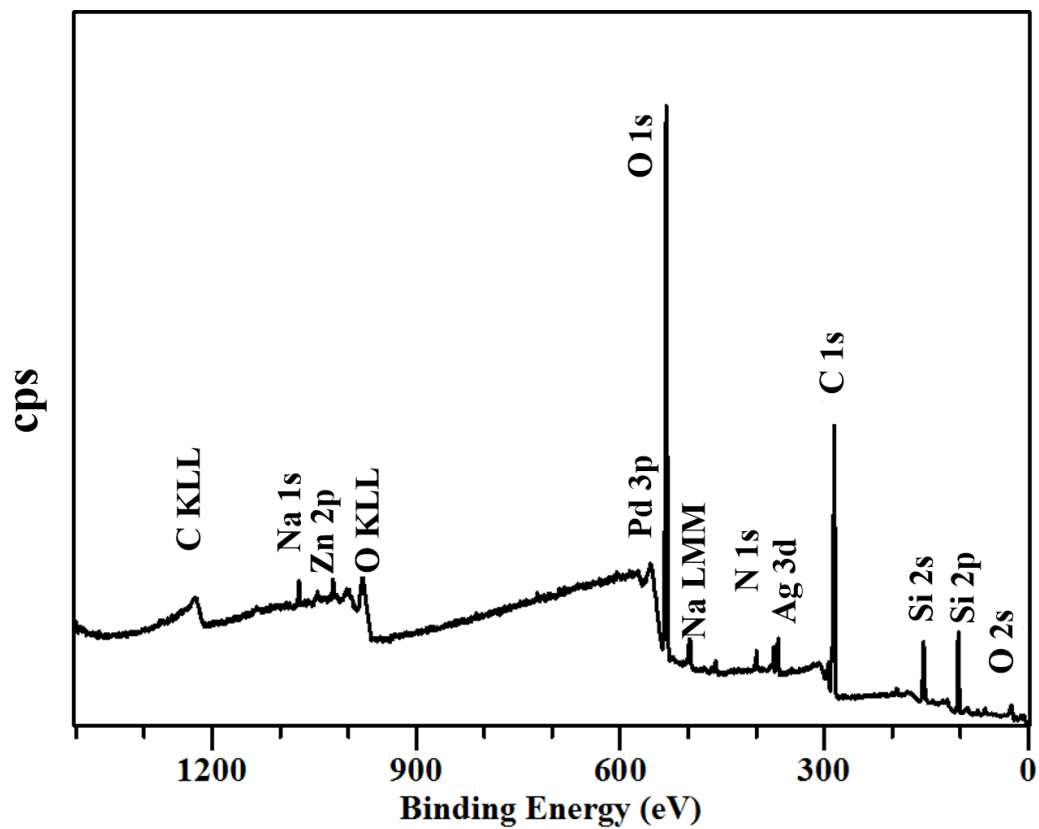


Figure A2 An XPS full-scan spectrum for fabricated silver-polymer composite using formulation 4.2.

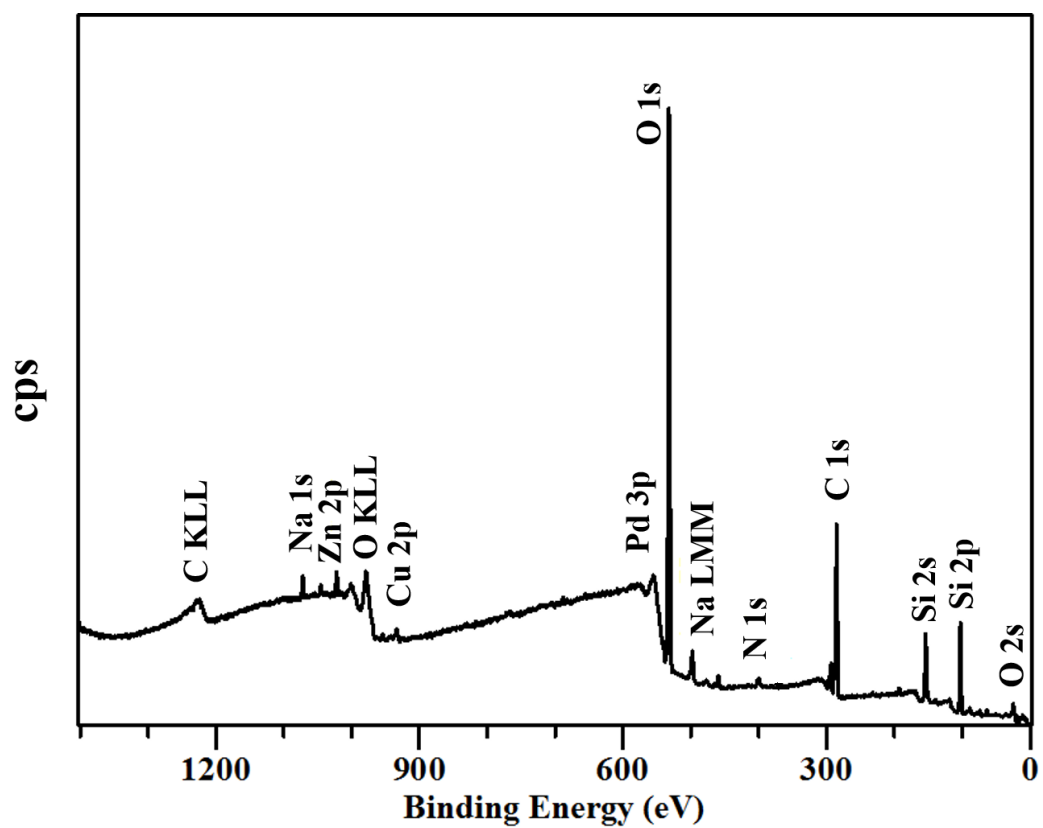


Figure A2 An XPS full-scan spectrum for fabricated copper-polymer composite.

Appendix B

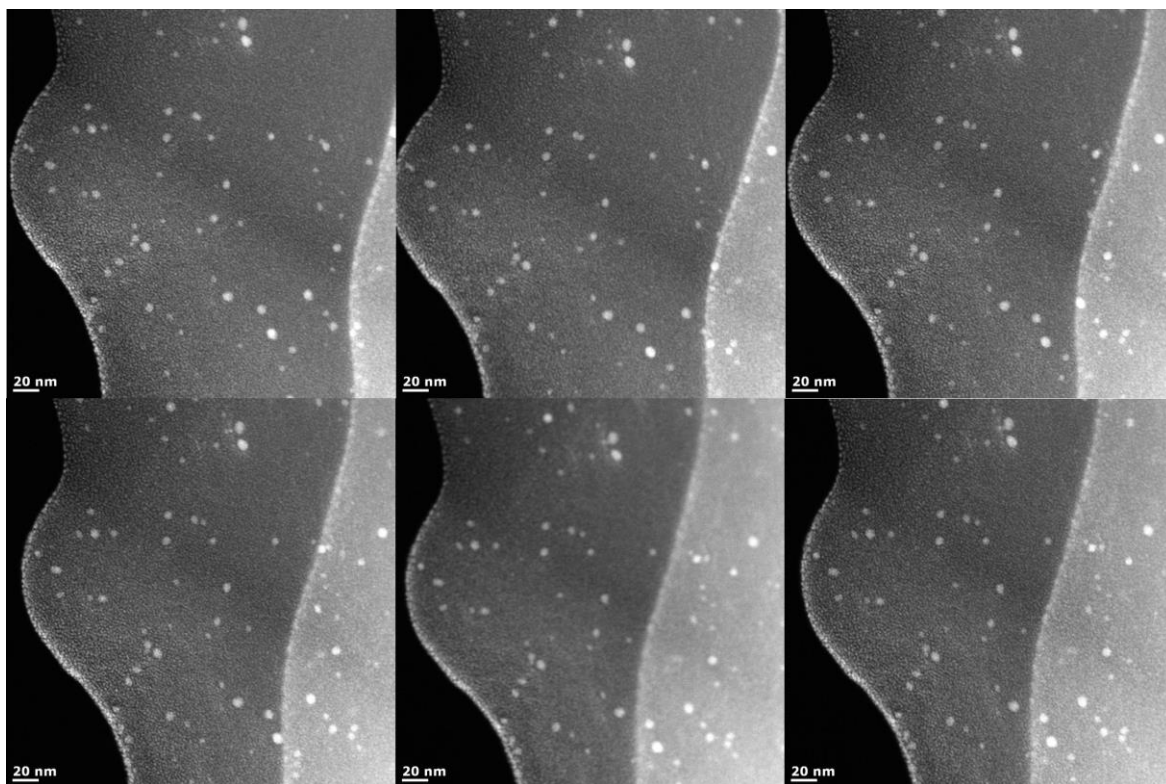


Figure B1 A group of DF-STEM images at different tilt angles to confirmed the 3D distribution of silver NPs.