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CONFINEMENT OF NANOSTRUCTURED CeO₂ INSIDE CARBON NANOTUBES

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Abstract

This study reveals confinement of nanostructured CeO_2 inside graphitised carbon nanofibers ($\text{CeO}_2@\text{GNF}$). A standard procedure has been developed for encapsulation of CeO_2 nanoparticles inside GNF. *In situ* preparation of CeO_2 encapsulated inside GNF, has been carried out by using gas phase thermal decomposition method and ionic liquid mediated method.

$\text{CeO}_2@\text{GNF}$ composites have been characterized by TGA, Raman, XRD, HRTEM, STEM and EDX techniques. Precursor loading was found to influence, particle size, location of CeO_2 , thermal stability and catalytic activity of $\text{CeO}_2@\text{GNF}$ composite. Besides being hollow nano container, GNF acts as a template for the growth of very small CeO_2 nanoparticles of size 3nm with high degree of crystallinity and dispersity. Catalytic properties of nanostructured CeO_2 confined inside GNF has been assessed in oxidation of cyclohexene. High conversion of the reactant, selective oxidation of allylic carbon centre and formation of selective oxidation product 2-cyclohexenenone are some of the notable features, attributed to the effect of spatial confinement of CeO_2 inside GNF.

To study metal-support interaction in a confined space, Pt/CeO_2 encapsulated in $\text{GNF}(\text{Pt}/\text{CeO}_2@\text{GNF})$ has been prepared. Addition of Pt into $\text{CeO}_2@\text{GNF}$ led to growth of Pt nanoparticles on step edges of CeO_2 nanoparticles at CeO_2 -GNF interface.

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Abbreviations

BMIBr

Definitions

1-butyl-3-methyl imidazolium bromide

CeO ₂ @GNF	Cerium oxide nanoparticles inside graphitised carbon nanofibers
CeO ₂ -GNF	Cerium oxide nanoparticles and graphitised nanofibers composite
Ce(tmhd) ₄	Tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)Ce(IV)
CNT	Carbon nanotube(s)
DWCNT	Double-walled carbon nanotube(s)
EDX	Energy dispersive X-ray spectroscopy
FWHM	Full width half maximum
GC-MS	Gas chromatography mass spectrometry
GNF	Graphitised carbon nanofiber(s)
¹ H NMR	Proton nuclear magnetic resonance
HOMO	Highest occupied molecular orbital
HRTEM	High resolution transmission electron microscopy
JCPDS	Joint committee on powder diffraction standards
LUMO	Lowest unoccupied molecular orbital
M NPs	Metal nanoparticles
MO NPs	Metal oxide nanoparticles
MOF	Metal organic framework
MWCNT	Multi-walled carbon nanotube(s)
nm	Nano metre
NPs	nanoparticles
SMSI	Strong metal support interaction
STEM	Scanning transmission electron microscopy
SWCNT	Single-walled carbon nanotube(s)
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
XRD	X-ray diffraction

1. Introduction

1.1 Confinement of metal/metal oxide at nanoscale

The principle of the encapsulation of metal nanoparticles inside a porous matrix has been widely used to prepare stable well dispersed nanoparticles grown inside hollow nanostructures and to prevent sintering of nanoparticles under harsh reaction conditions.^{1,2} Besides stability, nanoparticles offer many interesting properties as a result of their confinement,³⁻⁵ such as size controlled growth,⁶ unusual structural features,⁷ selectivity in catalysis,^{2,3} modification in redox behaviour,⁸ etc. .Therefore confinement of metal and metal oxide nanoparticles inside porous nanostructures has been an area of significant interest specifically for preparing stable nanoreactors to study chemical transformations at the nanoscale. Materials having porous structures, such as zeolites, metal organic frameworks (MOFs) and carbon nanotubes (CNTs) are potential containers for confinement of metal and metal oxide nanoparticles.

Metal nanoparticles encapsulated inside zeolites have been applied as nanoreactors for catalysis. Li et al.³ reported encapsulation of Pt inside hollow silicalite, that exhibits catalytic activity towards selected molecules due to restricted accessibility to only those molecules capable of diffusing through nanopores of silicalite structure. As a result, Pt NPs confined inside silicalite hollow crystals could hydrogenate toluene but not the bulky mesitylene (1,3,5-trimethylbenzene)³ (**Figure 1**). However, unconfined Pt NPs adsorbed over silica shows catalytic activity towards both. Selectivity towards the substrate and the negligible loss of catalytic activity even after 5 cycles in the Suzuki-Miyaura reaction has also been observed with Pd nanoparticles encapsulated inside zeolite.⁹ Also as a consequence of confinement inside zeolite, Pt NPs were prevented from catalyst poisoning.¹⁰

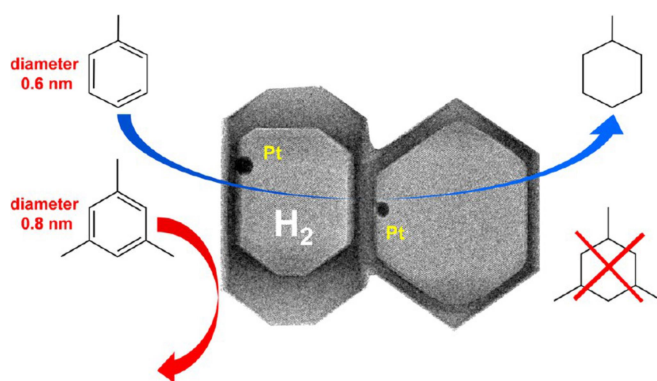


Figure 1 Selective hydrogenation of mono-alkylbenzenes over Pt NPs encapsulated in hollow silicalite.³

Like zeolites, metal organic frameworks (MOFs) are also effective for confining metal nanoparticles due to their porous structure. The porous structure of MOFs offers steric restriction to prevent aggregation of metal nanoparticles and thus produce uniformly distributed nanoparticles inside the pores of MOFs. Due to the confinement effect in the MOFs, small size (2-6 nm) Ag@Au core shell nanoparticles were prepared and applied as heterogeneous catalyst with significantly improved catalytic effect.¹¹ Similarly, confinement of Co_3O_4 inside hollow metal-organic framework provides a nanoreactor with improved performance for degradation of pollutant 4-chlorophenol (4-CP).¹² Besides providing stability to Co_3O_4 nanoparticles, metal-organic framework protects active sites of catalyst and provides adsorptive sites for enrichment of reactants near the catalyst and thus accelerates reaction rate.¹²

Looking beyond zeolites and MOFs, carbon nanotubes (CNTs) offer potential advantages for encapsulating guest molecules due to their unique tubular morphology with high thermal stability (ca. 700 °C in air and up to 2800 °C in vacuum) and mechanical strength (with tensile strength much higher than that of steel).¹³ In CNTs, curvature of CNT walls causes shifting of π electron density of graphene layers from concave inner to the convex outer surface resulting in electron density gradient, as a consequence, encapsulation of metal nanoparticles inside carbon nanotubes exhibit unusual properties distinct from those adsorbed outside the surface of CNTs.¹⁴ Therefore encapsulation of metals inside CNTs creates a separate class of materials having promising applications.

For example, γ -Fe nanoparticles confined inside CNT exhibit stability at room temperature, which is otherwise stable between 1185-1667K in the bulk.⁵ Similarly cobalt nanorods confined inside multiwalled carbon nanotubes (MWCNT) exhibit fcc structure which are otherwise stable in hexagonal form.¹⁵ Confined metal nanoparticles inside CNT, are also found to exhibit better catalytic performances than compared to those adsorbed outside the surface of CNTs. This improved catalytic activity of metal nanoparticles inside CNTs is attributed to the effect of spatial confinement at nanoscale,¹⁴ which can result from 4 key factors;

- i. **Electronic interaction of metal and metal oxide nanoparticles with CNT.** Electronic interaction takes place between confined metal/metal oxide nanoparticles and CNT host, as a consequence of this interaction, catalytic activity of confined catalysts can be affected. For example, Ru nanoparticles adsorbed outside double-walled carbon nanotube (DWCNT) exhibit higher electron density as compared to Ru nanoparticles confined inside DWCNT, suggesting electron transfer from Ru to DWCNT during confinement and thus higher rate of NH_3 synthesis with Ru adsorbed on DWCNT than Ru confined inside DWCNT.¹⁶ Khlobystov et al. also observed electron transfer from cobalt complexes to CNT as a result of confinement.¹⁷
- ii. **Restricted space of host matrix.** Due to restriction of space inside CNT, small size metal nanoparticles are prepared, and also agglomeration of nanoparticles is prevented. Since agglomeration of particles reduces the catalytic activity and lower chance of agglomeration inside CNT offers better catalytic activity to confined metal catalyst, for example, Rh-Mn nanoparticles confined inside CNT exhibit higher activity for syngas conversion due to the absence of nanoparticles aggregation.² Deactivation of iron oxide nanoparticle catalysts adsorbed outside CNT was observed due to agglomeration in contrast to the better catalytic performance of confined iron oxide nanoparticles inside CNT.¹⁸

- iii. **Enhanced reactant concentration inside CNT.** Due to confined space and interaction of reactant molecules with CNT, concentration of reactants increases inside CNT. As a consequence, proximity between the catalyst and reactants increases, and this accelerates the reaction rate. Theoretical study by Bao et al.¹⁹ suggests that, the increase in the concentration of the reactants CO and H₂ inside CNT is due to stronger interaction of both molecules with interior of CNT than with exterior.
- iv. **Enhanced rate of molecular uptake and release in CNT.** Transport of molecule through internal channels of CNTs becomes less hindered due to molecular ordering of incoming molecules inside CNTs. Because of lower transport resistance, the rate of reactant molecules getting in and product molecules going out becomes faster and this influences the rate of a catalytic reaction. For example, diffusion of n-heptane inside single-walled carbon nanotube (SWCNT) has been observed to be higher by a factor 35 than diffusion of n-heptane in bulk.²⁰

Due to such effects of spatial confinement at nanoscale, preparation of novel materials with tuned catalytic activity has attracted significant attention. A number of examples of confinement of different d-block (groups 6-11) metals/metal oxide nanoparticles inside CNTs (**Figure 2**) and their properties, have been demonstrated by several research groups as summarised in **Table 1**.

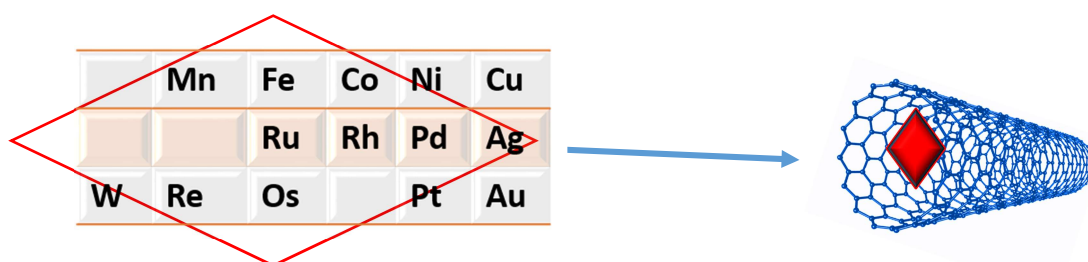


Figure 2 Schematic illustration of confinement of group 6-11 d-block elements inside carbon nanotube.

Table 1 Summary of confinement of d-block metals inside carbon nanotubes (CNTs) and their comparisons with metals adsorbed outside CNTs.

	M/MO NPs confined inside	M/MO NPs adsorbed outside	Effect of confinement	Properties/Applications	Ref.
1	Fe@SWCNT	Fe/SWCNT	Electron transfer from Fe to SWCNT	Oxidation of Fe in Fe@CNT is retarded	8
2	Ru@DWCNT	Ru/DWCNT	Electron transfer from Ru to DWCNT	Higher rate of NH ₃ synthesis in Ru/DWCNT	16
3	W@SWCNT Re@SWCNT Os@SWCNT			Formation of very small nanoparticles (~1nm) with high stability at elevated temperature.	6
4	Co@MWCNT	Co/MWCNT	Formation of uniformly distributed small size particles inside MWCNT	Higher rate of Fischer-Tropsch reactions with Co@MWCNT	21
5	CoFe ₅ @CNT	CoFe ₅ /CNT	Prevention of sintering and aggregation of particles	Higher rate of NH ₃ decomposition with CoFe ₅ @CNT	22
6	RhMn@CNT	RhMn/CNT	Prevention of aggregation of particles	16 times higher rate of syngas conversion with RhMn@CNT	2
7	Pd@CNT	Pd/CNT	Enrichment of reactants inside CNT channel	92% enantioselective hydrogenation of α,β -unsaturated carboxylic acid	23
8	Pt@MWCNT	Pt/MWCNT	Formation of small size particles inside MWCNT	Chemoselective hydrogenation of C=C in cinnamaldehyde over Pt@MWCNT	24
9	Cu@MWCNT	Cu/MWCNT	Formation of small size particles inside MWCNT and prevention from aggregation	Higher rate of hydrogenation of methyl acetate with Cu@MWCNT	25
10	Ag@MWCNT	Ag/MWCNT	Formation of grain boundaries and surface roughening of Ag, facilitating dissociation of H ₂ on Ag@MWCNT	Three times higher catalytic activity of Ag@MWCNT in hydrogenation of dimethyl oxalate	26
11	Au@MWCNT	Au/MWCNT	Interaction of Au with CNT facilitates dissociation of H ₂ on Au@MWCNT	Chemoselective hydrogenation of C=C in cinnamaldehyde over Au@MWCNT	27
12	TiO ₂ @MWCNT	TiO ₂ /MWCNT	Formation of more Ti ³⁺ or oxygen vacancies inside MWCNT	Enhanced visible light activity for degradation of methyl orange in TiO ₂ @MWCNT	28
13	Fe ₂ O ₃ @MWCNT	Fe ₂ O ₃ /MWCNT	Prevention of aggregation of particles	Higher rate of Fischer-Tropsch reaction and prevention of sintering of catalyst in Fe ₂ O ₃ @MWCNT	18
14	MnO ₂ @CNT	MnO ₂ /CNT	Formation of Mn ²⁺ /Mn ³⁺ redox couples	Enhanced capacitance of MnO ₂ in MnO ₂ @CNT	29

Similar to confinement of different metals in CNTs that can produce different materials with varying properties and applications, the choice of CNT as host matrices can influence the properties of the resultant catalyst.

1.2 Structure of carbon nanotubes (CNTs)

Based on the structure of CNTs, there can be different categories of nano containers to encapsulate host nanoparticles. CNTs can either be single-walled (SWCNTs) or multi-walled (MWCNTs). The simplest CNT has a single, one atom thick layer of graphite called, graphene, rolled up into a hollow cylinder and is called a single-walled carbon nanotubes (SWCNTs) having diameters of around 0.4–2 nm and are several micrometres long (**Figure 3a**). Depending on the way graphene sheet is wrapped SWCNTs can be armchair, zigzag and chiral nanotubes (**Figure 3c**).³⁰ Multiwalled carbon nanotubes (MWNTs), comprising multiple rolled up layers of graphene yielding cylindrical hollow structure (**Figure 3b**) of diameter 10-30 nm and interlayer spacing 0.34 nm.³¹ The name multiwalled nanotube is restricted to nanostructures with outer diameters of about 30 nm, above which the structures are called carbon nanofibers.³² Carbon nanofibers are described as a non-continuous one dimensional carbon nanoallotrope of cylindrical or conical shape, consisting of stacked and curved graphene sheets arranged in various ways.³³ One most important carbon nanofiber is graphitised carbon nanofibers (GNF).

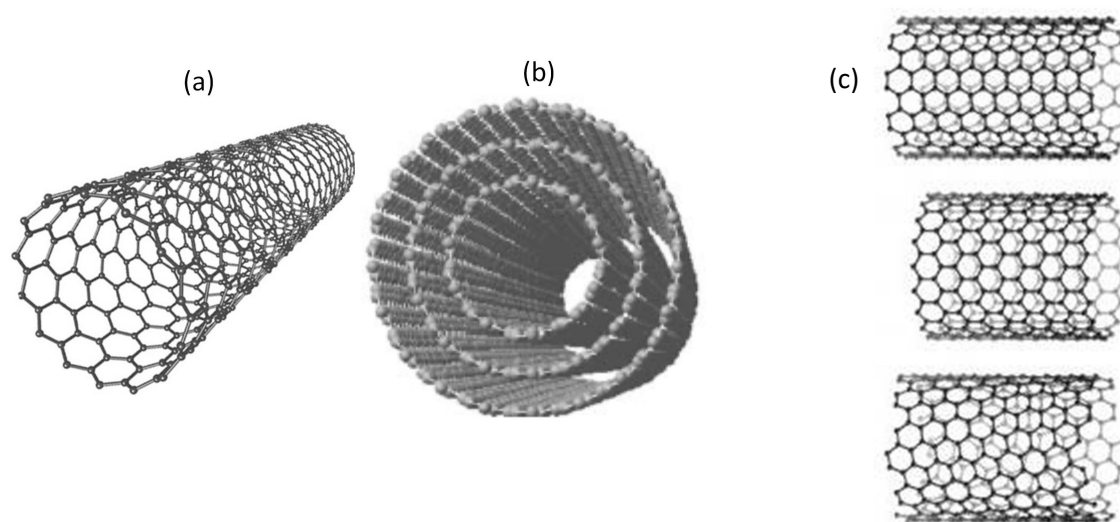


Figure 3 Schematic representation of; (a) single-walled carbon nanotubes (SWCNT),³⁴ (b) multi-walled carbon nanotubes (MWCNT),³⁵ and (c) SWCNTs of structure (From the top): armchair, zigzag and chiral.³⁰

1.2.1 Graphitised carbon nanofibers (GNF)

Unlike carbon nanotubes, which consist of concentric layers of graphene, in graphitised carbon nanofibers (GNF), the structures of the inner and outer surfaces are fundamentally different to each other. The outer surface of GNF consists of continuous, atomically flat cylindrical layers (ca. 50 to 60) of graphene, but the internal surface possesses a succession of step-edges formed by rolled-up sheets of graphene (3–4 nm high and spaced by 8–15 nm from each other) forming a robust hollow structure (**Figure 4b**).³⁶

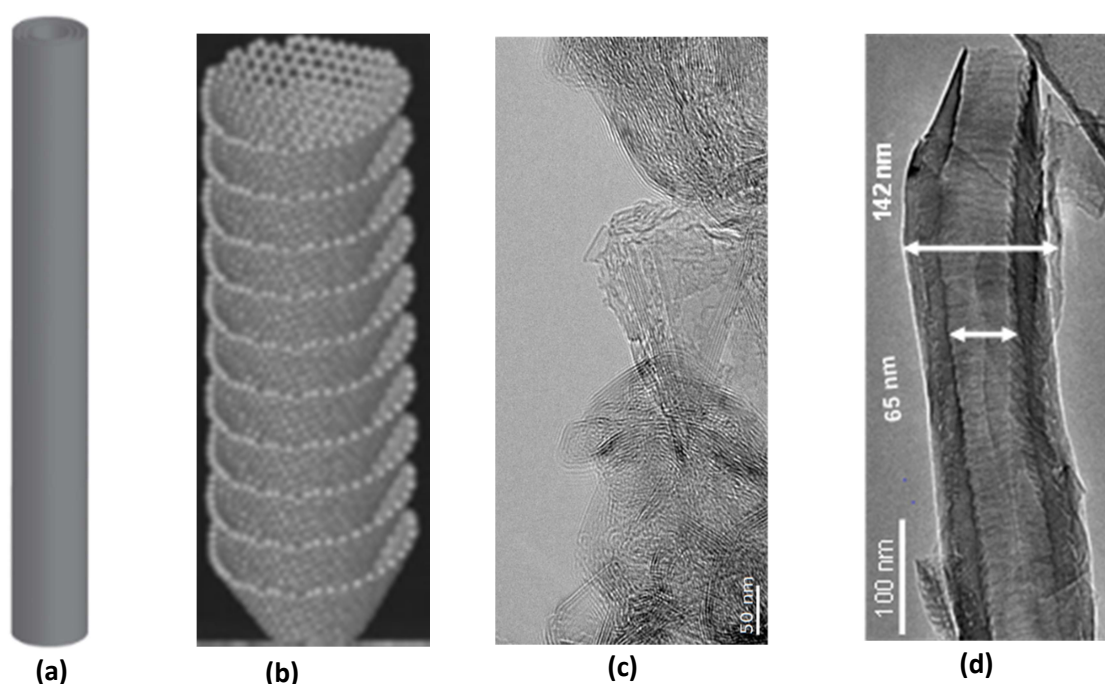


Figure 4 Schematic representation of innermost graphitic layers of (a) CNT and (b) GNF.³⁶ HRTEM images of (c) step edges of GNF(PR-19) and (d) cylindrical structure of GNF(PR-19).

High resolution transmission electron microscopy (HRTEM) analysis of GNF (PR-19) shows step edges (**Figure 4c**) and cylindrical structure (**Figure 4d**). These step edges can serve as potential anchoring points for guest nanoparticles. Hollow graphitised carbon nanofibers (GNF) are significantly wider than MWCNT (internal diameters typically above (50 nm)). **Figure 4d** shows HRTEM image of GNF (PR-19) having internal diameter 65 nm and external diameter 142 nm. Besides robust and hollow structure of

GNF, its wide internal channels facilitate effective transport of molecules through the tubular structure.^{4,37,38}, making GNF a most suitable candidate to study chemical reactions at nanoscale. In contrast, multiwalled carbon nanotubes (MWCNTs), consisting of layers of graphene parallel to the growth axis forming a set of concentric cylinders (**Figure 4a**), possess an atomically smooth interior, and hence, control of NP position through interactions with the nanotube surface is unfeasible.

Besides structural advantages, it is also demonstrated that both the kinetics,³⁸ and selectivity,^{4,37} of chemical reactions are fundamentally affected by confinement inside GNF. As a result of this spatial confinement, nanoscale chemical transformations in GNF nanoreactors exhibit distinct outcomes in comparison to the bulk solution or gas phase. For example, hydrosilylation reaction of phenylacetylene and triethylsilane in the nanoreactor having $[\text{Rh}_4(\text{CO})_{12}]$ catalyst confined inside GNF yields 8 fold increase in $\beta(\text{E})$ -vinyl silane in comparison to the reaction in bulk solution phase,³⁹ rate of cycloaddition reaction of alkynes and azides in Cu nanoparticles confined inside GNF is significantly higher than Cu NPs in bulk solution,³⁸ in oxygen reduction reaction Pt nanoparticles confined inside GNF retains electrochemical activity even after 50000 cycles, while the activity of Pt adsorbed on amorphous carbon dramatically decreases only after 10000 cycles.⁴⁰ These effects of confinement are the consequence of interactions between carbon nanostructures (CNT), reactants and products, which are summarised by Khlobystov¹³ (**Table 2**).

Table 2 Interactions between CNT, reactants & products in carbon nanoreactors.¹³

Interactions between CNT and catalyst	Interactions between CNT and reactants	Interactions between CNT and products
enhanced stability of catalyst inside nanotube	attractive interactions between nanotube interior and reactant molecules leading to higher local concentration and effective pressure inside nano-reactors	restriction of reaction space inside nanotube favouring formation of one product (e.g., linear isomer) over another (e.g., branched isomer)
electron transfer between catalyst and interior	alignment of reactant molecules within nanotube facilitating reaction	efficient transport of product molecules from nano-reactor to bulk phase
surface of nanotube altering catalytic activity	van der Waals or electron transfer interactions between reactants and nanotube interior lowering activation energy	
chemical reactions between metal catalyst and nanotube interior leading to transformations of CNT sidewall		

Taking advantages of GNF over MWCNT Khlobystov et al. have reported GNF as nano reactor to study chemical transformations in a confined space.³⁹ Nanostructured metals encapsulated inside hollow structure of GNF, have shown superior catalytic performances in comparison to free standing or surface-adsorbed nano catalysts. To give a few examples, nanoparticles (NPs) of rhodium (Rh) and rhodium-platinum (RhPt) alloy embedded inside GNF for regioselective hydrosilylation of terminal alkynes,³⁷ Au NPs encapsulated inside GNF for oxidation of silane by hydrogen peroxide,⁴ Pt NPs inside GNF for oxygen reduction reaction,⁴⁰ and Pd complexes inside GNF for Heck reaction.⁴¹ Besides high selectivity and conversion, GNF nanoreactor having catalyst inside, exhibits good recyclability and stability of catalyst,^{38,40} thus representing a superior nano container to study chemical transformations at nanoscale.

Although many investigations have been done for d-block metals inside carbon nanotubes and their catalytic applications have been extensively studied, lanthanides and their compounds have been studied significantly less. Being different from d-block elements, lanthanides can offer a new class of materials when confined in CNTs.

1.3 Nanostructured lanthanide oxides

Compared to d-block elements lanthanides exhibit unique distinct properties due to 4f-orbitals, deeply buried inside the atom and shielded from external environment by overlying 5s and 5p orbitals (**Figure 5a**).⁴² This contracted nature of 4f orbital has a substantial effect on their physicochemical properties, leading to wide range of applications of lanthanides (**Figure 5b**).⁴³ Due to partially filled 4f orbitals, lanthanide oxides exhibit unique electronic, optical, magnetic and catalytic properties.⁴⁴ Based on the f-f electronic transitions lanthanide oxides are also applied as lasers, light emitting diodes (LEDs) and biological markers.⁴⁵

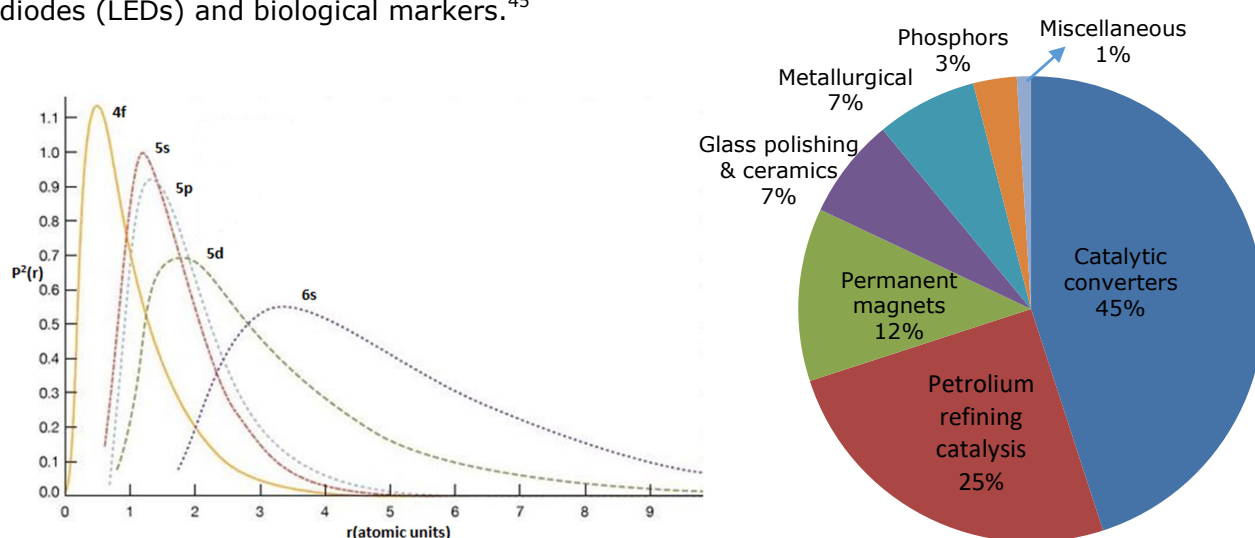


Figure 5 (a) Electron probability function for 4f, 5s, 5p, 5d and 6s orbitals of gadolinium ($P^2(r)$ = radial probability function, r = distance from the nucleus),⁴² (b) Pie chart of applications of lanthanides (1996).⁴³

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
58	59	60	61	62	63	64	65	66	67	68	69	70	71

Figure 6. Elements of lanthanide series.

1.3.1 CeO₂ as catalyst

Among lanthanides (La-Lu) (**Figure 6**), cerium is the most applied element in the field of catalysis in its oxide form known as ceria (CeO₂). Fortunately, it is the most abundant lanthanide, about 0.0046% of the earth's crust by weight (64 ppm).⁴⁶ The high abundance, with its outstanding catalytic activity has made CeO₂ widely used as catalyst and an effective alternative to noble metal catalysts. Compared to its bulk counterpart, nanoparticles of CeO₂ exhibit improved activities due to their size effects and their unique physical and chemical properties. As a result, CeO₂ nanoparticles have been used in heterogeneous catalysis as supporting material,⁴⁷ solid-oxide fuel cells,⁴⁸ solar cells,⁴⁹ high temperature oxidation protection material,⁵⁰ antioxidants,⁵¹ and potential pharmacological agents.⁵² The remarkable catalytic activity of CeO₂ is due to its ability to undergo interconversion between $\text{Ce}^{3+} \rightleftharpoons \text{Ce}^{4+}$. Depending on the reaction conditions, it exists as CeO₂ (Ce⁴⁺) under oxidizing conditions and Ce₂O₃ (Ce³⁺) under reducing conditions. As a consequence of this interconversion, CeO₂ releases oxygen from its structure at moderate temperatures (<600 °C).⁵³ The non-stoichiometry of oxygen within the material creates oxygen vacancy while reducing Ce⁴⁺ to Ce³⁺. This behaviour makes ceria useful for oxygen storage and release applications. Also, due to this redox behaviour, CeO₂ nanoparticles have been used as catalyst for many important redox reactions, such as, preparation of imines from alcohols and amines,⁵⁴ oxidation of cyclohexene,⁵⁵ oxidation of CO to CO₂^{47b} and hydrogenation of CO₂ to methanol.⁵⁶

Further, the catalytic performance of CeO₂ is greatly influenced by its size, shape and morphology,⁵⁷ which is attributed to change in surface area, mesoporous structures, pore volumes, and generation of oxygen vacancies. For example, rate of oxidation of CO over CeO₂ nanotube is 3 times higher than that of the bulk ceria,⁵⁸ and flowerlike CeO₂

microspheres exhibit higher catalytic activity than normal CeO₂ nanoparticles.⁵⁹ It is also observed that the decrease in the size of CeO₂ results in unique properties. CeO₂ nanoparticles of size 3-4 nm, supporting Au NPs enable an increase in rate of CO oxidation by two orders magnitude as compared to Au NPs supported on bulk ceria.⁶⁰ This has been attributed to generation of more O vacancies in smaller CeO₂ nanoparticles.⁶¹ Due to this size-property relationship, many groups have prepared CeO₂ nanoparticles of different sizes and shapes such as nanospheres,⁶² nanorods,⁶³ nanotubes,⁵⁸ shuttle-shaped,⁶⁴ nanowires,⁶⁵ and flower-like,⁶⁵ by various methods (**Table 3**). Still controllable preparation of ultra-small CeO₂ nanoparticles with high dispersity remains a significant challenge. Apart from size controlled synthesis of CeO₂ nanoparticles, it is important for a CeO₂ catalyst to improve the stability of its redox properties and to prevent deactivation of CeO₂ under harsh reaction conditions. Encapsulation of CeO₂ nanoparticles in a core-shell system, where CeO₂ is protected by an outer shell structure is an efficient way to produce stable catalyst. Besides stability, the effect of spatial confinement of CeO₂ nanoparticles can also be studied.

Table 3 Preparation of CeO₂ nanoparticles of different morphologies and sizes, and their applications.

	Method of preparation	Morphology & size	Application	Ref.
1	Hydrothermal	Nanospheres, 100-250 nm Nano rods, 50-200 nm length Nanocubes, 36 nm	Ferromagnetism Photocatalyst Oxygen storage capacity	62 63 66
2	Solvothermal	Shuttle shaped, 500-700 nm	CO oxidation	64
3	Chemical precipitation	Rods, 80-100 nm	Band gap variation of CeO ₂	67
6	Sol gel	Nanoarchitecture(not discrete particles), 10 nm Ceria microspheres, 50-100 nm	Improved electrical conductivity Removal of pollutants from waste water	68 69
7	Reversed micelles/microemulsion	Ultrafine particles, 2-6 nm Polycrystalline aggregates, 8 nm	Oxidation of CO Reduction in band gap of CeO ₂	70 71
8	Spray pyrolysis	Ceria powder, 10 to 155 nm	High thermal stability with conserved surface area	72
9	Supercritical solvent(CO ₂)	Nanowires, 5 nm diameter	Hydrogenation of nitroarenes	65
10	Ionic liquid assisted	Nanoflower like, 14 nm	CO oxidation	57

1.3.2 CeO₂ as catalyst support

Interactions of metal nanoparticles with oxide supports can significantly enhance the performance of supported catalysts. CeO₂ has been used as a support for noble metal catalysts such as Pt,⁷³ Au,^{47b} Cu,^{74,75} Rh,⁷⁶ for many important applications like hydrogenation of benzene,⁷⁷ and toluene,⁷⁸ oxidation of CO to CO₂,⁷⁹ and hydrogenation of CO₂ to methanol.^{74,75} The role of a metal oxide support for metal catalyst is not limited to providing high surface area for stabilisation of metal nanoparticles. It renders a hybrid metal- metal oxide junction for redox reactions to take place at the interface between the catalyst and support. Based on the nature of oxide support, the catalytic activities of metal catalyst can be modified. Broadly, metal oxide supports can be categorised as reducible metal oxides (CeO₂) and non-reducible metal oxides (SiO₂, Al₂O₃ and aluminosilicates). CeO₂ being a reducible support exhibits improved catalytic activities in comparison to non-reducible supports.⁸⁰ This distinction is mainly due to strong metal-support interaction (SMSI) effect. Pt supported on CeO₂ (Pt/CeO₂) is a system having such SMSI effect. As a result of the interaction with CeO₂, a large electronic perturbation takes place in Pt nanoparticles leading to change in their chemical properties. In Pt/CeO₂ nanostructure, two types of metal-oxide (MO) interactions are observed, electron transfer from Pt to CeO₂ and transfer of activated oxygen from CeO₂ to Pt.⁸¹ These interactions between Pt and CeO₂ can be explained in two ways.

One is due to the generation of oxygen vacancy in nanostructured CeO₂ as represented in **equation 1**. Each released O atom leaves behind an oxygen vacancy (V_O) and creates two Ce³⁺ cations by transferring electrons to two Ce⁴⁺ cations. This generation of V_O involves three steps, (1) transfer of two electrons from O²⁻ to two Ce⁴⁺ cations, (2) elimination of O atom and (3) relaxation of crystal lattice (**Figure 7**).⁸² In ultra-small CeO₂ nanoparticles, the gap between the highest occupied molecular orbital (HOMO); 2p orbitals of O and lowest unoccupied molecular orbital (LUMO); 4f orbitals of Ce is less in comparison to bulk CeO₂.⁸² As a result, electron transfer from O²⁻ to Ce⁴⁺ becomes easier and the energy needed for oxygen vacancy creation (E_{vac}) is less. It has been observed

that, E_{vac} for nano CeO_2 (0.8 eV) < E_{vac} for bulk CeO_2 (2.25 eV). As a consequence, the oxygen vacancy generation becomes easier in nano ceria.

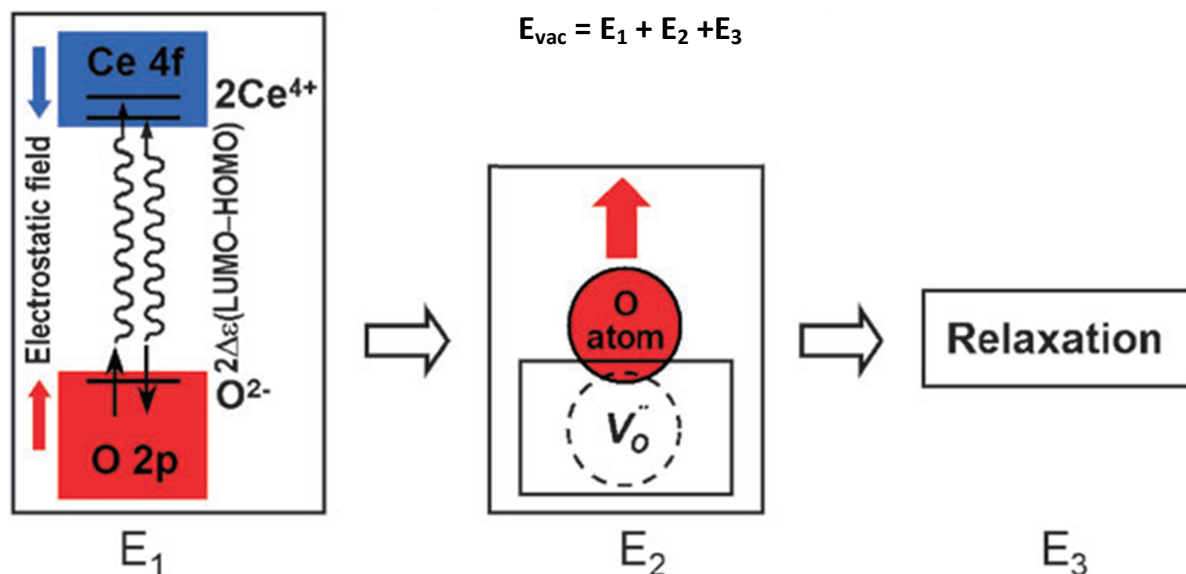
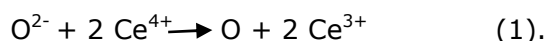


Figure 7 Illustration of oxygen vacancy generation in nano ceria.⁸² E_{vac} = The energy needed for generation of oxygen vacancy, E_1 = energy required for electron excitation, E_2 = energy required for removal of O atom and E_3 = energy gained from relaxation of crystal lattice.

Further, the energy gap between filled 5d orbitals (HOMO) of Pt and empty 4f orbitals (LUMO) of Ce is small.⁸¹ As a result, there is electron transfer from Pt (5d) to Ce (4f) and transfer of activated O to Pt takes place, which generates Ce^{3+} at the interfaces. This is purely a nanoscale effect which does not happen in ordered bulk CeO_2 ,⁸¹ and therefore nanostructured Pt/ CeO_2 has been used for important catalytic reactions, such as, hydrogen generation in water gas shift reaction, where dissociation of O-H bond in water becomes enhanced due to Pt/ CeO_2 combination,⁷³ hydrogenation of crotonaldehyde to produce butanol,⁸³ and chemoselective hydrogenation of nitro arenes,⁸⁴ oxidation of CO to CO_2 .⁷⁹ The combination of Pt and ceria clearly gives a useful material but what would happen if Pt and CeO_2 are brought in contact at nanoscale and are confined inside hollow carbon nanostructures? To address the question, Pt/ CeO_2 nanoparticles need to be encapsulated for studying metal-support interaction (MSI) in a confined space.

1.3.3 Confinement of nanostructured CeO₂

A few attempts made to study confinement of CeO₂ in silica and polymer matrices have been reported and are summarised in **Table 4**. The observations reveal interesting outcomes of confinement. For example, Kitagawa et al.⁸⁵ prepared ceria nanoparticles confined inside porous coordination polymer and showed that ceria in the pores contains higher concentration of Ce³⁺ than bulk synthesised ceria, and because of high amount of Ce³⁺ it acts as good O₂ adsorbent. Increased catalytic stability, prevention from coke formation on surface of Ni nanoparticles in Ni/CeO₂@SiO₂,⁸⁶ increase in reactant concentration inside nanoreactor accelerating rate of reaction,⁸⁷ increase in oxygen vacancy creation,⁸⁵ are key results of confinement of CeO₂ nanoparticles inside host matrices, suggesting importance of studying confinement effect of nanostructured CeO₂.

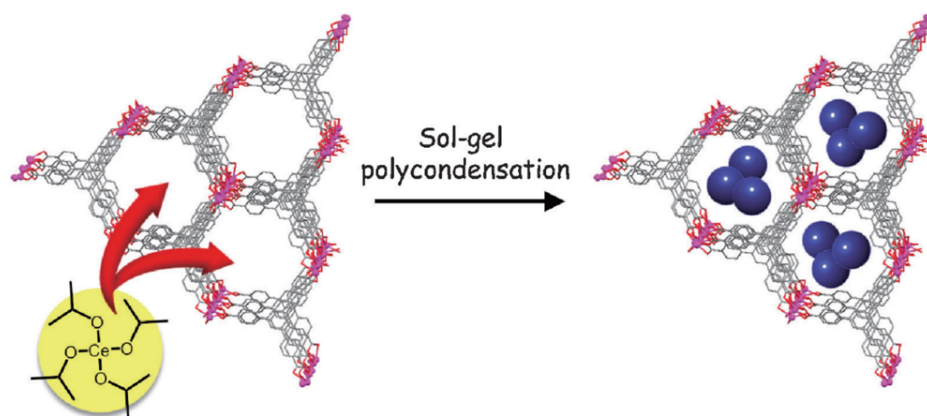


Figure 8 Schematic presentation of CeO₂ encapsulated inside porous coordination polymer.⁸⁵

Table 4 Confinement effects on nanostructured CeO₂.

	Method of preparation	Host matrix for confinement	Effect of confinement	Application	Ref.
1	Sol-gel condensation	Porous coordination polymer (PCP)	Increased Ce ³⁺	Oxygen adsorption	85
2	Ultrasonic irradiation	Mesoporous silica (Ni/CeO ₂ @SiO ₂)	Increased concentration of reactants near catalyst	Steam reforming of propylene glycol	88
3	Microemulsion	Silica (Ni/CeO ₂ @SiO ₂)	Increased catalytic activity and stability, prevents coke formation on Ni surface	Dry reforming of methane	86
4	Thermal impregnation	Titania nanotube (CeO ₂ @TiO ₂)	Increased local concentration of reactant	Selective catalytic reduction of NO	87

1.4 Scope for further investigation

Confinement of d-block metals inside carbon nanotubes has been studied extensively (**Table 1**), but attempts to study confinement of CeO₂ inside nanostructured carbon are rare. At present, 46 papers have been published on CeO₂ nanoparticles adsorbed on carbon nanotubes with only one study of CeO₂ nanoparticles inside carbon nanotube. Confinement effect on CeO₂ inside carbon nanotubes has been studied with oxidative dehydrogenation of ethyl benzene in presence of CO₂ and enhanced catalytic activity has been observed. CeO₂ being a reducible oxide can exhibit distinct outcomes as a consequence of confinement inside CNTs. Inside a nanoscale host, formation of ultra-small CeO₂ nanoparticles is more likely, which can lead to formation of more oxygen vacancies and Ce³⁺ cations. Both of these facts are central to catalytic activity of CeO₂, and therefore confinement of CeO₂ is worth studying. Further, graphitised carbon nanofibers being a superior nanocontainer, are therefore an ideal host structure for preparation of CeO₂ nanoparticles confined inside GNF and to evaluate its catalytic activity.

Similarly catalytic importance of Pt nanoparticles supported on CeO₂ nanoparticles (Pt/CeO₂) has been studied but confinement of Pt/CeO₂ has not been attempted by any group. The nanoscale effects of the metal-support interaction could produce interesting results under confinement which remains unexplored. Ceria being a reducible oxide support makes a strong metal-support interaction with Pt due to generation of oxygen vacancies at the Pt-CeO₂ interface, which is more probable with small size CeO₂ nanoparticles. Since confinement could lead to the formation of small size CeO₂ nanoparticles, the interactions between the catalyst and ceria are expected to be enhanced in Pt/CeO₂ encapsulated within a nanocontainer.

2. Aims and objectives

Due to the catalytic importance of CeO_2 and superior performance of GNF as hollow nanocontainer, this project is aimed at investigating the effect of nanostructured CeO_2 encapsulated in GNF. The aim of this project is to develop a standard procedure for preparation of CeO_2 inserted in GNF and to test its catalytic effect in redox reactions at nanoscale.

The specific objectives to achieve this aim are as follows:

- To develop a standard procedure for synthesis of CeO_2 encapsulated inside GNF.
 - i. by gas phase decomposition of volatile β -diketonate complex of cerium; $\text{Ce}(\text{tmhd})_4$ {tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato) $\text{Ce}(\text{IV})$ } as ceria precursor.
 - ii. by ionic liquid mediated method using hydrated ionic compound ($\text{CeBr}_3 \cdot x\text{H}_2\text{O}$) as ceria precursor.
- To characterise CeO_2 encapsulated inside GNF and evaluate its catalytic activity in oxidation reaction.
- To synthesise CeO_2 supported Pt nanoparticles embedded inside GNF for evaluation of metal-support interaction in a confined space.

3. Results and discussion

3.1 Preparation and characterisation of CeO₂ nanoparticles inside graphitised carbon nanofibers (CeO₂@GNF) by gas phase decomposition method

3.1.1 Shortening the length of GNF

In order to encapsulate CeO₂ nanoparticles inside hollow nanostructures and to perform chemical reactions in a confined space, the diameter and length of GNF must be suitable for easy transport of reactants to, and products from, its internal cavity. Smaller diameters with a greater length of GNF retards the diffusion rate and as a result the rate of chemical reaction becomes reduced. It has been observed that, the rate of catalytic dehydrogenation of ethyl benzene inside carbon nanotube is increased by 5% on reducing the length of carbon nanotubes from approximately 300 to 150 nm.⁸⁹ Therefore, cutting of long carbon nanotubes is essential to meet the demand of short nanoreactors. There are a number of different methods for cutting carbon nanotubes, for example mechanical methods, such as ball milling, oxidative methods using reagents, such as, nitric acid,⁹⁰ mixture of nitric and sulphuric acid,⁹¹ potassium permanganate,⁹² using catalytic metal and metal oxide nanoparticles, such as nickel oxide (NiO NPs),⁹³ iron (Fe NPs),⁹⁴ and silver (Ag NPs).⁹⁵ Among all these methods, ball milling is a clean process that effectively controls the length of carbon nanotubes without significant damage to it. Effectiveness of this method for making short length nanotubes has been demonstrated by Solomonsz et al.⁹⁶ who reported 4 fold increase in percentage of dehydrogenative silylation product using GNF shortened by ball milling process. Therefore, in this work graphitised carbon nanofibers (PR-19) were subjected to ball milling to reduce their length (**Figure 9**).

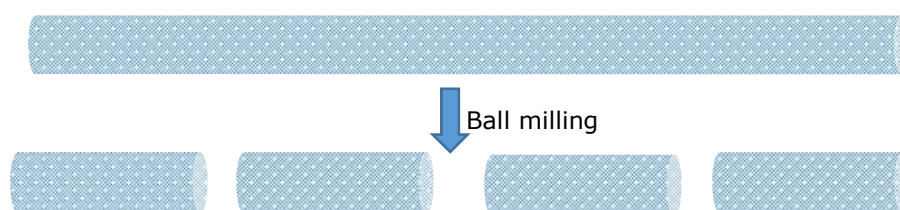


Figure 9 Schematic illustration of shortening the length of GNF by ball milling.

3.1.2 β -diketonate complex of cerium as precursor material

β -diketonate complexes of lanthanides are known for their applications as potential precursors for synthesis of highly pure lanthanide oxides. For synthesis of lanthanide oxides by thermal decomposition, these β -diketonate complexes have to be volatile with low sublimation temperature. To prepare lanthanide oxide encapsulated inside carbon nanotubes, these volatile complexes are suitable because they can readily sublime to gas phase under low pressure and enter inside nanotubes. Gas phase provides less hindered diffusion⁹⁷ of these precursor molecules inside nanotubes unlike liquid phase, which is driven by capillary forces of nanotubes. Volatility of these complexes can be achieved by using bulky or fluorinated ligands. One of such β -diketonate complexes of Ce(IV) is tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)Ce(IV), also represented as Ce(tmhd)₄. Due to its stability and low sublimation temperature (140 °C) Ce(tmhd)₄ is a suitable precursor for preparation of CeO₂ nanoparticles.

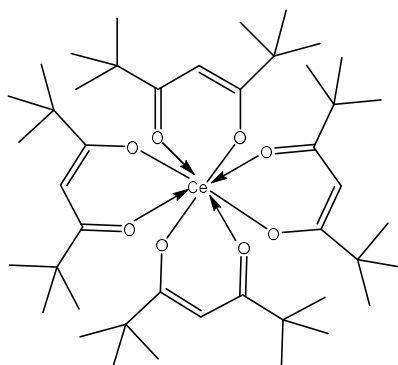


Figure 10 Tetrakis (2,2,6,6-tetramethyl-3,5-heptanedionato)Ce(IV), [Ce(tmhd)₄].

3.1.3 Method of preparation of CeO₂ inside graphitised carbon nanofibres (CeO₂@GNF)

CeO₂ nanoparticles in graphitised carbon nanofibers (CeO₂@GNF) have been prepared by heating a volatile precursor with graphitised carbon nanofibers (GNFs) (**Figure 11**). Prior to filling, graphitised carbon nanofibers were ball milled to reduce their length. The precursor Ce(tmhd)₄ was mixed with GNF, sealed under vacuum in a glass ampoule and heated above its sublimation temperature to ensure sublimation of Ce(tmhd)₄ and

diffusion inside hollow structure of GNFs to form the $[\text{Ce}(\text{tmhd})_4@\text{GNF}]$ composite. The sample was then rapidly cooled in ice cold water to facilitate condensation of precursor molecule inside GNF.⁶ Then the $[\text{Ce}(\text{tmhd})_4@\text{GNF}]$ composite was heated under argon atmosphere at temperature above the decomposition temperature of the $\text{Ce}(\text{tmhd})_4$ to decompose into CeO_2 nanoparticles inside GNF. In order to study the effect of precursor concentration on formation of CeO_2 nanoparticles, three different amounts of the cerium complex have been mixed with a fixed mass of GNF under same reaction conditions.

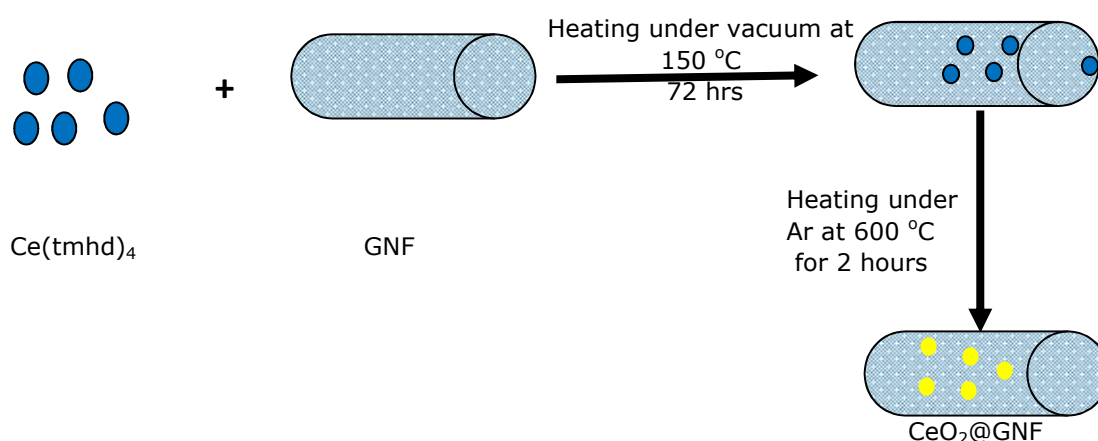


Figure 11 Schematic illustration of preparation of CeO_2 nanoparticles inside graphitised carbon nanofibers from gas phase decomposition of tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)Cerium(IV) $[\text{Ce}(\text{tmhd})_4]$.

3.1.4 Characterisation of CeO_2 nanoparticles encapsulated inside GNF ($\text{CeO}_2@\text{GNF}$)

3.1.4.1 Thermogravimetric analysis (TGA)

To ascertain the loading of CeO_2 in $\text{CeO}_2@\text{GNF}$ nanocomposite and to study its thermal stability, thermogravimetric analysis was carried out. **Figure 12** depicts thermogravimetric curves of cerium complex $\text{Ce}(\text{tmhd})_4$, GNF, and $\text{CeO}_2@\text{GNF}$ with different concentrations of precursor. The total weight loss occurred from 25 to $1000\text{ }^\circ\text{C}$ is found to be around 92-94%, which corresponds to carbon gasification due to combustion of GNF and the residual mass beyond $600\text{ }^\circ\text{C}$ corresponds to CeO_2 . Increase in residual mass of CeO_2 is in good agreement with the increase in amount of precursor. The $\text{CeO}_2@\text{GNF}$ nanocomposite starts to combust at around $400\text{ }^\circ\text{C}$, which is much lower

than the combustion temperature of pure GNF (700 °C). This is due to catalytic effect of CeO_2 which accelerates the combustion of GNF in air.^{94,98,99} This is a consequence of noncovalent interaction between CeO_2 nanoparticles and GNF,¹⁰⁰ where CeO_2 coordinates to π bonds ($\text{C}=\text{C}$) of GNF. As a result of this coordination $\text{C}=\text{C}$ bonds become weakened and thus GNF combusts at a low temperature.¹⁰¹ TGA profiles also indicate a decrease in thermal stability of CeO_2 @GNF nanocomposite with increase in amount of precursor (**Figure 12 b**), which is due to enhanced catalytic effect of CeO_2 nanoparticles with an increased concentration of ceria precursor. Again, one step decomposition of CeO_2 @GNF in thermogram reveals uniform oxidation, which is attributed to the formation of stable CeO_2 @GNF nanocomposite, negating the formation of CeO_2 and GNF separately.

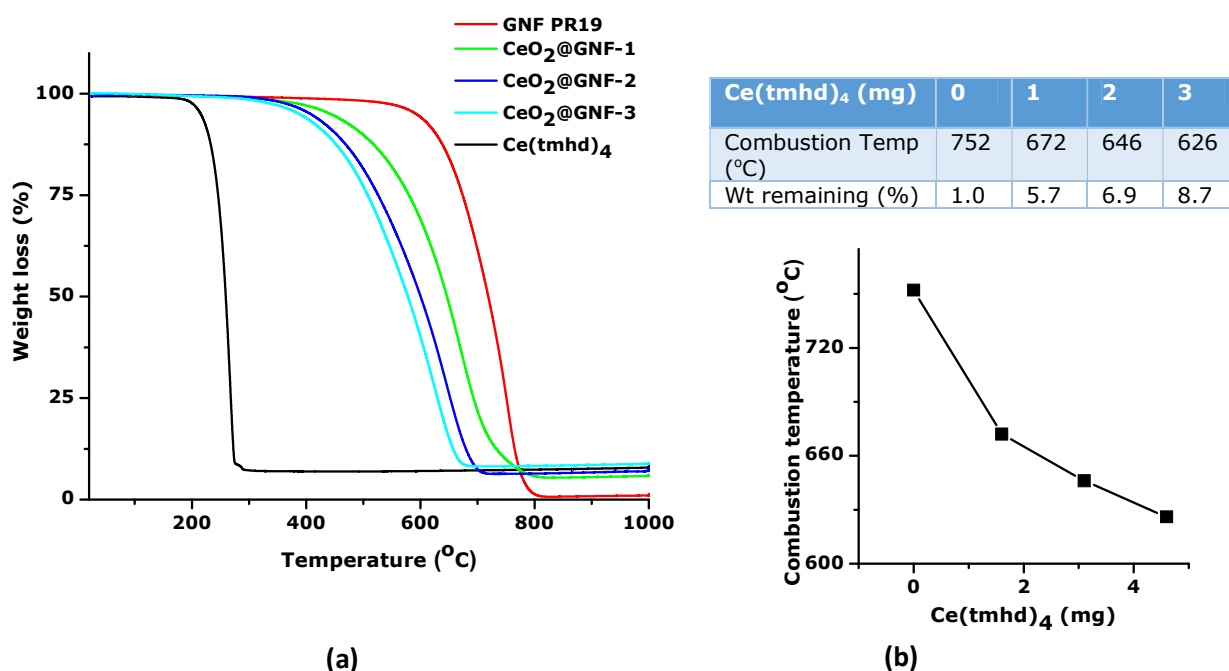


Figure 12 TGA curves of precursor $\text{Ce}(\text{tmhd})_4$, GNF, CeO_2 @GNF made with different amount of precursor (1,2 & 3 mg) denoted as CeO_2 @GNF-1, CeO_2 @GNF-2 and CeO_2 @GNF-3 respectively, (b) variation of combustion temperature of CeO_2 @GNF with amount of precursor.

3.1.4.2 Raman spectroscopy

Results obtained from TGA suggesting formation of CeO_2 and GNF nanocomposite is further supported by Raman spectroscopy. **Figure 13** depicts Raman spectra of GNF and CeO_2 @GNF nanocomposites made with different concentrations of precursor. The Raman

spectra of GNF consist of two characteristic bands: the G mode or tangential mode at 1571 cm^{-1} that corresponds to the movement in opposite directions of two neighbouring carbon atoms in a graphitic sheet, and the D mode or disorder mode at 1343 cm^{-1} which is activated by any defect that breaks the translational symmetry.⁹⁹ Usually the D- to G-band intensity ratio (I_D/I_G) is typically taken as a measure of surface disorder in carbon nanotubes. The I_D/I_G ratio increased for $\text{CeO}_2@\text{GNF}$ nanocomposites in comparison to GNF. This is potentially due to structural disorder of GNF resulted due to shortening/opening and thermal treatment during the preparation of composites.⁸⁹ Apart from the D and G bands, a band at 456 cm^{-1} is observed in Raman spectra of $\text{CeO}_2@\text{GNF}$ which is the feature of Ce-O bond,⁹⁹ confirming the formation of CeO_2 in the nanocomposite. Since Raman signals of CeO_2 inside GNF are obscured by 50-60 layers of carbon, so the observed Raman band for Ce-O corresponds to CeO_2 outside the GNF. The low intensity Ce-O band indicates low amount of CeO_2 adsorbed outside the surface of GNF, indicating most of the CeO_2 nanoparticles are encapsulated inside GNF.

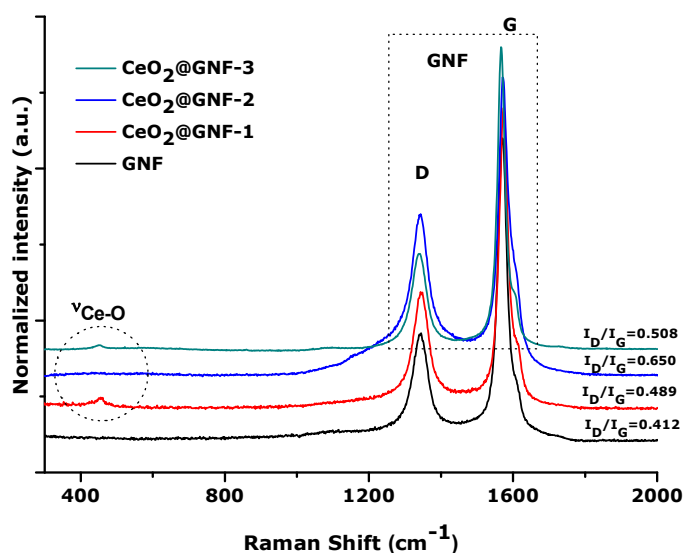


Figure 13 Raman spectra of GNF and $\text{CeO}_2@\text{GNF}$ made with different amounts of precursor (1,2 & 3 mg) denoted as $\text{CeO}_2@\text{GNF}$ -1, $\text{CeO}_2@\text{GNF}$ -2 and $\text{CeO}_2@\text{GNF}$ -3 respectively. The dotted circle indicates the characteristic Raman bands of CeO_2 , and the dotted square frame indicates the characteristic Raman bands of graphitised carbon nanofibers (GNF).

3.1.4.3 Powder X-ray diffraction

Though TGA and Raman measurements suggest formation of CeO_2 and GNF nanocomposite but to further ascertain the formation of CeO_2 and to identify its crystal structure the powder X-ray diffraction measurements were carried out. **Figure 14** depicts XRD patterns of graphitised carbon nanofibers and CeO_2 encapsulated in GNF with three different concentrations of precursor (1, 2 & 3 mg). The XRD patterns reveal GNF is integrated part in all three materials. The diffraction peaks of GNF at $2\theta = 26^\circ$, 42.4° , 44.6° , 54.4° and 77.4° correspond to (002), (100), (101), (104) and (110) planes of graphitic lattice,¹⁰² and are unchanged in CeO_2 @GNF composite. In CeO_2 @GNF-1 no prominent extra peaks corresponding to CeO_2 are observed, which can be attributed to low amount of precursor with very small size of CeO_2 nanoparticles well dispersed inside GNF. However for CeO_2 @GNF-3, with highest amount of $\text{Ce}(\text{tmhd})_4$ (3mg), XRD pattern shows four peaks at $2\theta = 28.3^\circ$, 32.8° , 47.3° , 56.3° corresponding to (111), (200), (220), and (311) crystal planes of CeO_2 (JCPDS card no. 43-1002) which are less prominent in CeO_2 @GNF-1 and CeO_2 @GNF-2. The XRD patterns show crystalline nature of CeO_2 with face centred cubic fluorite crystal structure.¹⁰³

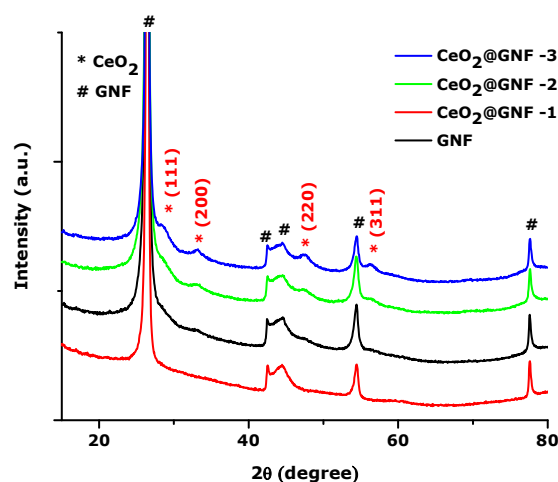


Figure 14 Powder XRD patterns of, GNF, and CeO_2 @GNF made with different amounts of precursor (1, 2 & 3 mg) denoted as CeO_2 @GNF-1, CeO_2 @GNF-2 and CeO_2 @GNF-3 respectively. Diffraction peaks corresponding to GNF are marked as # and those of CeO_2 as *.

For CeO₂@GNF-3, the crystallite size of the CeO₂ were calculated from the full width half maximum (FWHM) of the (111) peak at $2\theta = 28^\circ$ by using Scherrer's equation,¹⁰⁴ (eq. 2.).

$$D = K\lambda/B \cos\theta \text{ ----- (2)}$$

Where, D is the average crystallite size, λ is the wavelength of the X-ray radiation used, K is a constant taken as 0.9, θ is the diffraction angle, and B is the full width of the diffraction line at half the maximum intensity (FWHM) measured in radian.

The mean size was found to be 9 nm. The fact that CeO₂ peaks became more prominent for sample CeO₂@GNF-3 prepared with large amount of Ce(tmhd)₄ is due to increase in size of CeO₂ nanoparticles and is consistent with previous reports.¹⁰⁵

3.1.4.4 Transmission electron microscopy (TEM) and Energy dispersive X-ray spectroscopy (EDX)

Although TGA, Raman and XRD results all suggest formation of a nanocomposite of CeO₂ and GNF, the location of CeO₂, inside or outside GNF, could only be ascertained from TEM. Therefore transmission electron microscopic analysis was performed to confirm encapsulation of CeO₂ nanoparticles inside hollow structure of graphitised carbon nanofibers (GNF). Besides providing information about location of CeO₂ nanoparticles inside GNF, TEM analysis shows, particle size, crystal structure, atomic scale arrangements and lattice planes with d-spacing. **Figure 15** shows high resolution transmission electron microscopy (HRTEM) images of CeO₂@GNF nanocomposites. TEM reveals CeO₂ nanoparticles are well dispersed inside the GNF and fairly uniform in size. The mean size of the particles are found to be of diameter 4, 6 & 8 nm for precursor amount of 1,2 & 3 mg respectively. At low amount of precursor, CeO₂ nanoparticles are observed to be embedded inside GNF, however at higher amounts of precursor (3mg), besides encapsulation of most of the CeO₂ nanoparticles inside GNF, a few are found to be adsorbed on the outer surface of GNF (**Figure 16 d**). This can be attributed to the internal volume of GNF that can accommodate a fixed amount of nanoparticles, beyond which, nanoparticles gets deposited on the outer surface of GNF. Formation of CeO₂ nanoparticles is further confirmed by the high resolution TEM images (**Figure 16a-b**) of CeO₂ nanoparticles showing clear (111) fringes with interplanar d spacing of 0.32 nm.

EDX analysis revealing presence of C, Ce and O further reaffirms formation of $\text{CeO}_2\text{@GNF}$ nanocomposite. **Figure 16c** shows atomic steps of CeO_2 nanoparticles obtained when electron beams of TEM are exactly parallel to the lattice planes of the sample.

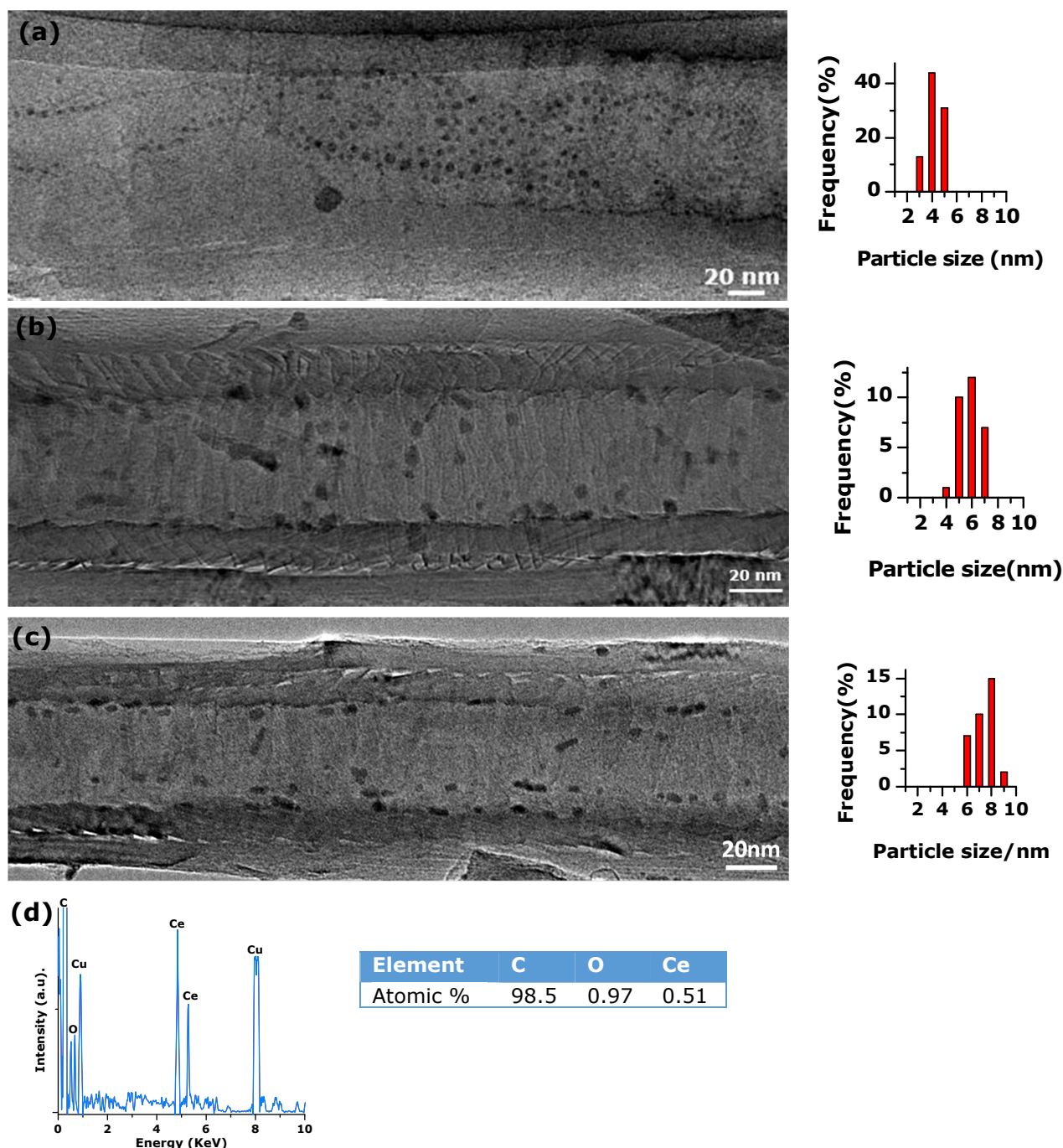


Figure 15 Studies of the CeO_2 nanoparticles encapsulated inside GNF ($\text{CeO}_2\text{@GNF}$) by transmission electron microscopy. (a-c) HRTEM images of $\text{CeO}_2\text{@GNF}$ made with 1, 2 & 3 mg $\text{Ce}(\text{tmhd})_4$ and their corresponding size distribution histograms of CeO_2 nanoparticles, (d) EDX spectra and atomic % of elements in $\text{CeO}_2\text{@GNF}$ with 3 mg $\text{Ce}(\text{tmhd})_4$ in the inset table. Cu peaks are from the TEM grid.

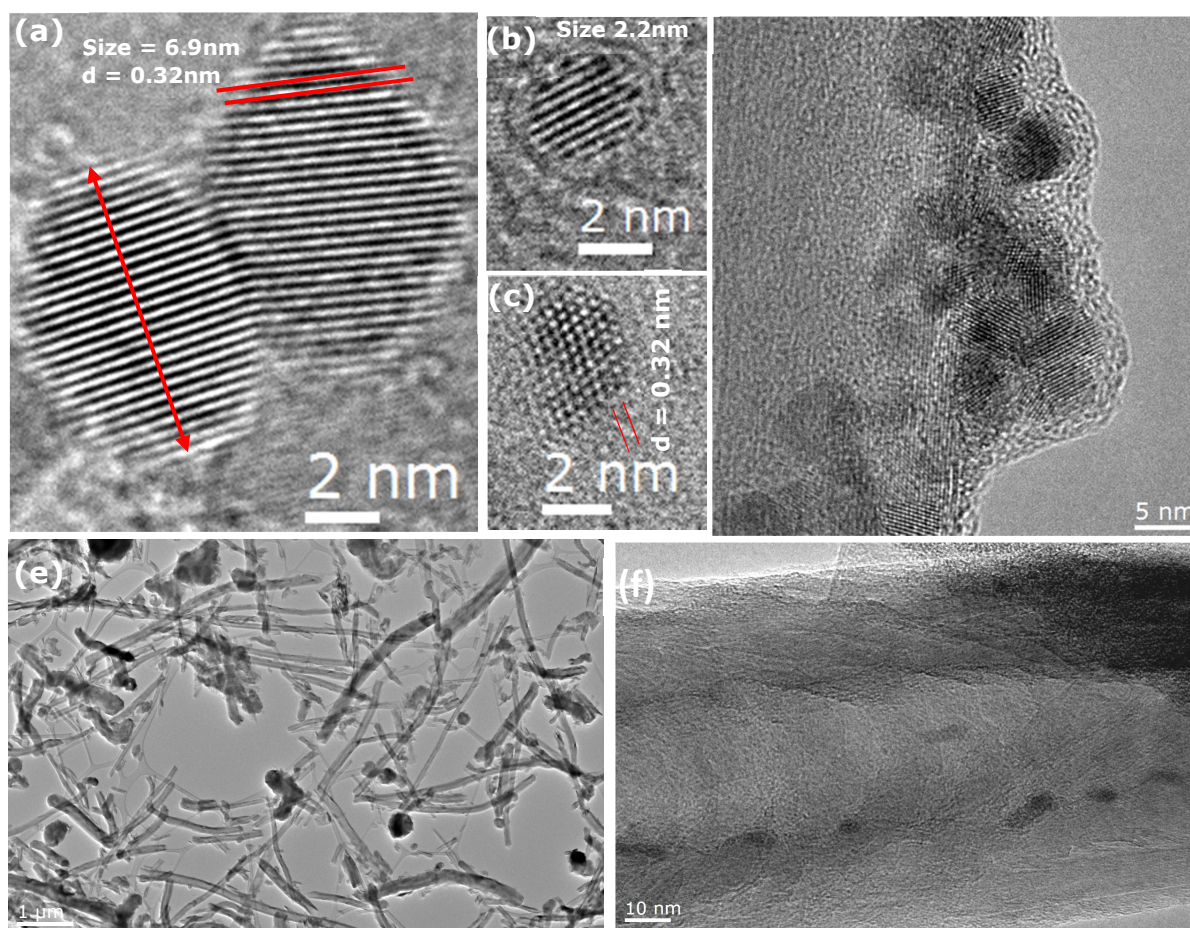


Figure 16 HRTEM images of the CeO₂ nanoparticles encapsulated inside GNF, (a) CeO₂@GNF-3, (b) CeO₂@GNF-1 with their interplaner spacings, (c) atomic steps of CeO₂, (d) CeO₂ nanoparticles adsorbed on the outer surface of GNF, (e) low magnification images of CeO₂@GNF (globules appearing are due to damaged GNFs during ball milling) and (f) CeO₂ nanoparticles deposited on step edges of GNF.

3.2 Preparation and characterisation of CeO₂ nanoparticles inside graphitised carbon nanofibers using ionic liquid mediated method

3.2.1 Ionic liquid

Ionic liquids comprising a cationic organic moiety and anion, represent a separate class of polar solvents which exist in liquid form at low temperature (below 100 °C). Many advantages including, thermal stability, low toxicity, nonflammability, negligible vapour pressure, low surface tension and ability to dissolve inorganic salts have increased the applications of ionic liquids. Usually, to embed metal oxides/metal nanoparticles inside carbon nanotubes, volatile precursors having low sublimation temperature are used and for this, organometallic complexes of metals are found to be most suitable class of precursors. Precious organometallic precursors being moisture sensitive, need special precautions while carrying out reactions and thus pose limitations. However, while metal salts are cost effective, they normally exist in hydrated form and exhibit very high melting temperature, making them unsuitable for encapsulation inside carbon nanotubes using gas phase or liquid phase. Further, ionic liquids due to presence of aliphatic alkyl chain and symmetry of cation, exhibit low surface tension. For example, BMIMPF₆ (1-butyl-3-methylimidazolium hexafluorophosphate) exhibit surface tension 38 mN.m⁻¹, significantly below the threshold surface tension of 180 mN.m⁻¹,¹⁰⁶ which could make the confinement of BMIMPF₆ inside multiwalled carbon nanotubes¹⁰⁷ possible. Therefore ionic liquids can be utilised to prepare metal nanoparticles from hydrated ionic precursors of metals and encapsulate them inside carbon nanotubes. Limited attempts have been made to prepare CeO₂ nanoparticles using ionic liquid.^{57,108} Zhang et al. have prepared SWCNT and CeO₂ nanocomposite by adding shuttle shaped CeO₂ nanoparticles into SWCNT in presence of ionic liquid BMIMPF₆ (1-butyl-3-methylimidazolium hexafluorophosphate).¹⁰⁹ But no attempt was made for ionic liquid mediated preparation of nanocomposite of CeO₂ nanoparticle in carbon nanotubes. Also, a few questions still remain to be investigated, such as, the role of ionic liquid in synthesis of metal oxide nanoparticles inside carbon nanotubes, the role of carbon nanotubes in growth of metal

oxide nanoparticles using ionic liquid. In order to answer these questions, the preparation of CeO₂-GNF composite using ionic liquid, 1-butyl-3-methylimidazolium bromide (BMIBr) and ceria precursor, CeBr₃.xH₂O has been attempted in this project.

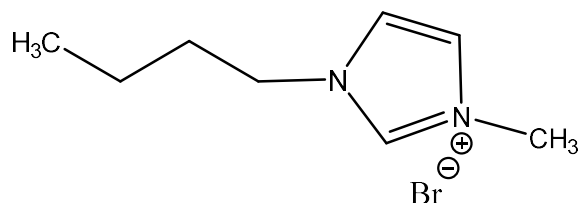


Figure 17 1-butyl-3-methylimidazolium bromide (BMIBr).

3.2.2 Method of preparation of CeO₂ nanoparticles inside graphitised carbon nanofibers

CeBr₃.xH₂O and 1-butyl-3-methyl imidazolium bromide (BMIBr) were taken in 1:3 molar ratio and heated in oven at 110 °C with graphitised carbon nanofibers (GNF) in an open vial. Since precursor is a hydrated salt, so it was heated in open vial to allow the water molecules to evaporate after heating at 110 °C. A salt is formed [BMI]₃[CeBr₆]¹¹⁰ at 1:3 molar ratio and at 110 °C (**eq. 3**) and becomes adsorbed into GNF to form [BMI]₃[CeBr₆]@GNF. Since the [BMI]₃[CeBr₆] complex decomposes at 300 °C, so in order to ensure its complete oxidation into CeO₂, the material; [BMI]₃[CeBr₆]@GNF was subjected to heating at 430 °C in air (**Figure 18**). Before reaching at this procedure, an attempt was made to prepare the complex [BMI]₃[CeBr₆]@GNF in two steps. In the first step BMIBr and CeBr₃.xH₂O were mixed and heated at 110 °C in air to prepare [BMI]₃[CeBr₆] and in the second step GNF was mixed into it and heated at 430 °C in air. But it did not result formation of CeO₂-GNF composite, instead, yellow powders of CeO₂ was separately observed with GNF after oxidation at 430 °C in air. To investigate the effect of amount of ceria precursor on formation of CeO₂ nanoparticles, three different amounts of CeBr₃.xH₂O and BMIBr were used at a fixed concentration of GNF. Also to study the effect of the temperature on formation of CeO₂ nanoparticles, the [BMI]₃[CeBr₆]@GNF was heated above its decomposition temperature of [BMI]₃[CeBr₆], at 330, 430 and 530 °C.

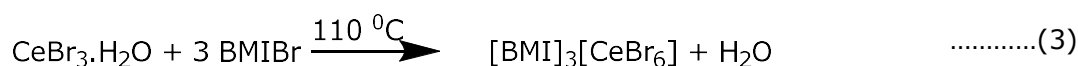


Figure 18 Schematic illustration of ionic liquid mediated preparation of nanocomposite of CeO₂ nanoparticles in GNF (CeO₂-GNF) from CeBr₃.xH₂O precursor.

3.2.3 Characterisation of CeO₂-GNF nanocomposite

3.2.3.1. UV-Visible absorption spectroscopy

UV-visible absorption spectroscopy was used to monitor the progress of reaction between BMIBr, CeBr₃.xH₂O and GNF. For comparison 2 vials were taken. One containing CeBr₃.xH₂O and 1-butyl-3-methyl imidazolium bromide (BMIBr) in 1:3 molar ratio (sample-1) and in the other vial containing 10 mg GNF with CeBr₃.xH₂O and 1-butyl-3-methyl imidazolium bromide (BMIBr) in the same molar ratio of 1:3 (sample-2). In order to form [BMI]₃[CeBr₆], both vials were heated at 110 °C for 2 hours and slowly cooled.

Figure 19 shows UV-visible absorption spectra of both the samples and starting materials in ethanol.

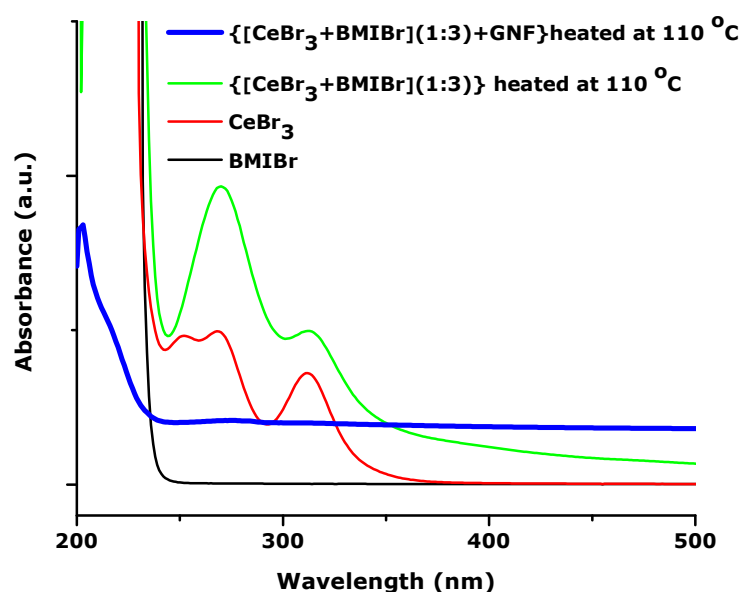


Figure 19 UV-visible absorption spectra of BMIBr, CeBr₃, (CeBr₃+BMIBr) heated at 110 °C and (CeBr₃+BMIBr+ GNF) heated at 110 °C.

The absorption spectra of sample-1 shows bands at $\lambda_{\max}$ 312 nm and 269 nm, which are attributed to 4f-5d transitions,¹¹¹ of Ce^{3+} in $[\text{BMI}]_3[\text{CeBr}_6]$. However in the spectra of sample-2 containing GNF these bands were absent, thus indicating encapsulation of $[\text{BMI}]_3[\text{CeBr}_6]$ complex in GNF. This observation is similar to a previous report on the formation of adduct of SWCNT and Vaska's complex.¹¹² The non-zero contribution to optical density after adding GNF is due to light scattering effect of GNF.

3.2.3.3 Thermogravimetric analysis (TGA)

UV-visible spectroscopy indicates formation of the adduct between GNF and $[\text{BMI}]_3[\text{CeBr}_6]$, and to study its thermal stability, thermogravimetric analysis (TGA) was carried out. A single step decomposition in TGA shows formation of CeO_2 -GNF nanocomposite and is stable up to 500 °C (**Figure 20**). The combustion temperature of the CeO_2 -GNF nanocomposite is lower than the GNF. This reduction in combustion temperature of CeO_2 -GNF nanocomposite can be attributed to the presence of CeO_2 , which catalytically promotes combustion of GNF. Coordination of CeO_2 to $\text{C}=\text{C}$ bonds in GNF weakens the strength of $\text{C}=\text{C}$ bonds and thus lowers the combustion temperature of GNF.¹⁰¹ On increasing amount of precursor, the combustion temperature is decreasing (**Figure 20b**). This is accounted for the increase in catalytic effect with increase in the amount of precursor. The residual mass left beyond 650 °C corresponds to CeO_2 in CeO_2 -GNF nanocomposite.

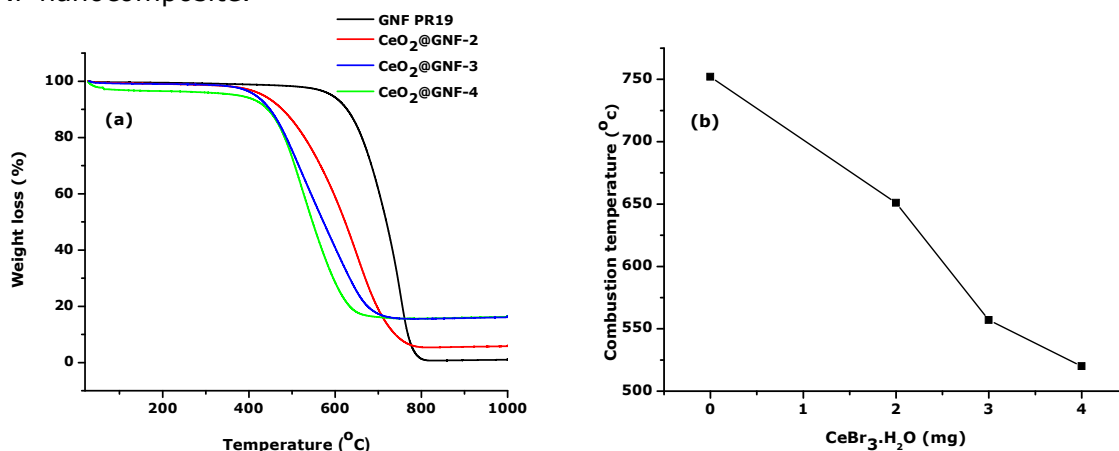


Figure 20 TGA curves of, (a) GNF, CeO_2 -GNF nanocomposites made with different amounts of precursor (2, 3 & 4 mg) denoted as CeO_2 -GNF-2, CeO_2 -GNF-3 and CeO_2 -GNF-4 respectively, (b) variation of combustion temperature of CeO_2 -GNF with amount of precursor.

3.2.3.4 Powder X-ray diffraction

To support the observation of TGA suggesting formation of CeO₂-GNF nanocomposite X-ray diffraction analysis was carried out. **Figure 21** shows X-ray diffraction pattern of CeO₂-GNF prepared, with different amounts of precursor CeBr₃.xH₂O(a) and at different temperatures (b). In the X-ray diffraction pattern, peaks observed at $2\theta = 28.5^\circ, 33.2^\circ, 47.6^\circ, 56.3^\circ$ and 69.6° corresponds to CeO₂ lattice planes (111), (200), (220), (311) and (400) respectively(JCPDS: 78-0694). This corresponds to a typical fluorite structure of cerium oxide (CeO₂)¹¹³. The diffraction peaks of GNF at $2\theta = 26^\circ, 42.4^\circ, 44.6^\circ, 54.4^\circ$ and 77.4° correspond to (002), (100), (101), (104) and (110) planes of graphitic lattice of GNF.¹⁰² The appearance of diffraction peaks of cerium oxide, besides those corresponding to GNF, confirms formation of cerium oxide nanoparticles adsorbed on GNF. It is also observed that, as the amount of precursor increases, the intensity of peaks increases (**Figure 21a**). This can be attributed to formation of small size nanoparticles at low amount of precursor and as amount of precursor increases particle size increases. Furthermore, as the temperature increases peaks become more intense (**Figure 21b**). Increase in the intensity of the peaks corresponds to increase in crystallinity of CeO₂ with increase in temperature.¹¹⁴ In the X-ray diffraction patterns of CeO₂@GNF (**Figure 14**) prepared by gas phase decomposition method, the peak corresponding to CeO₂ lattice plane (110) at $2\theta = 77.4^\circ$ does not appear. This could be attributed to the fact that, in gas phase decomposition method the CeO₂ nanoparticles are encapsulated inside GNF, however in ionic liquid mediated preparation CeO₂ nanoparticles are adsorbed on the outer surface of GNF.

Formation of CeO₂ is further confirmed from the characteristic band for $\nu_{\text{Ce-O}}$ at 456 cm^{-1} in the Raman spectrum of CeO₂-GNF-3 nanocomposite (**Figure 21c**). The bands at 1350 and 1578 cm^{-1} correspond to the characteristic D and G bands of GNF. The I_D/I_G ratio which is typically taken as a measure of surface disorder in carbon nanotubes, increases for CeO₂-GNF nanocomposites in comparison to GNF. This can be attributed to the surface disorder due to interaction with ionic liquids.

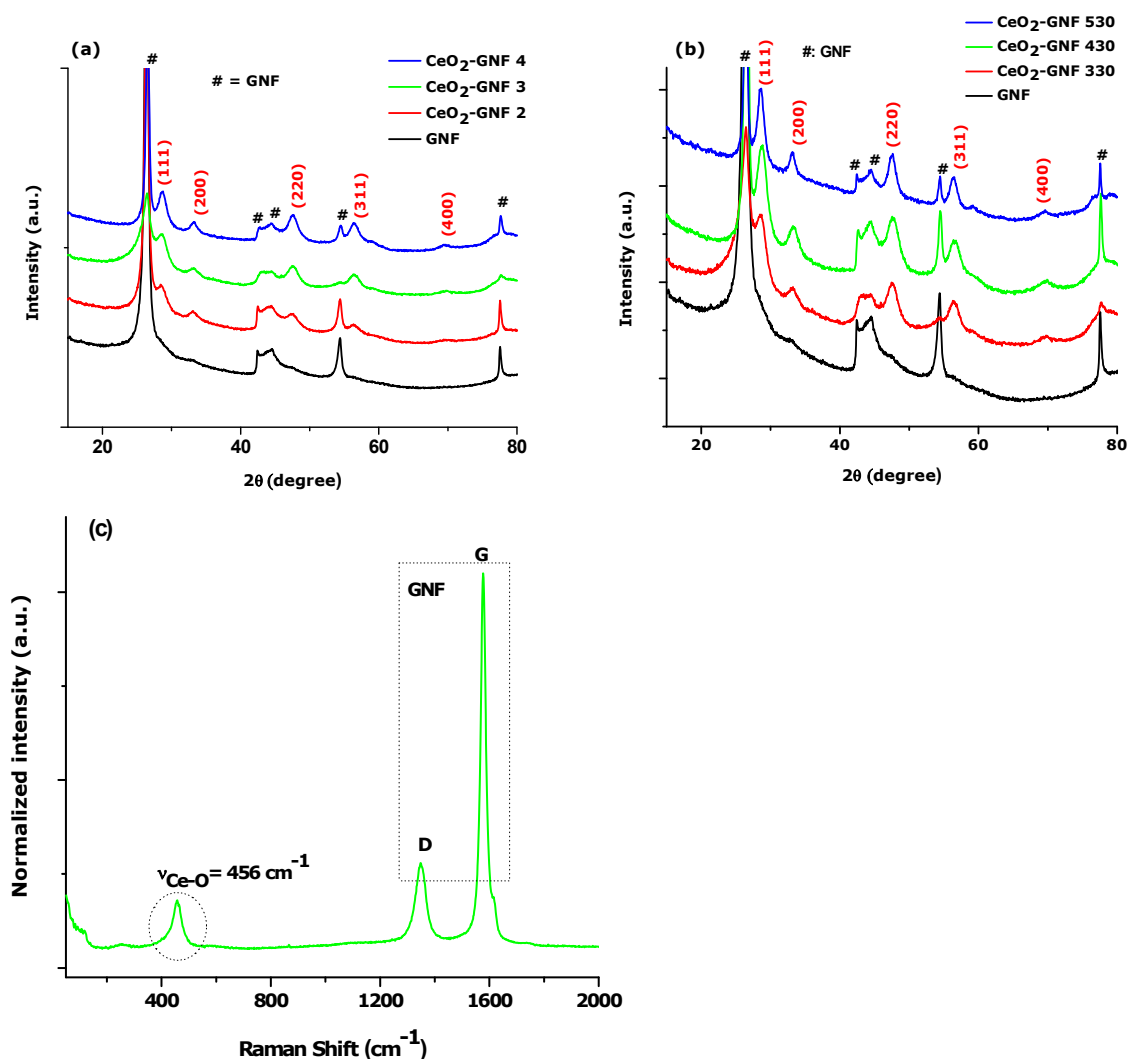


Figure 21 Powder X-ray diffraction (PXRD) patterns of CeO₂-GNF nanocomposites prepared (a) at varied amount of precursor (CeO₂-GNF-2, CeO₂-GNF-3 and CeO₂-GNF-4 corresponding to 2, 3 and 4 mg CeBr₃.xH₂O respectively), (b) at varied temperatures (CeO₂-GNF 330, CeO₂-GNF 430 and CeO₂-GNF 530 corresponding to CeO₂-GNF-3 prepared at decomposition temperatures 330, 430 and 530 °C), (c) Raman spectrum of CeO₂-GNF-3 (The dotted circle indicates the characteristic Raman band of CeO₂, and the dotted square frame indicates the characteristic Raman bands of graphitised carbon nanofibers (GNF)).

3.2.3.5 Transmission electron microscopy (TEM) and Energy dispersive X-ray spectroscopy (EDX) analysis

TGA, XRD, Raman results suggest formation of CeO₂-GNF nanocomposite but to ascertain size and location of CeO₂ particles in GNF, TEM analysis was carried out. TEM images of CeO₂-GNF show CeO₂ particles are formed both inside (**Figure 22a-b**) and outside GNF (**Figure 22e-f**). But hollow structures of most of the GNFs were disintegrated into nontubular carbon nanostructures. TEM images also confirm that CeO₂ nanoparticles are adsorbed on the nontubular carbon nanostructures forming a nanocomposite (**Figure 22c**). Though no attempt was made to prepare any metal or metal oxide nanoparticles inside carbon nanotubes using ionic liquid, previous work¹⁰⁷ showed encapsulation of ionic liquids inside carbon nanotubes without disruption of nanotubes. Therefore disintegration of tubular structure of GNFs could be due to thermal treatment of GNF with ionic liquid. Well dispersed CeO₂ nanoparticles of size 4-9 nm were formed on carbon nanostructure. High resolution image of **Figure 22b** shows atomic arrangement of CeO₂ with inter planner d spacing of 0.32 nm corresponding to (111) lattice planes of CeO₂ crystal lattice and that of GNF is 0.34 nm (**Figure 22d**). Further CeO₂ formation is confirmed by EDX analysis, which shows the atomic % composition of Ce and O (**Figure 22g**). The Ce:O ratio suggests formation of CeO₂. Also absence of Br and N in EDX spectrum confirms complete decomposition of ionic liquid.

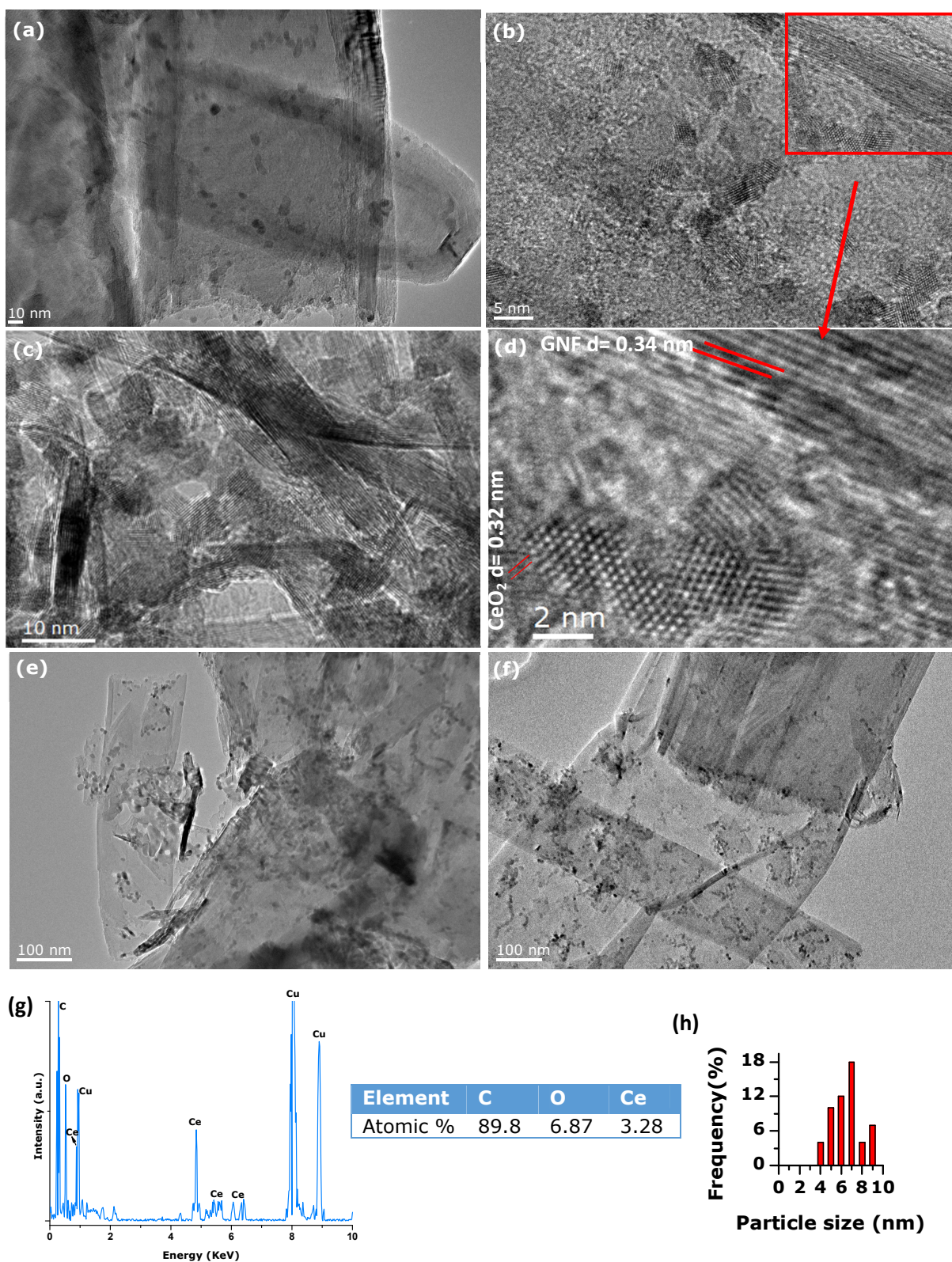


Figure 22 HRTEM images of the CeO_2 -GNF composite prepared by ionic liquid mediated method. (a-b) CeO_2 nanoparticles inside GNF, (c) CeO_2 nanoparticles adsorbed on disrupted graphitised carbon nanofibers, (d) high resolution image of b, (e-f) images showing GNFs disrupted, (g) EDX spectra of CeO_2 -GNF nanocomposite (Cu peaks are from the TEM grid) & (h) particle size distribution.

3.2.3.6 Role of GNF in formation of CeO₂ nanoparticles

To study the effect of graphitised carbon nanofibers (GNF) on formation CeO₂, CeBr₃.xH₂O was heated with BMIBr at 1:3 molar ratio, both in absence and presence of GNF, in air at 330 °C, above the decomposition temperature of [BMI]₃[CeBr₆]. Powder X-ray diffraction (PXRD) (**Figure 23a**) did not show any evidence of formation of CeO₂ in absence of GNF. However in presence of GNF at 330 °C, CeO₂ nanoparticles are formed, as evident from the X-ray diffraction pattern (**Figure 23b**). This can be attributed to, heterogeneous nucleation of CeO₂ nanoparticles on GNF, where, GNF acts as a substrate and it stimulates the growth of CeO₂ nanoparticles on its surface by lowering the activation energy required for formation of CeO₂ nanoparticles. The CeO₂-GNF interfacial energy overcomes the activation barrier for growth of CeO₂ nanoparticles. That can explain why the CeO₂ nanoparticles are formed in heterogeneous phase but not in the homogenous phase without GNF at same temperature. This selective growth of nanoparticles on heterogeneous substrate has also been observed in previous reports.¹¹⁵ Furthermore, on heating CeBr₃.xH₂O with BMIBr at 1:3 molar ratio at 430 °C forms yellow ceria and HRTEM images confirm formation of nanorods (**Figure 24a-c**). These nanorods are not grown as single crystalline but are the result of self organized CeO₂ nanoparticles with clearly recognised boundaries (**Figure 24c**). Formation of CeO₂ nanorods in absence of GNF at higher temperature confirms the heterogeneous nucleation process stimulated by GNF surface. Though in absence of GNF substrate CeO₂ is formed but the particles are organized into nanorods. Therefore GNF as a heterogeneous substrate, not only controls the growth of CeO₂ particles but also controls the particle size and dispersion on its surface. XRD pattern of CeO₂ nanorods (**Figure 23c**) with peaks at $2\theta = 28.5^\circ, 33^\circ, 47.4^\circ, 56.2^\circ, 59.1^\circ, 69.3^\circ, 77^\circ$ and 79.2° corresponds to lattice planes (111), (200), (220), (311), (222), (400), (331) and (420) respectively (JCPDS 34-0394) of the cubic fluorite type CeO₂.¹¹³ HRTEM image of CeO₂ nanorod shows interplaner spacing $d = 0.25$ nm corresponding to (200) planes of CeO₂ (**Figure 24e**). However, the interplaner spacing $d = 0.32$ nm of CeO₂ nanoparticles formed on GNF corresponds to (111) planes of CeO₂. This shows that GNF surface also

orients the plane specific growth of CeO_2 crystal lattice. EDX showing absence of Br and N confirms complete decomposition of ionic liquid and formation of CeO_2 (**Figure 24d**).

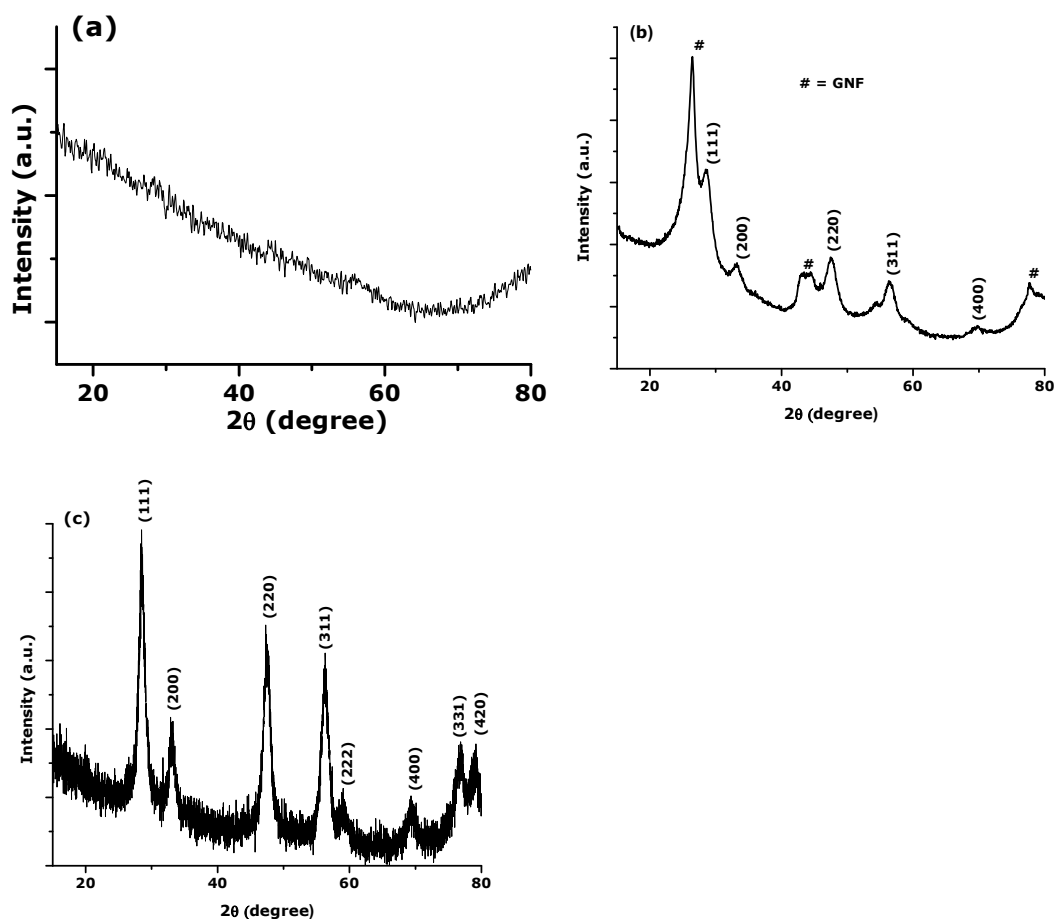


Figure 23 Powder X-ray diffraction patterns of, (a) $\text{CeBr}_3 + \text{BMIBr}$ after heating at 330 °C, (b) $\text{CeBr}_3 + \text{BMIBr} + \text{GNF}$ after heating at 330 °C, (c) $\text{CeBr}_3 + \text{BMIBr}$ after heating at 430 °C.

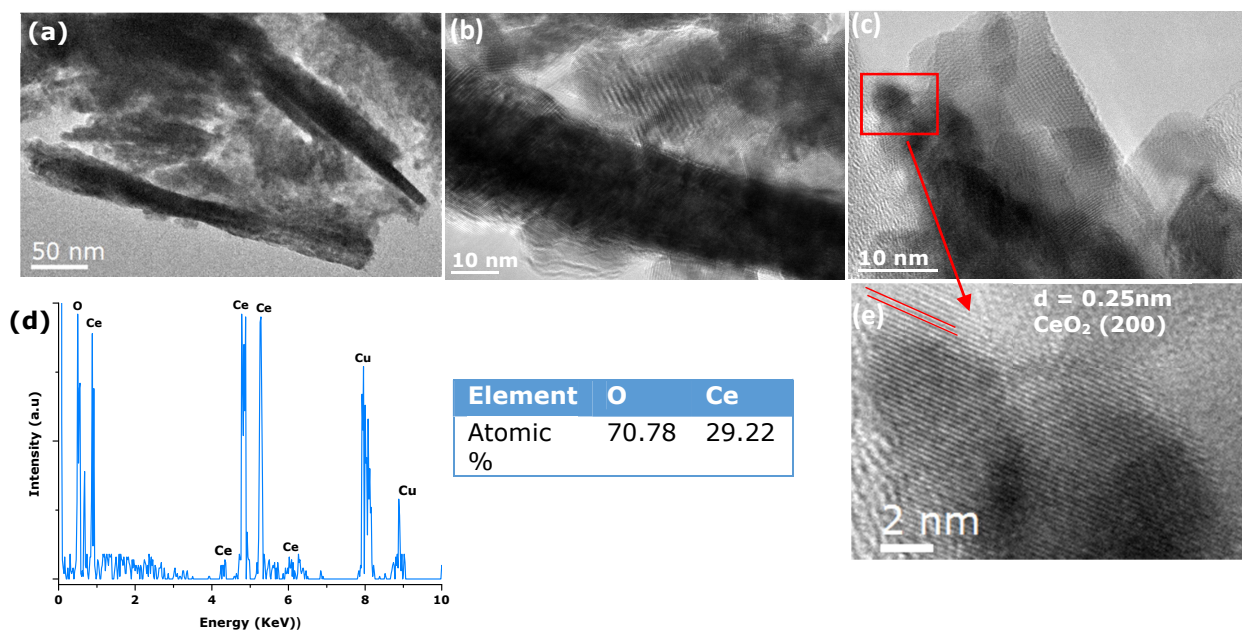


Figure 24 TEM images of CeO₂ nano rods (a-c), high magnification image of c (e) and EDX spectrum of CeO₂ nanorod with the elemental composition in the inset table (d). (Cu peaks are from the TEM grid).

3.2.3.7 Role of ionic liquid in formation of CeO₂ nanoparticles

CeBr₃.xH₂O, a hydrated precursor having very high melting temperature (~ 730 °C), is not suitable for preparation of CeO₂ nanoparticles encapsulated inside GNF, by simple thermal decomposition method like Ce(tmhd)₄. Therefore, ionic liquid, 1-butyl-3-methylimidazolium bromide (BMIBr) was mixed with CeBr₃.xH₂O in 1:3 molar to form a complex [BMI]₃[CeBr₆] having decomposition temperature 300 °C.¹¹⁰ On heating this complex beyond 300 °C in air and in the presence of GNF, it diffuses into GNF and is oxidised to CeO₂. To ascertain the role of ionic liquid, only CeBr₃.xH₂O and GNF were heated at same temperature 430 °C. It was observed that, CeBr₃ and GNF remain separate as a mixture without forming a composite as is evident from a nonuniform two-step decomposition in TGA, which is expected to be a single step in case of a composite (**Figure-25a-b**). The appearance of two distinct peaks centred at 503 and 685 °C in weight derivative curve suggests that CeBr₃ is not attached to the surface of GNF. This observation illustrates unevenly distributed CeBr₃ and GNF in the mixture. During combustion of the mixture, the portion of GNF that is in contact with CeBr₃ oxidises at

low temperature (503 °C) because CeBr_3 accelerates the combustion of GNF and the remaining portion of the GNF oxidises at higher temperature (685 °C). The result is consistent with previous report on composite of nickel nanoparticles in MWCNT.¹⁰⁵ Therefore, the indispensable role of the ionic liquid for formation of CeO_2 -GNF nanocomposite is confirmed.

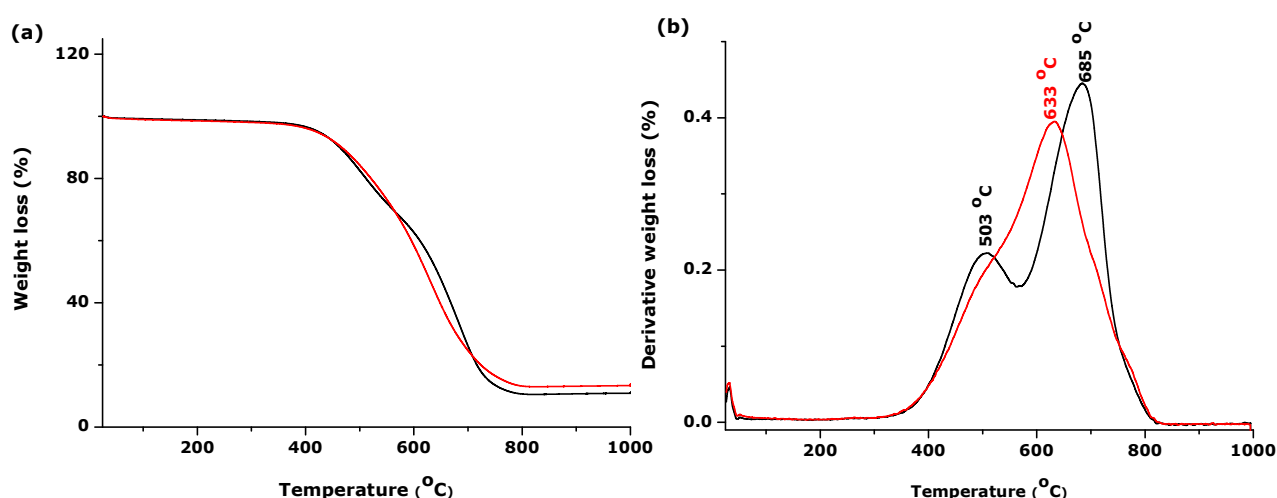


Figure 25 (a) TGA and (b) DTG curves of CeBr_3 +GNF (black) and CeBr_3 +GNF +BMIBr (red) prepared by heating at 330 °C in air.

Therefore, ionic liquid is important for bringing down the melting point of precursor by forming a complex with it, and for interaction between imidazolium cation and GNF that triggers $[\text{BMI}]_3[\text{CeBr}_6]$ complex to be adsorbed on GNF.

Based on the results from XRD, TGA, Raman and TEM it is concluded that, highly stable, well-dispersed crystalline CeO_2 nanoparticles are formed with GNF as CeO_2 -GNF nanocomposite.

Although CeO_2 -GNF nanocomposite is formed by ionic liquid mediated method, the structure of GNF is partially disrupted. Therefore, to investigate the reason for disintegration of the GNF structure, whether the precursor, CeBr_3 or the ionic liquid is responsible for this, an experiment was carried out by heating a mixture of GNF and

BMIBr at 430 °C. TEM analysis of the resulted material confirms the role of ionic liquid BMIBr in disintegration of the GNF into non-tubular carbon nanostructures. HRTEM images **(Figure 26)** show the outer layers of GNFs are unravelled into carbon nanoribbons as a result of thermal treatment of BMIBr and GNF. Though whole structure of GNF is not disrupted, a hybrid structure comprising partially exfoliated GNF and carbon nanoribbons are formed. This can be accounted for the interaction between the imidazolium cation in ionic liquid and π electron system of GNF. Previous reports also established such interaction between cationic part of ionic liquid and MWCNT¹¹⁶⁻¹¹⁸ which is also known as cation- π interaction.¹¹⁹ Fukushima et al.¹¹⁸ reported untangling of carbon nanotubes by imidazolium based ionic liquids, due to cation- π interactions between π -electrons of the carbon nanotubes and the imidazolium cation. But none of the reported works on ionic liquid and CNTs suggest such disruption of the physical structure of the CNT.^{111,120-124} However, the reaction with ionic liquids leading to exfoliation of graphites into graphene nanoribbons has been reported by many research groups.¹²⁵⁻¹²⁹ Exfoliation of graphites has been ascribed to the cation- π interaction between ionic liquids and graphites. As a result of this interaction, intercalation of imidazolium cation in graphitic layers¹²⁸ and weakening of van der Waals forces of attraction between graphitic layers,¹³⁰ take place. This leads to exfoliation of graphites into graphene nanoribbons. In a similar manner, partial exfoliation of GNF into carbon nanoribbons can be attributed to cation- π interaction. Furthermore, since this structural disruption is taking place in the absence of the CeBr₃, the role of cerium is negated. Therefore, it is confirmed that the ionic liquid, BMIBr has the role in structural disruption of GNF. Imidazolium cation gets intercalated between graphitic layers of GNF, and weakens the van der Waals force of attraction between layers. As a result stacked graphitic cones of GNF slides out and collapses into nanoribbons.

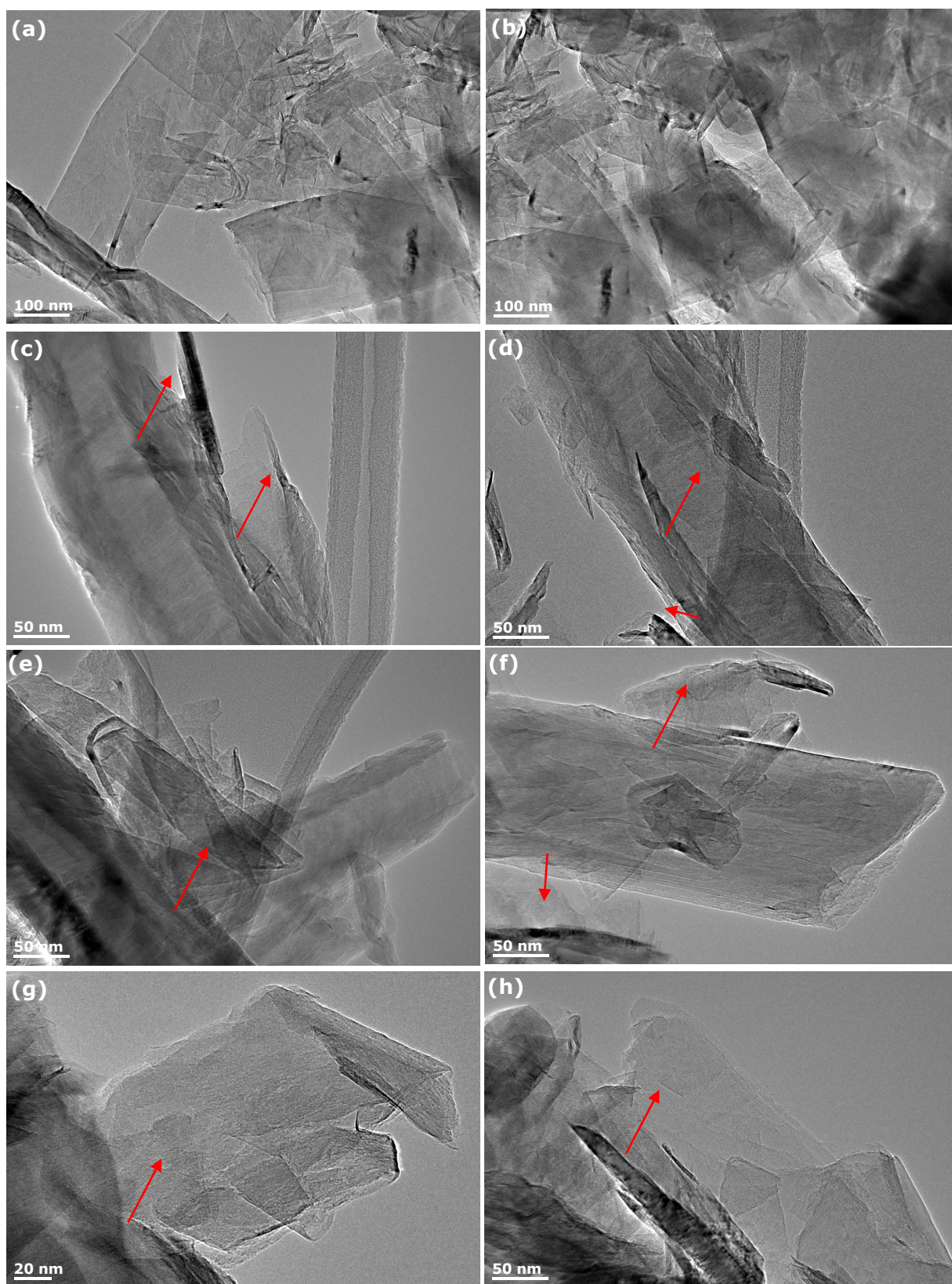


Figure 26 HRTEM images of GNF + BMIBr heated at 430 °C in air. Exfoliated GNF forming tubular structure and nanoribbon (a-b), broken outer layers of GNF (c-f) and GNFs disintegrated into carbon nanoribbons (g-h). Arrows show the outer surface of GNF is unravelled into carbon nanoribbons.

Though the motivation behind this experiment was to synthesize CeO_2 nanoparticles encapsulated inside GNF using ionic liquid as a driver to pull CeBr_3 inside hollow structure of GNF but the partially disrupted structure of GNF resulted into adsorption of CeO_2 nanoparticles on a hybrid carbon nanostructure comprising both tubular and non-tubular morphology. CeO_2 nanoparticles deposited on this hybrid carbon nanostructure can have possible applications in electrocatalysis, where nanoribbons can provide greater electroactive surface area and tubular structure would provide electrical conductivity.

3.3 Comparison between gas phase decomposition method and ionic liquid mediated method for preparation of CeO_2 encapsulated inside GNF

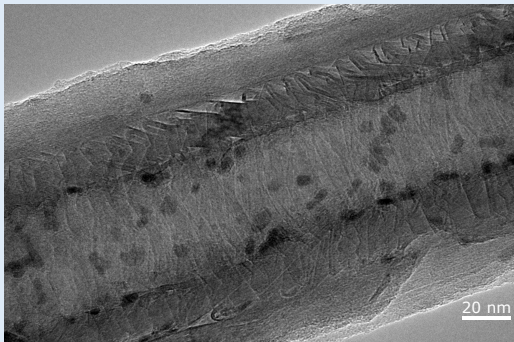
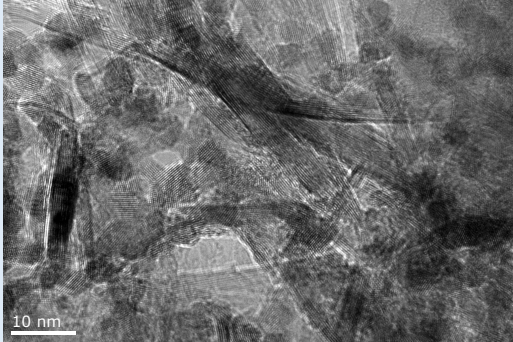
Gas phase decomposition method utilises volatile cerium complex sublimed at $150\text{ }^\circ\text{C}$ under vacuum followed by thermal decomposition to CeO_2 under argon. Ultra-small CeO_2 particles of size 2-4 nm, well-dispersed inside GNF hollow structure and adsorbed on the step edges of GNF were prepared by this method. Encapsulation of CeO_2 inside hollow structure of GNF makes the composite a potential nanoreactor and thus suitable for studying nanoscale catalysis in a confined space.

However, ionic liquid mediated synthesis involves hydrated cerium salt, unsuitable for sublimation, which on mixing with ionic liquid forms complex of low decomposition temperature. Thermal treatment of the ionic liquid complex with GNF, in air forms well dispersed CeO_2 nanoparticles of size 4-8 nm as CeO_2 -GNF nanocomposite. But disintegration of GNF into nontubular carbon structures make it unsuitable for studying nanoscale catalysis in a confined space. However, with the small size and well dispersed particles adsorbed on carbon nanofibres, this CeO_2 -GNF nanocomposite could be a suitable heterogeneous catalyst.

Gas phase decomposition of $\text{Ce}(\text{tmhd})_4$ is the suitable method for *in situ* preparation of CeO_2 encapsulated inside GNF. The comparison between two methods is summarised in

Table 5.

Table 5 Comparison of methods of preparation of CeO₂ and GNF nanocomposite

Gas phase decomposition	Ionic liquid mediated method
GNF structure is retained	Most of the GNF structures are ruptured
Prepared under vacuum and argon	Prepared under air in and open vessel
Volatile precursor used	Hydrated precursor (salt) used
Suitable to study catalysis in confinement	Not suitable to study catalysis in confinement
 CeO ₂ @GNF	 CeO ₂ -GNF

4. Catalysis by CeO₂ nanoparticles encapsulated inside GNF (CeO₂@GNF)

4.1. Oxidation reaction

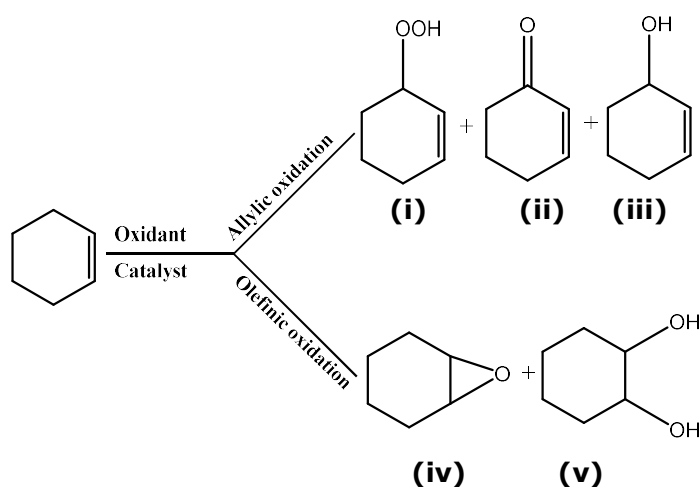


Figure 26 Illustration of possible products generated from oxidation of cyclohexene through allylic and olefinic oxidation, (i) 2-cyclohexenyl hydroperoxide, (ii) 2-cyclohexenone, (iii) 2-cyclohexenol, (iv) cyclohexane epoxide & (v) 1,2-cyclohexanediol.

To evaluate the catalytic activity of CeO₂ confined inside GNF, an oxidation reaction was tested using CeO₂@GNF nanoreactor. Keeping in mind, the redox properties (Ce⁴⁺/Ce³⁺) of CeO₂, which makes it a potential oxidation catalyst, the tested reaction was the oxidation of cyclohexene with *tert*-butylhydroperoxide (TBHP) as an oxidant. This reaction was chosen, because oxidation of cyclohexene can proceed through two different routes¹³¹: allylic oxidation and olefinic oxidation (**Figure 26**), leading to formation of five main oxidation products, such as cyclohexane epoxide, 1,2-cyclohexanediol, 2-cyclohexenyl hydroperoxide, 2-cyclohexenol and 2-cyclohexenone.¹³²⁻¹³⁵ The selectivity of all these cited products varies with the catalyst, oxidant, temperature, time, pressure and solvent.^{136,137} Therefore, this reaction can provide key insights about performance of nanoreactor CeO₂@GNF in terms of selective oxidation of carbon centres (either allylic or olefinic).

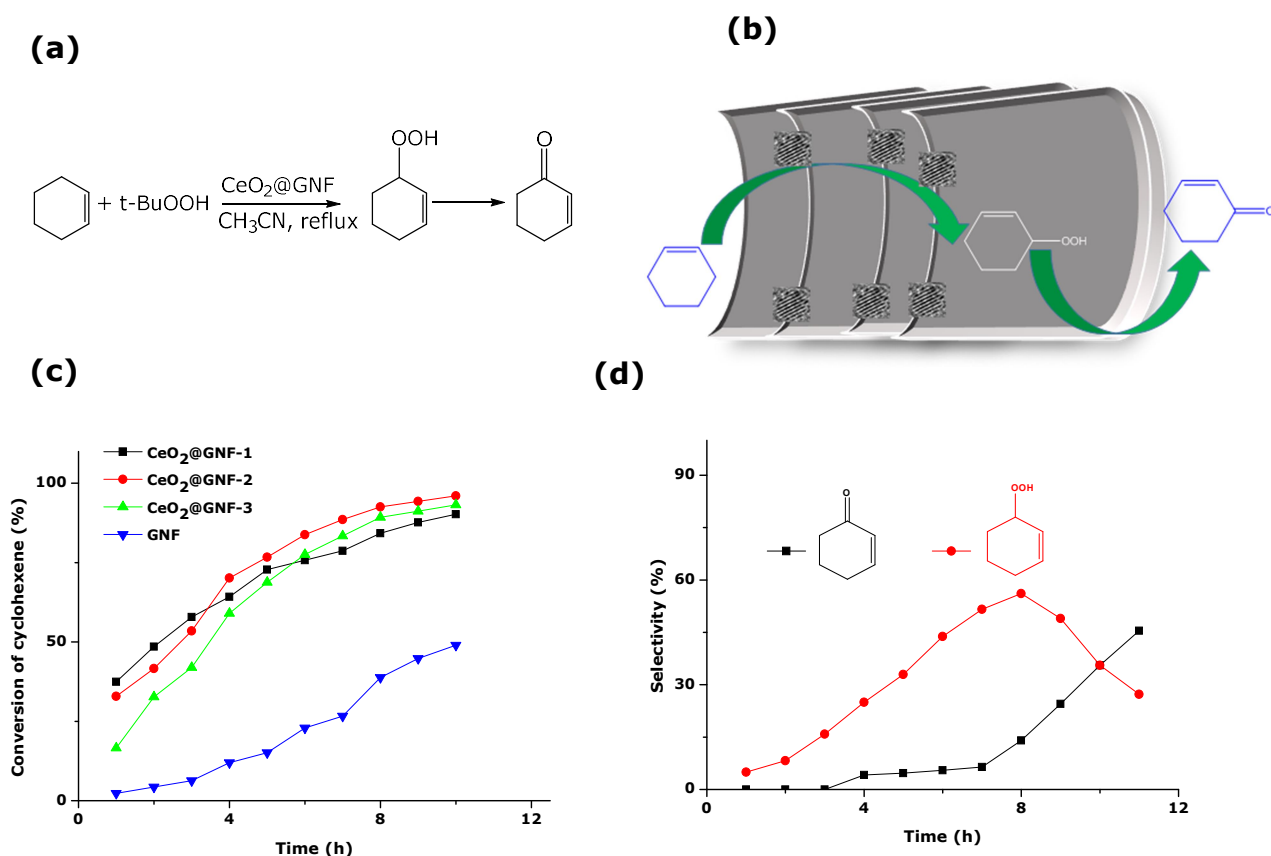


Figure 27 (a) Allylic oxidation of cyclohexene catalysed by $\text{CeO}_2@\text{GNF}$ nanoreactor, (b) schematic illustration of 2-cyclohexenone production from cyclohexene inside $\text{CeO}_2@\text{GNF}$, (c) conversion of cyclohexene catalyzed by $\text{CeO}_2@\text{GNF}$ nanoreactors made with different amounts CeO_2 (4.7, 5.9 and 7.7 wt%) denoted as $\text{CeO}_2@\text{GNF-1}$, $\text{CeO}_2@\text{GNF-2}$ and $\text{CeO}_2@\text{GNF-3}$ respectively. (d) Selectivity of 2-cyclohexenone vs 2-cyclohexenyl hydroperoxide.

In order to confirm the catalytic effect of $\text{CeO}_2@\text{GNF}$, the control reaction was carried out in its absence under same reaction condition. The low conversion of the reactant cyclohexene (23%) in absence of nanoreactor indicates that the reaction is spontaneous to some extent under tested reaction conditions. Furthermore, to evaluate catalytic effect of GNF, the reaction was carried out with GNF under same reaction conditions. The conversion (48%) of cyclohexene suggests the catalytic effect of GNF. This catalytic effect of GNF is attributed to decomposition of TBHP promoted by defect sites of GNF.¹³⁸ Finally, the resultant catalytic effect of $\text{CeO}_2@\text{GNF}$ was ascertained from significantly high conversion of cyclohexene (96%) on carrying out the reaction in presence of the nanoreactor $\text{CeO}_2@\text{GNF}$ (**Figure 27c**). The enhancement in catalytic activity can be attributed to increase in local concentration of reactant nearer to CeO_2 inside the confined space of GNF. Besides high conversion of reactant, formation of a highly

selective product 2-cyclohexenone through a selective intermediate 2-cyclohexenyl hydroperoxide, demonstrates the superior catalytic performance of the nanoreactor $\text{CeO}_2\text{@GNF}$ (**Figure 27a-b**). With cyclohexene conversion, decrease in concentration of 2-cyclohexenyl hydroperoxide and increase in that of 2-cyclohexenone (**Figure 27d**) confirms the formation of 2-cyclohexenone from 2-cyclohexenyl hydroperoxide intermediate. Throughout the reaction it was observed, 2-cyclohexenyl hydroperoxide as the only intermediate, suggesting the reaction proceeds through selective oxidation at allylic carbon centre of cyclohexene, which is another advantage of carrying out this reaction with the nanoreactor $\text{CeO}_2\text{@GNF}$. In contrast, the previous reports on oxidation of cyclohexene with TBHP yield mixture of 2-cyclohexenone, 2-cyclohexenol and cyclohexeneepoxide¹³⁹ as major products.

Voort et al.¹⁴⁰ reported formation of both cyclohexeneepoxide and 2-cyclohexenyl hydroperoxide as products of cyclohexene oxidation by TBHP, suggesting the reaction proceeds through both allylic and olefinic oxidation pathway. Also in this work, the control reaction with GNF yielding mixture of both 2-cyclohexenol and 2-cyclohexenone, proves the effect of CeO_2 .

Furthermore, in this reaction, the major advantage of the nanoreactor; $\text{CeO}_2\text{@GNF}$ was observed to be the small amount of catalyst. In previous reports catalyst (CeO_2) was used in the range of 50 to 100 mg, however in this work very small amount of catalyst; $\text{CeO}_2\text{@GNF}$ (5.9 wt% of CeO_2) has been used. Macedo et al.¹⁴¹ used 30 mg of CeO_2 nanorods for oxidation of cyclohexene using TBHP as oxidant yielding both 2-cyclohexenyl hydroperoxide and 2-cyclohexenone as a mixture of products. 95 mg of CeO_2 (3-5 nm), and VO_2/CeO_2 nanoparticles were used as catalysts for oxidation of cyclohexene with H_2O_2 ¹⁴² and TBHP¹⁴⁰ respectively. Therefore, selective oxidation of allylic carbon yielding exclusive product 2-cyclohexenone using minimum quantity of catalyst for high conversion of cyclohexene demonstrates distinct feature of the nanoreactor $\text{CeO}_2\text{@GNF}$ (**Table 6**).

Table 6 Comparison of this work with literature.

Catalyst	Oxidant	Amount of catalyst (mg)	Amount of cyclohexene (mmol)	Reaction time(h) / Temp(C)	Cyclohexene conversion (%)	Selectivity (%)		Ref.
						Enone	Enol	
CeO ₂ @GNF-2	70% TBHP	10(10mgGNF + 5.9 wt% CeO ₂)	2.9	10/80	96	50	0	This work*
CeO ₂ nanorods	70%TBHP	30	1.5	24/55-105	22	<14	<14	141
VO ₂ /CeO ₂	70%TBHP	100	29	6/65	45	18	5	139
CeO ₂	H ₂ O ₂	95	10	24/82-85	76	67	33	142
Mn/CeO ₂	O ₂	30	1	4/110	52	52	26	55

*Reaction conditions: 2.9 mmol of cyclohexene (0.3 ml), 5.8 mmol of TBHP (1.6 ml), 1,4-dichlorobenzene (0.213 g) as internal standard, 2.5 ml of acetonitrile as solvent, stirred under reflux, Conversion = (Cyclohexene consumed/initial cyclohexene) x 100, Selectivity = (Cyclohexenone/cyclohexenone + 2-cyclohexenyl hydroperoxide) x 100, Enone: 2-cyclohexenone, Enol: 2-cyclohexenol.

The performance of nanoreactor demonstrating additive effect of both CeO₂ and GNF can be attributed to the effect of spatial confinement of CeO₂ inside tubular structure of GNF. The additive effect can be attributed to three factors: (1) well dispersed CeO₂ nanoparticles of very small size (3-8 nm) prepared inside GNF, providing larger surface area for adsorption of substrate molecules, (2) the exclusive contribution of geometrical effect of the channel structure of GNF, increases concentration of reactant inside nanoreactor leading to effective interaction between reactant and catalyst CeO₂ adsorbed on graphitic step edges (TEM image in **Figure 16f**), resulting in maximum conversion of reactant and (3) easy diffusion of reactant and product molecules to and from nanoreactor and localised interaction of reactant molecules with CeO₂ makes the nanoreactor effective even with small amount of catalyst. This observation is similar to the effect of spatial confinement effect of other catalysts inside carbon nanotubes yielding highly selective products, previously reported by our group.^{4,37}

Table 7 Cyclohexene conversion with varying CeO₂ loading.

Material	CeO ₂ wt%	GNF(mg)	Particle size (nm)	Conversion of cyclohexene(%)
CeO ₂ @GNF-1	4.7	10	4	90
CeO ₂ @GNF-2	5.9	10	6	96
CeO ₂ @GNF-3	7.7	10	8	93

In order to study the effect of CeO₂ loading on catalytic activity we have tested CeO₂@GNF with three different concentrations of CeO₂ (4.7, 5.9 and 7.7 wt%) (**Table 7**). It was observed that, the catalytic activity of the nanoreactor is not increasing linearly with the amount of CeO₂ (**Figure 27c**). After 10 hours of reaction conversion of cyclohexene is lowest for 4.7 wt% CeO₂ and highest for 5.9 wt% of CeO₂. Though conversion is decreasing with further increase in the amount of CeO₂ to 7.7 wt%, its not very significant and could be within the error of ¹H NMR spectroscopy measurement. This variation in catalytic activity can be attributed to two factors, size and extent of encapsulation of CeO₂ nanoparticles inside GNF.

First, considering the effect of size of CeO₂ nanoparticles, from XRD and TEM analysis it is evident that, the size of CeO₂ is increasing with increase in the amount of cerium precursor. Catalytic activity is increasing as size of CeO₂ nanoparticles increases from 4 to 6 nm and decreasing with further increase in particle size to 8 nm. This nonlinear (volcano like) variation of catalytic activity with particle size is consistent with previous reports of oxidation reactions involving decomposition of oxidants H₂O₂¹⁴³ and O₂¹⁴⁴ by Au nanoparticles.

Second, there is a variation in extent of confinement of particles inside GNF with amount of precursor. As TEM confirms, for higher amount of CeO₂ (7.7 wt%) though most of the particles are encapsulated inside but few particles are grown on the outer surface of GNF. Since the particles deposited outside the surface of GNF are deprived of the localised concentration effect of reactants they exhibit low activity. This decrease in extent of confinement could be assigned for reduction in catalytic activity of CeO₂@GNF

with highest content of CeO₂, which further validates the superior activity of CeO₂ confined inside GNF.

Based on the results a plausible mechanism for catalytic oxidation of cyclohexene is proposed (**Figure 28**). Though cyclohexene oxidation with TBHP (t-BuOOH) can proceed through both free radical and epoxidation route but formation of 2-cyclohexenyl hydroperoxide, with no evidence of formation of epoxide, during the reaction confirms formation of products through selective oxidation of allylic carbon centre through free radical mechanism only. According to the proposed mechanism, the reaction of t-BuOOH on the surface of CeO₂ nanoparticles, that involves coordination of oxygen atom of t-BuOOH to cerium followed by formation of radicals t-BuO[•] and [•]OH takes place in the first step. CeO₂ nanoparticles behave as initiator in homolytic cleavage of t-BuOOH (**equation 4**), the similar process has been previously described for other catalysts.¹⁴⁵⁻

¹⁴⁸ The free radical t-BuO[•] extracts allylic hydrogen from cyclohexene to form cyclohexenyl radical, which becomes trapped by atmospheric O₂ to form 2-cyclohexenyl peroxide radical.^{149,150} The role of atmospheric oxygen was also ascertained by negligible conversion after 10 hours of the reaction conducted under argon. The 2-cyclohexenyl peroxide radical abstracts hydrogen from allylic CH₂ of another molecule of cyclohexene to form 2- cyclohexenyl hydroperoxide,^{151,152} evidence of its presence is confirmed by both ¹H NMR spectroscopy and GC-MS analysis. This homolytic abstraction of hydrogen is also energetically favourable (bond energy of RCOO-H = 90 Kcal mol⁻¹, and that of allylic C-H bond is 85 Kcal mol⁻¹).¹⁵³ Furthermore, 2-cyclohexenyl hydroperoxide is catalytically decomposed by CeO₂ to the product cyclohexenone,^{154,155} and regenerates the catalyst for completion of cycle.



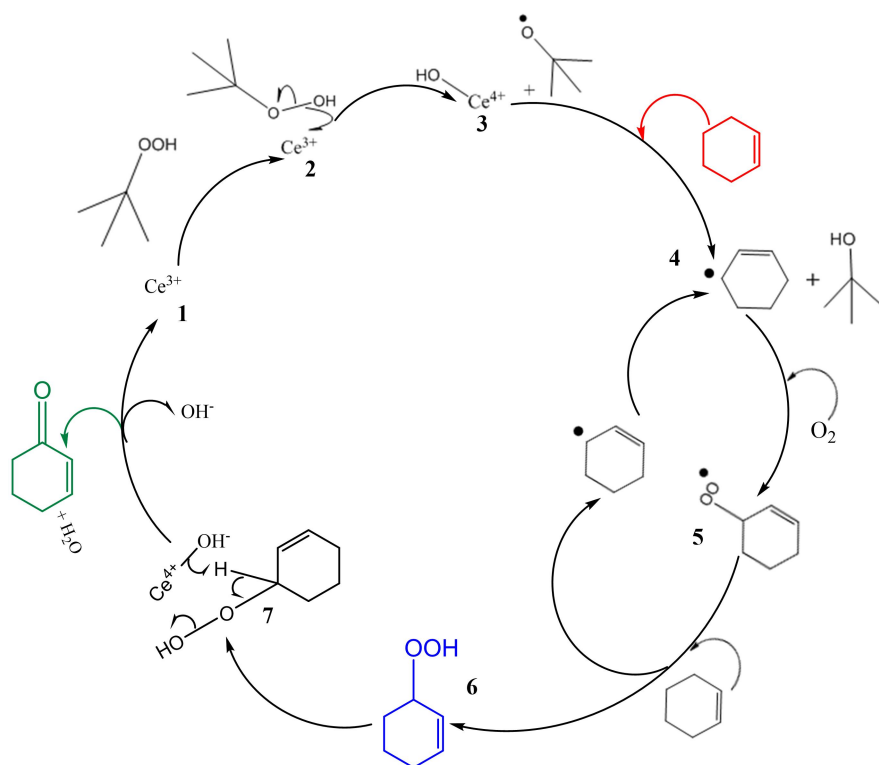


Figure 28 Proposed mechanism of cyclohexene oxidation in $\text{CeO}_2@\text{GNF}$ nanoreactor.

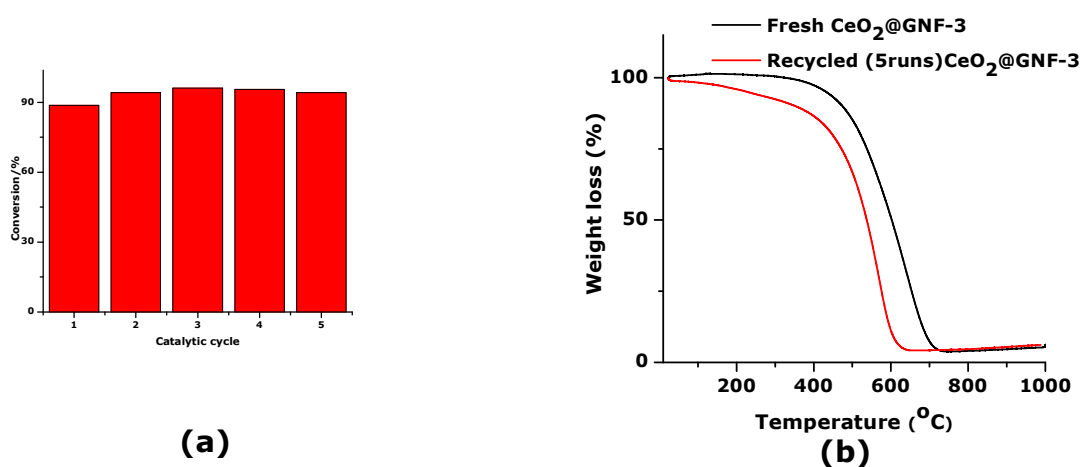


Figure 29 Reusability of $\text{CeO}_2@\text{GNF}$ nanoreactor in the oxidation of cyclohexene (a) & TGA curve of fresh and recycled (5 runs) $\text{CeO}_2@\text{GNF}$ (b).

In order to study the recyclability of the $\text{CeO}_2@\text{GNF}$ nanoreactor, we have evaluated the catalytic activity of $\text{CeO}_2@\text{GNF}$ for five runs. After each run the catalyst was filtered and washed repeatedly by methanol and kept overnight for drying in oven at 65°C in open vial. The conversion of cyclohexene was found to be increasing till 3rd run with a very

small decrease starting from 4th run (**Figure 29a**). Increase in conversion after first run can be attributed to cleaning of surface of catalyst due to reaction conditions. Also CeO₂ oxide being a redox catalyst, possibly is regenerated after first cycle, when heated in oxygen atmosphere overnight.⁵⁴ TGA profiles (**Figure 29b**) of fresh and recycled CeO₂@GNF shows no significant loss of CeO₂ content even after five cycles, indicating the high stability of nanoreactor, which can be assigned to encapsulation of CeO₂ inside robust hollow container GNF. Although there is no loss of CeO₂ but change in TGA profile after five cycles, suggesting decrease in combustion temperature of CeO₂@GNF composite could be due to change in size of CeO₂ nanoparticles.

5. Preparation and characterisation of Pt/CeO₂ nanoparticles inside graphitised carbon nanofibers (Pt/CeO₂@GNF)

5.1 Method of preparation of Pt/CeO₂ encapsulated inside GNF (Pt/CeO₂@GNF)

Pt nanoparticles supported on CeO₂ nanoparticles (Pt/CeO₂) were encapsulated inside graphitised carbon nanofibers in two steps (**Figure 30**). In first step, CeO₂ nanoparticles were deposited inside GNF by gas phase decomposition of tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)Ce(IV)[Ce(tmhd)₄] using the same procedure (**section 3.1.3**). In second step Pt nanoparticles were grown inside CeO₂@GNF by gas phase decomposition of platinum (II) acetylacetonate [Pt(acac)₂]. CeO₂@GNF and Pt(acac)₂ were sealed in glass ampoule under vacuum and heated above the sublimation temperature of Pt(acac)₂ to ensure its sublimation and penetration inside CeO₂@GNF to form Pt(acac)₂ – CeO₂@GNF. The sample was then rapidly cooled in ice cold water to facilitate condensation of Pt(acac)₂ molecules inside the GNF. Then it was opened and again sealed under argon and heated at 500 °C to decompose Pt(acac)₂–CeO₂@GNF into Pt nanoparticles and grow on already existing CeO₂ nanoparticles inside GNF.

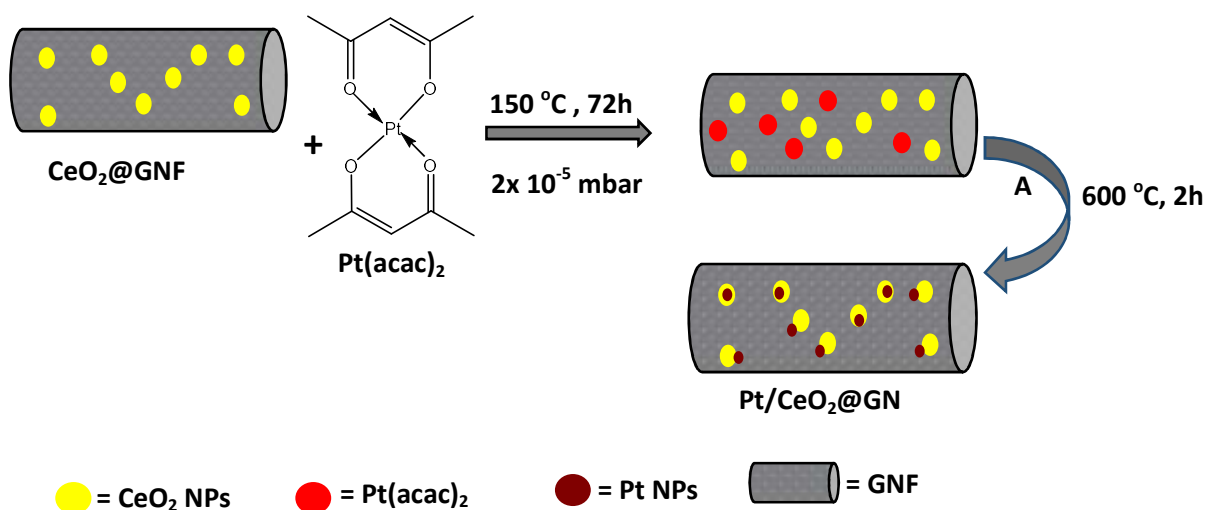


Figure 30 Schematic illustration of preparation of Pt/CeO₂ encapsulated inside graphitised carbon nanofibers (Pt/CeO₂@GNF).

5.2 Characterisation of Pt/CeO₂ encapsulated inside GNF (Pt/CeO₂@GNF)

5.2.1 Thermogravimetric analysis (TGA)

To confirm loading of Pt with CeO₂ embedded inside GNF, thermogravimetric analysis (TGA) was carried out. **Figure 31a** depicts the TGA of fresh GNF, CeO₂@GNF and Pt/CeO₂@GNF in air. The Pt/CeO₂@GNF is stable up to 500 °C, and a single step decomposition between 500 to 700 °C suggests formation of a composite material instead of a mixture of both. TGA curves show decrease in combustion temperature of composites in comparison to pure GNF. This is attributed to the catalytic effect of Pt and CeO₂, that accelerates combustion of GNF in air. Coordination of Pt and CeO₂ to C=C bonds in GNF weakens the C=C bonds, resulting lowering in combustion temperature of GNF.¹⁰¹ Addition of Pt into CeO₂ further lowers the combustion temperature, this suggests synergistic effect of both Pt and CeO₂. Residual mass beyond 700 °C corresponds to CeO₂ and Pt/CeO₂. There is an increase in residual mass observed for Pt/CeO₂@GNF, which is attributed to addition of Pt to CeO₂@GNF.

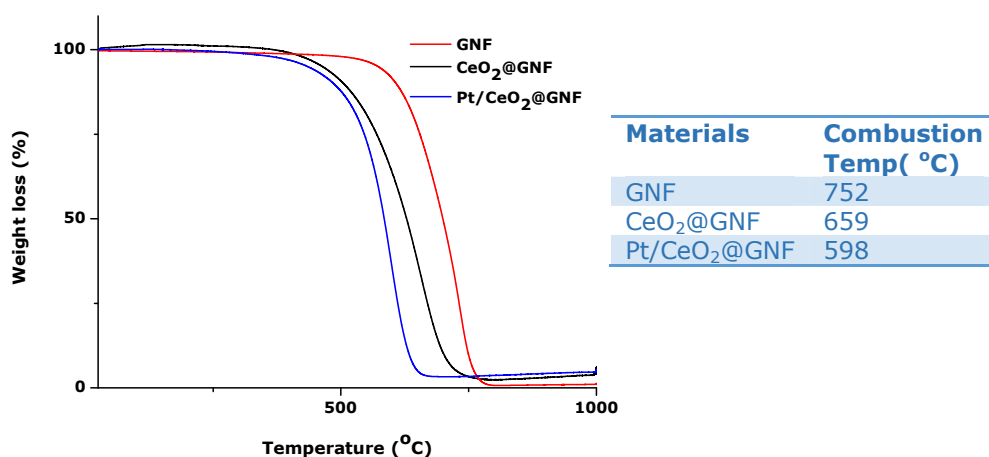


Figure 31 Thermogravimetric analysis of GNF, CeO₂@GNF and Pt/CeO₂@GNF, inset table shows combustion temperature of all the three materials.

5.2.2 Powder X-ray diffraction

In addition to TGA, to further confirm the formation Pt/CeO₂@GNF nanocomposite powder X-ray diffraction analysis was carried out. **Figure 32** shows XRD patterns of Pt/CeO₂@GNF, CeO₂@GNF and GNF. Long scan (14 hours with very slow scanning rate) XRD pattern of Pt/CeO₂-GNF shows a peak at $2\theta = 38^\circ$, which corresponds to (111) plane of Pt nanoparticles.^{84,156} The Pt peak is observed besides the peaks of GNF, confirms presence Pt NPs with GNF. Peaks corresponding to CeO₂ are not visible due to low amount of precursor and very small size of nanoparticles well dispersed inside the graphitised carbon nanofibers. This observation is consistent with the earlier XRD pattern obtained for CeO₂ inside GNF, where CeO₂ peaks were absent at low amount of precursor. So presence of Pt in CeO₂@GNF composite is ascertained from TGA and XRD but location of particles, particle size and elemental composition could only be confirmed by transmission electron microscopy.

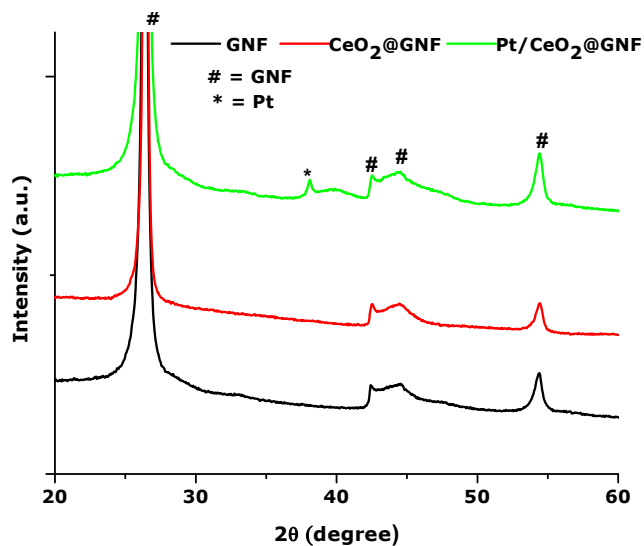


Figure 32 XRD patterns of graphitised carbon nanofibers (GNF), CeO₂ NPs inside GNF (CeO₂@GNF) and Pt NPs deposited on CeO₂ NPs inside GNF (Pt/CeO₂@GNF).

5.2.3 Transmission electron microscopy (TEM) and Energy dispersive X-ray spectroscopy (EDX)

In order to study the particle size and their location, HRTEM analysis was carried out (**Figure 33**). The average size of both Pt and CeO₂ nanoparticles ranges between 2 to 4 nm (**inset in Figure 33d**). Most of the nanoparticles are encapsulated inside the graphitised carbon nanofibers (GNF) (**Figure 33a-b**). Pt nanoparticles are found to be adsorbed on the edges of CeO₂ nanoparticles besides separately grown Pt and CeO₂ nanoparticles. A high degree of lattice alignment between Pt metals on CeO₂ was observed in HRTEM analysis. A HRTEM image of selected particle (**Figure 33c**) reveals contact between Pt and CeO₂ particles with clearly resolved lattice fringes having a d spacing 0.31 nm corresponding to (111) planes of CeO₂ and 0.23 nm corresponding to (111) planes of Pt nanoparticles. The elemental composition of nanoparticles was further ascertained for both Pt and CeO₂, by EDX analysis on a selected particle showing overlapping of lattice fringes (**Figure 33e-f**). A close look at the location shows atomic steps and the interatomic distances obtained by line profiles along a-a' (d=0.31 nm) and b-b' (d=0.22 nm) are consistent with (111) spacings of both CeO₂ and Pt respectively (**Figure 33g**), which again supports the adsorption of Pt on the edges of CeO₂ nanoparticles. In order to get a conclusive evidence to establish the fact that, Pt and CeO₂ particles are in contact, Scanning transmission electron microscopy (STEM) analysis was carried out. STEM analysis can easily distinguish between Pt and CeO₂ nanoparticles based on their transmitted intensity. Since Pt has higher atomic number than Ce, the transmitted electron intensity of Pt is higher than cerium, so in STEM images (**Figure 34a-c**) bright spots corresponds to Pt and less intense spots corresponds to CeO₂. Further to ensure, Pt and CeO₂ particles are in contact, viewing the sample from different angles was desirable. Therefore, images of a selected area was taken by tilting the sample at three different angles (0, 5 and 10 degrees) along x-axis (**Figure 34a-c**). The tilted images show that Pt nanoparticles are in contact with CeO₂ and there is adsorption of Pt nanoparticles on edges of CeO₂.

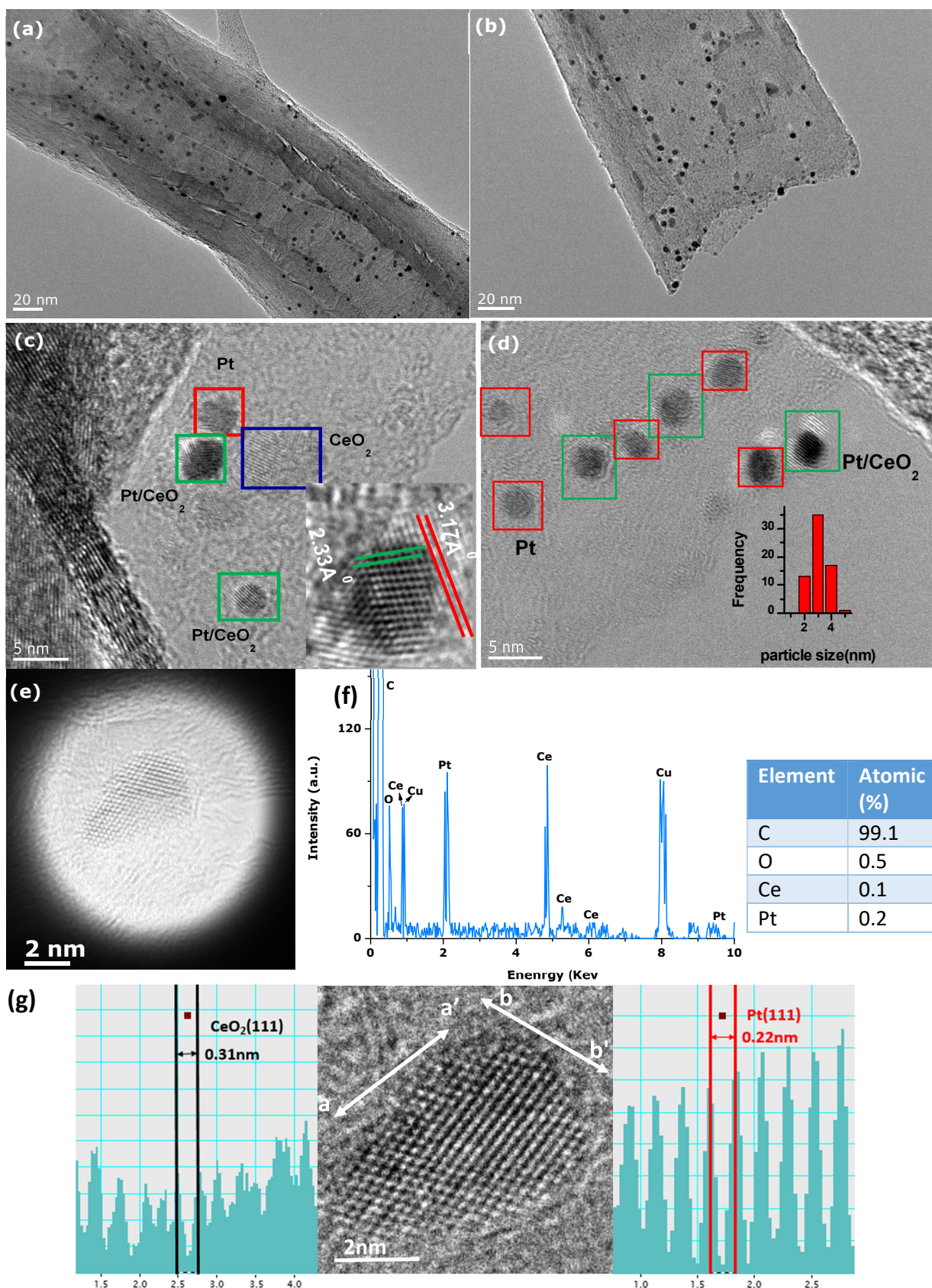


Figure 33 HRTEM analysis of (a-b) Pt/CeO₂ NPs inside GNF(Pt/CeO₂@GNF), (c) lattice fringes of CeO₂ and Pt NPs (inset shows Pt/CeO₂), (c-d) rectangles red: Pt NPs, blue: CeO₂ NPs, green: Pt/CeO₂ NPs (e) selected area for EDX analysis (f) corresponding EDX spectrum with elemental composition in the inset table, (Cu in EDX spectrum is from TEM grid), (g) atomic steps with corresponding line profiles showing the d-spacings of (111) planes of CeO₂ along a-a' and Pt along b-b'.

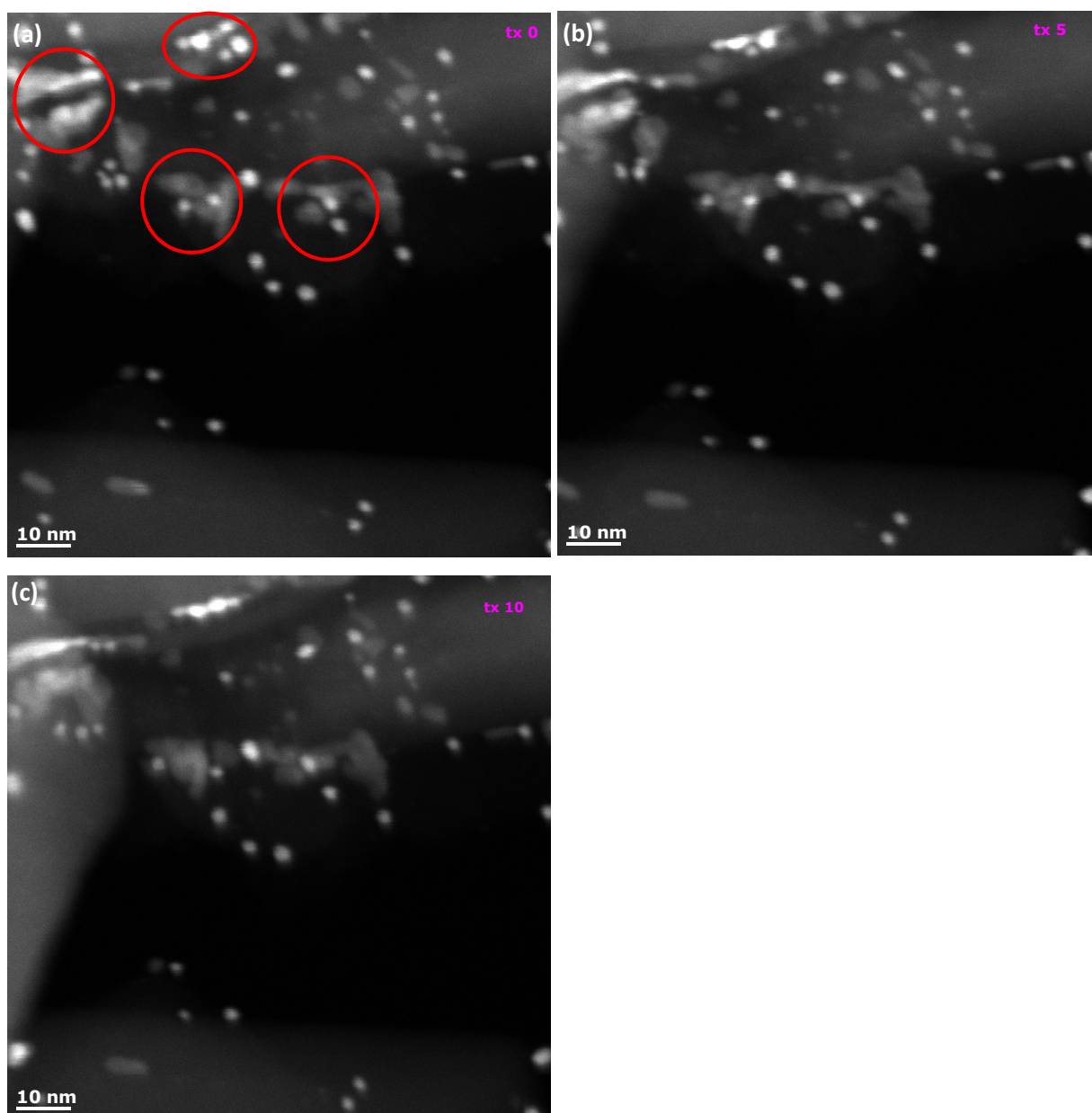


Figure 34 STEM images of Pt/CeO₂@GNF sample tilted along x-axis at angles (a) 0° (b) 5° and (c) 10°. Bright and less intense spots corresponds to Pt and CeO₂ respectively. Encircled zones shows contact between Pt and CeO₂ nanoparticles.

This observation of Pt nanoparticles adsorbed on the atomic terraces of CeO₂ is also consistent with previous reports. A computational modelling study on bonding between Pt and CeO₂ in Pt/CeO₂/Cu predicts growth of Pt particles on step edges of CeO₂ (**Figure 35c**).⁸¹ Wang et al. also demonstrated that, Pt particles are adsorbed adjacent to CeO₂ on CNT¹⁵⁶ through cyclic voltammetry (CV) studies. CV measurement of electroactive surface area of Pt, in Pt deposited on CNT (Pt-CNT) and Pt deposited on CeO₂-CNT

(Pt/CeO₂-CNT) shows no significant difference, suggesting that, Pt surface is not fully covered by CeO₂ and thus supports the fact that, Pt is adsorbed adjacent to CeO₂. This preferential nucleation of Pt particles adjacent to CeO₂ is due to defects on the step edges of CeO₂(111) planes.¹⁵⁶ Scanning tunneling microscopy (STM) and dynamic scanning force microscopy (SFM) studies on step structure of CeO₂ revealed that, the (111) planes of CeO₂ exhibit steps with (001) and (110) nanofacets (**Figure 35a-b**).¹⁵⁷ The defects on these nanofacets are due to missing oxygen atoms and kink sites (having low coordinated oxygen atoms) on CeO₂ edges. In Pt/CeO₂@GNF, being embedded inside, interaction between CeO₂ and GNF creates Ce³⁺ at the interface generating oxygen vacancies and thus creates more defects at the interface. Since density of these defects are more at the CeO₂-GNF interface, the nucleation of Pt takes place preferentially at the edges of (111) planes of CeO₂. A similar observation was also made by Lykhach et al.¹⁵⁸ where, the nucleation of Pt nanoparticles is influenced by defect density on CeO₂ surface.

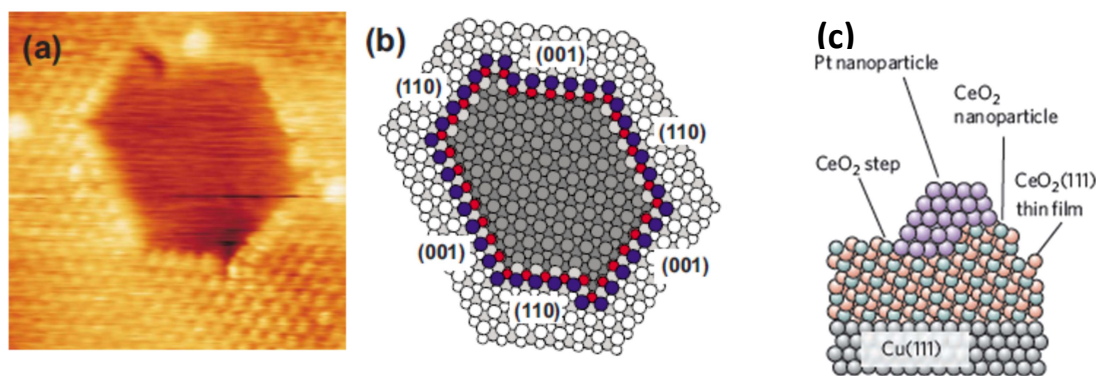


Figure 35 (a) Atomically resolved topographic SFM image of (111) plane of CeO₂, (b) corresponding model¹⁵⁷, (c) Model of Pt-CeO₂(111)/Cu(111) showing growth of Pt on edges of CeO₂.⁸¹

Therefore based on the results obtained from TGA, XRD, HRTEM, EDX and STEM, it is concluded that, Pt and CeO₂ nanoparticles are encapsulated inside GNF. Some Pt

nanoparticles are preferentially adsorbed on the step edges of (111) planes of CeO₂ at the interfaces of CeO₂-GNF due to the presence of defects.

6. Conclusions

A standard procedure has been developed to prepare CeO₂ nanoparticles encapsulated inside graphitised carbon nanofibers (GNF) by gas phase thermal decomposition of volatile cerium precursor [Ce(tmhd)₄]. Experimental findings confirm encapsulation of crystalline CeO₂ of size 4 nm inside GNF. Increasing amount of precursor material affects both growth factor and size distribution of CeO₂ nanoparticles. Thermal stability and catalytic activity of CeO₂@GNF nanoreactor are also affected by the amount of precursor. CeO₂ nanoparticles deposited on the step edges of GNF acts as effective catalytic sites. Decrease in thermal stability of nanocomposite was observed with increase in the precursor amount due to catalytic effect of CeO₂ which promotes combustion of GNF. Selective oxidation of allylic carbon centre in cyclohexene demonstrates catalytic activity of CeO₂@GNF. Size dependent catalytic activity and high stability even after five cycles of the reaction are the notable features of CeO₂@GNF nanoreactor.

Ionic liquid mediated method was not found to be an effective method for encapsulation of CeO₂ inside GNF, although CeO₂-GNF nanocomposite was prepared with very small and well dispersed crystalline CeO₂ nanoparticles. The role of both ionic liquid and GNF was found to be important for preparation of CeO₂ nanoparticles. GNF acts as an effective template for growth of small and well dispersed CeO₂ nanoparticles, whereas CeO₂ nanoparticles are organised into nanorods in absence of GNF. Ionic liquid reduces decomposition temperature of high melting cerium salt by forming a complex with it. Due to the interaction between imidazolium cation of ionic liquid and π electrons of GNF, the structure of GNF were partially exfoliated.

To study confinement of nanostructured CeO₂ inside GNF, gas phase decomposition method was found to be suitable. Ionic liquid mediated method is unsuitable as tubular

structures of graphitised carbon nanofibres are exfoliated and CeO_2 particles are mostly adsorbed on outer surface of exfoliated GNF.

Growth of Pt nanoparticles on CeO_2 encapsulated in GNF resulted in adsorption of Pt nanoparticles on the step edges of CeO_2 at the interface of CeO_2 -GNF. Besides their growth on the edges of CeO_2 nanoparticles, Pt nanoparticles are grown separately inside GNF.

7. Future works

Keeping in mind the excellent catalytic activity of Pt for hydrogenation reactions and the importance of conversion of CO_2 into valuable chemicals, nanostructured Pt/ CeO_2 encapsulated inside GNF can be applied to study hydrogenation of CO_2 . Our preliminary result suggests exclusive formation of ethanol as the product. So the future work would be focused on optimization of the reaction conditions for production of ethanol from CO_2 . Effects of parameters like concentration and particle size of both Pt and CeO_2 , temperature and pressure, on hydrogenation products will be investigated.

Though ionic liquid based method did not succeed in confining CeO_2 inside GNFs, very small size and well dispersed CeO_2 nanoparticles were adsorbed on carbon fibres leading to formation of a composite material. This can be applied as a heterogeneous catalyst to study catalysis of redox chemical reactions and yield of products that will be compared with the products formed with catalysts encapsulated inside the CeO_2 @GNF nanoreactor. This will reveal catalytic efficiency of CeO_2 nanoparticles, confined inside GNFs and adsorbed on the surface of carbon nanofibres. Our attempt to study the effect of confinement on charge of Ce through EELS could not yield any information due to multiple layers of carbon fibres but XPS analysis and other surface techniques of CeO_2 -GNF composite could be carried out to investigate the properties, like charge, of the adsorbed CeO_2 catalyst over the surface of carbon nanofibres. This may provide useful information about the surface and properties of this catalyst and allow for future

understanding and development to enhance CeO₂ nanomaterials for many future applications.

The CeO₂@GNF nanoreactor could be applied for other important chemical reactions, those that are known to be catalysed by CeO₂ nanoparticles, such as, oxidation of CO to CO₂,^{47b} hydrogenation of CO₂ to methanol.⁵⁶ Effects of confinement of CeO₂ catalyst inside CNTs will be evaluated for selectivity of products in useful chemical reactions, such as, selective catalytic reduction of NO_x with NH₃,¹⁵⁹ synthesis of methanol by hydrogenation of organic carbonates¹⁶⁰ carbon-carbon (C-C) bond formation by Michael addition reaction of active methylene compounds to conjugated alkenes¹⁶¹ and catalytic desulfurization of CH₃SH.¹⁶² Since electron densities vary in outer and inner surface of CNTs, confinement of CeO₂ inside CNTs could influence charge on Ce in CeO₂. Thus, investigation will be made on the effect of confinement on charge of Ce, that will further demonstrate the advantage of confining CeO₂. Excellent recycling of CeO₂ even after 5 cycles of the reactions illustrates stability of CeO₂ when confined inside GNFs.

With the knowledge developed in this project it would be interesting to confine other lanthanide oxides inside graphitised nanofibres, as they possess very useful magnetic and thermal properties. Praseodymium oxide is well known as one of the most attractive lanthanide oxides due to its electrical¹⁶³ and catalytic^{164,165} properties. Appropriate β -diketonate complex of Pr having low sublimation temperature will be chosen as precursor for encapsulation of Praseodymium oxide nanoparticles inside GNFs using the developed method for CeO₂. Resultant electrical, thermal and magnetic properties of Praseodymium oxide confined inside GNFs will be explored.

Overall, this project has laid the foundation to study encapsulation of cerium and other lanthanide elements in CNTs, and proposed a new set of materials for catalytic and electromagnetic applications.

8. Experimental

8.1 General

All reagents and solvents were purchased from Sigma-Aldrich and were used as received. Tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)cerium(IV)(99.9% Ce) was purchased from Strem Chemicals, USA., 1-butyl-3-methyl imidazolium bromide from Sigma-Aldrich, cerium(III)bromide hydrate (99%) from Alfa Aesar, USA, graphitised carbon nanofibers (GNF) PR19 from Pyrograf products and cyclohexene (>99%) from Sigma Aldrich, Japan. Conventional glass apparatus were used in experimental procedures.

Prior to use GNF was ball milled using Retsch MM40 Ball Miller with 5ml jars and 12mm SS balls at a frequency of 10 per second for 90 minutes.

^1H NMR spectra were recorded at room temperature using a Bruker Advance-DPX-300 spectrometer (TopSpin 1.3 PL4). Proton 16 scan experiments were run with CDCl_3 and CD_3CN as solvents. Spectra were analysed using MestReNova software.

GCEIMS analysis of samples were recorded using Mass Spectrometer: JEOL AccuTOF GCX (JEOL Ltd., Tokyo, Japan) and Gas Chromatograph: Agilent 7890B (Agilent Technologies Inc, Wilmington, USA). Spectra were run from the neat samples.

UV-Vis absorption spectra were recorded at room temperature using 1cm quartz cuvettes in ethanol as solvent. The samples were run using a Perkin-Elmer Lambda 25 UV/Vis spectrometer over a wavelength range of 200-900 nm. Spectra were analysed using UV WinLab Es software.

Transmission electron microscopy (TEM) micrographs were acquired by Prof. Andrei Khlobystov and Dr. Alessandro La Tore. STEM micrographs were acquired by Dr. Michael Fay. The microscope used was a JOEL 2100F TEM field emission gun microscope. Samples were prepared by dispersing in methanol and were sonicated for 30 second to 1 minute before spotting. Samples were spotted on copper grid mounted with a lacey carbon film (Agar Scientific UK) and allowed to dry naturally. Particle size and d-spacings

were calculated by using Gatan Digital Micrograph software. Energy dispersive X-ray spectroscopy (EDX) measurements were performed using same microscope.

Raman spectra of samples were acquired by Dr. Graham A. Rance using Horiba-Jobin-Yvon LabRAM HR spectrometer. Spectra were baseline corrected using a linear fitting model.

The powder x-ray diffraction patterns were recorded using a PANalytical X'Pert Pro diffractometer equipped with a Cu K(α) radiation source ($\lambda = 1.5432$, at 40 kV and 40 mA) in Bragg-Brentano geometry using a Si zero background holder. Few drops of isopropyl alcohol were added to all samples on sample holder for good adhesion. The parameters for a typical measurement were; Start angle 5° , Stop angle: 120° , Step Size: 0.05250, Time/step: 6080 s, scan speed: 0.002200/s.

The thermogravimetric analysis of samples were carried out using a TA Q500 Thermogravimetric Analyser. All samples were analysed in air using a platinum pan at heating rate $10^\circ/\text{min}$ from 20 to 1000°C with an isotherm for 10 minutes at 1000°C , air flow: 60 mL/min.

8.2 Preparation of CeO_2 nanoparticles encapsulated inside graphitised carbon nanofibers ($\text{CeO}_2@\text{GNF}$) using gas phase decomposition method

Ball milled graphitised carbon nanofibers (PR19) and cerium complex, $\text{Ce}(\text{tmhd})_4$ of certain quantity (**Table-8**) were taken in a pyrex glass ampoule. The ampoule was then sealed under high vacuum (2.9×10^{-5} mbar) and heated at 150°C in an oil bath for 72 hours for sublimation of cerium complex and diffusion inside hollow structure of GNFs. After 72 hours, the ampoule was immediately put in ice cold water for 10 minutes before opening. The sample was then taken in another pyrex glass ampoule and sealed under argon. Before filling argon, the ampoule was evacuated at 1.6×10^{-2} mbar. This process, of evacuation of ampoule (1.6×10^{-2} mbar) followed by argon filling, was repeated thrice to ensure complete removal of O_2 or moisture. Then the ampoule was sealed and was heated at 600°C for 2 hours followed by slow cooling for 8 hours to a final temperature 20°C . The heating was performed in an auto programmed oven. After cooling the

ampoule was opened and CeO_2 encapsulated inside GNF ($\text{CeO}_2\text{@GNF}$) was used for further characterization and applications. The conditions of preparation of $\text{CeO}_2\text{@GNF}$ with varied precursor concentrations are summarised in **Table 8**.

Table 8 Reaction parameters for preparation of $\text{CeO}_2\text{@GNF}$.

Materials	Quantity of precursor [Ce(tmhd) ₄](mg)	Quantity of GNF(PR19)(mg)	Sublimation temperature(°C)
$\text{CeO}_2\text{@GNF-1}$	1	10	150
$\text{CeO}_2\text{@GNF-2}$	2	10	150
$\text{CeO}_2\text{@GNF-3}$	3	10	150

8.3 Preparation of CeO_2 -GNF composite by using ionic liquid mediated method

$\text{CeBr}_3 \cdot x\text{H}_2\text{O}$ and 1-butyl-3-methyl imidazolium bromide (BMIBr) were taken in 1:3 molar ratio in a glass vial. 10 mg of ball milled graphitised carbon nanofibres (PR19) was added into this mixture. Then the open vial containing the mixture of all three ($\text{CeBr}_3 \cdot x\text{H}_2\text{O}$, 1-butyl-3-methyl imidazolium bromide (BMIBr) and graphitised carbon nanofibres (GNF)) was heated in an oven at 110 °C for 2 hours followed by slow cooling of the sample for 8 hours to a final temperature of 20 °C. The reagents were heated at 110 °C for formation of the complex $[\text{BMI}]_3[\text{CeBr}_6]$ and its diffusion inside GNF to form $[\text{BMI}]_3[\text{CeBr}_6]\text{-GNF}$. In order to oxidise the $[\text{BMI}]_3[\text{CeBr}_6]$ complex into CeO_2 , the same vial was again heated at 430 °C in an oven for 2 hours followed by slow cooling for 8 hours to a final temperature of 20 °C. Temperature was controlled by auto programming in the oven.

To investigate the role of ionic liquid and GNF in formation of CeO_2 , varied amount of precursor and ionic liquid was taken and decomposed at different conditions (**Table 9**).

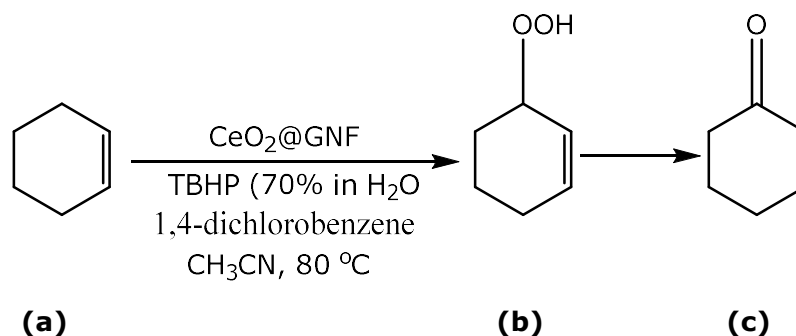
Table 9 Amount of reagents and decomposition temperature for preparation of CeO₂-GNF composite by ionic liquid mediated method.

Materials	Amount of Precursor CeBr ₃ .xH ₂ O (mg)	Amount of ionic liquid BMIBr (mg)	Amount of GNF (mg)	Decomposition temperature(°C)
CeO ₂ -GNF-2	2	3.5	10	430
CeO ₂ -GNF-3	3	5.1	10	430
CeO ₂ -GNF-4	4	6.9	10	430
CeO ₂ -GNF 530	3	5.1	10	530
CeO ₂ -GNF 630	3	5.1	10	630
CeO ₂ nanorod	3	5.1	Nil	430

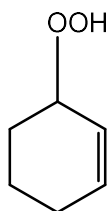
8.4 Preparation of Pt/CeO₂ encapsulated inside graphitised carbon nanofibers (Pt/CeO₂@GNF)

Pt/CeO₂ nanoparticles were encapsulated inside graphitised carbon nanofibers in two steps. In the first step, CeO₂ nanoparticles were encapsulated inside GNF by following the procedure mentioned in **section 8.2**. CeO₂@GNF-1 (10mg) and Pt(acac)₃ 0.2 mg were sealed in a glass ampoule under vacuum (2.9×10^{-5} mbar) and heated at 140 °C in an oil bath for 72 hours to ensure sublimation of platinum precursor and penetration inside CeO₂@GNF. The sample was then rapidly cooled in ice cold water. After opening, the material was transferred to another glass ampoule and again sealed under argon. Before filling argon, the ampoule was evacuated at 1.6×10^{-2} mbar. The process of evacuation (1.6×10^{-2} mbar) followed by argon filling was repeated thrice and then the ampoule was sealed. The ampoule containing Pt(acac)₃ encapsulated in CeO₂@GNF was heated in an oven at 500 °C for 2 hours and slowly cooled for 8 hours to a final temperature 20 °C. The material Pt/CeO₂ encapsulated inside GNF (Pt/CeO₂@GNF) was recovered and used for characterizations and applications. The temperature was controlled by auto programming in the oven.

8.5 Reaction procedure for allylic oxidation of cyclohexene in nanoreactor of CeO₂ inside GNF



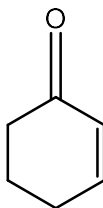
The catalytic oxidation of cyclohexene, with tert-butylhydroperoxide TBHP (Aldrich, 70 wt% in H₂O) as an oxidant was carried out in CeO₂@GNF nanoreactor taken in a two-necked glass round-bottom flask equipped with a magnetic stirrer and a reflux condenser open to air. In a typical reaction, a mixture of 2.9 mmol of cyclohexene (0.3 ml), 5.8 mmol of TBHP, 10 mg CeO₂@GNF and 0.213 g of 1,4-dichlorobenzene as internal standard were taken in 2.5 ml of acetonitrile and stirred at 80 °C. The course of reaction was followed by ¹H NMR spectroscopy. For the study of the kinetics, aliquots were taken from the reaction bulk after every hour. The final products were characterized by ¹H NMR and gas chromatography (GC-MS). The ¹H NMR spectra in appendix-I shows, the decrease in concentration of the intermediate 2-cyclohexenyl hydroperoxide with respect to time and formation of the product 2-cyclohexenone. Before the reaction starts, at 0 hour, concentration of 2-cyclohexenyl hydroperoxide is nill and is decreasing as the reaction proceeds from 3 hours to 11 hours. GC MS of products were matched with those of respective compounds.



2-cyclohexenyl hydroperoxide **(b)**

¹H NMR (300 MHz, 297 K, CD₃CN, δ , ppm): 9.40(bs, 1H), 5.96 (m, 1H), 5.74(m, 1H), 4.37(m, 1H), 2.2 -1.21 (m, 6H)

GCMS m/z :114



2-cyclohexenone (**c**)

^1H NMR (300 MHz, 297 K, CD_3CN , δ , ppm): 7.0 (m, 1H), 6.07 (d, 1H), 2.4-2.2 (m, 6H)

GCMS m/z :96

For recycling, the catalyst was recovered by filtration, washed with methanol and kept in oven for drying overnight at 60 °C in an open vial. The catalyst was again reused under the same reaction conditions mentioned above with freshly loaded reactants. The recycling reaction was conducted five times. The catalytic performances were reported in terms of cyclohexene conversion and selectivity towards products. They were calculated following the expressions below:

Conversion (%) = (consumed cyclohexene/initial cyclohexene) x 100

Selectivity of product (%) = (Moles of individual product/ Moles of total products formed) x 100.

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10. References

1. L. Li, D. L. King, J. Liu, Q. Huo, K. Zhu, C. Wang, M. Gerber, D. Stevens and Y. Wang, *Chem. Mater.*, 2009, **21**, 5358–5364.
2. X. Pan, Z. Fan, W. Chen, Y. Ding, H. Luo and X. Bao, *Nat. Mater.*, 2007, **6**, 507–511.
3. S. Li, T. Boucheron, A. Tuel, D. Farrusseng and F. Meunier, *Chem. Commun.*, 2014, **50**, 1824–1826.
4. A. La Torre, M. d. C. Gimenez-Lopez, M. W. Fay, G. A. Rance, W. A. Solomonsz, T. W. Chamberlain, P. D. Brown and A. N. Khlobystov, *ACS Nano*, 2012, **6**, 2000–2007.
5. H. Kim and W. Sigmund, *J. Cryst. Growth*, 2005, **276**, 594–605.
6. T. W. Chamberlain, T. Zoberbier, J. Biskupek, A. Botos, U. Kaiserb and A. N.

-
- Khlobystov, *Chem. Sci.*, 2012, **3**, 1919-1924.
7. E. Philp, J. A. Sloan, I. Kirkland, R. R. Meyer, S. Friedrichs, J. L. Hutchison and M. L. H. Green, *Nat. Mater.*, 2003, **2**, 788-791.
 8. W. Chen, X. Pan, X. Bao, *J. Am. Chem. Soc.*, 2007, **129**, 7421 -7426.
 9. C. Dai, X. Li, A. Zhang, C. Liu, C. Song and X. Guo, *RSC Adv.*, 2015, **5**, 40297-40302.
 10. S. Li, C. Aquino, L. Gueudré, A. Tuel, Y. Schuurman and D. Farrusseng, *ACS Catal.*, 2014, **4**, 4299-4303.
 11. H. L. Jiang, T. Akita, T. Ishida, M. Haruta, and Q. Xu, *J. Am. Chem. Soc.*, 2011, **133**, 1304-1306.
 12. T. Zeng, X. Zhang, S. Wang, H. Niu, and Y. Cai, *Environ. Sci. Technol.*, 2015, **49**, 2350-2357.
 13. A. N. Khlobystov, *ACS Nano*, 2012, **5**, 9306-9312.
 14. X. Pan and X. Bao, *Acc. Chem. Res.*, 2011, **44**, 553- 562.
 15. S. Liu, J. Zhu, Y. Mastai, I. Felner and A. Gedanken, *Chem. Mater.*, 2000, **12**, 2205 -2211.
 16. S. Guo, X. Pan, H. Gao, Z. Yang, J. Zhao and X. Bao, *Chem. Eur. J.*, 2010, **16**, 5379-5384.
 17. L. J. Li, A. N. Khlobystov, J. G. Wiltshire, G. A. D. Briggs and R. J. Nicholas, *Nat. Mater.*, 2005, **4**, 481-485.
 18. R. M. M. Abbaslou, A. Tavassoli, J. Soltan and A. K. Dalai, *Appl. Catal. A: Gen.*, 2009, **367**, 47-52.
 19. J. Guan, X. Pan, X. Liu and X. Bao, *J. Phys. Chem. C*, 2009, **113**, 21687-21692.
 20. P. Kondratyuk, Y. Wang, J. Liu, J. K. Johnson and J. T. Yates, Jr., *J. Phys. Chem. C*, 2007, **111**, 4578-4584.
 21. M. Trepanier, A. K. Dalai, and N. Abatzoglou, *Appl. Catal. A: Gen.*, 2010, **374**,

-
- 79–86.
22. J. Zhang, J. O. Muller, W. Zheng, D. Wang, D. S. Su and R. Schlogl, *Nano Lett.*, 2008, **8**, 2738–2743.
 23. Z. Guan, S. Lu and C. Li, *J. Catal.*, 2014, **311**, 1–5.
 24. H. X. Ma, L. C. Wang, L. Y. Chen, C. Dong, W. C. Yu, T. Huang and Y. T. Qian, *Catal. Commun.*, 2007, **8**, 452–456.
 25. D. Wang, G. Yang, Q. Ma, M. Wu, Y. Tan, Y. Yoneyama and N. Tsubaki, *ACS Catal.*, 2012, **2**, 1958 – 1966.
 26. J. Zheng, X. Duan, H. Lin, Z. Gu, H. Fang, J. Li and Y. Yuan, *Nanoscale*, 2016, **8**, 5959–5967.
 27. X. Zhang, Y. C. Guo, Z. Cheng Zhang, J. S. Gao and C. M. Xu, *J. Catal.*, 2012, **292**, 213–226.
 28. W. Chen, Z. Fan, B. Zhang, G. Ma, K. Takanabe, X. Zhang and Z. Lai, *J. Am. Chem. Soc.*, 2011, **133**, 14896 –14899.
 29. W. Chen, Z. Fan, L. Gu, X. Bao and C. Wang, *Chem. Commun.*, 2010, **46**, 3905–3907.
 30. J. Sloan, A. I. Kirkland, J. L. Hutchison and M.L. H. Green, *Acc. Chem. Res.*, 2002, **35**, 1054–1062.
 31. M Scarselli, P Castrucci and M De Crescenzi, *J. Phys.: Condens. Matter*, 2012, **24**, 313202, 1–36.
 32. A. Jorio, M. S. Dresselhaus and G. Dresselhaus, *Carbon Nanotubes: Advanced Topics in the Synthesis, Structure, Properties, and Applications* (New York: Springer), 2008.
 33. (a) A. V. Melechko, V. I. Merkulov, T. E. McKnight, M. A. Guillorn, K. L. Klein, D. H. Lowndes, M. L. Simpson, *J. Appl. Phys.*, 2005, **97**, 041301–39. (b) M. Inagaki, Y. Yang, F. Y. Kang, *Adv. Mater.*, 2012, **24**, 2547–2566. (c) A. Ramos, I. Camean

-
- and A. B. Garcia, *Carbon*, 2013, **59**, 2-32.
34. <http://www.carbonallotropes.com/carbon-nanotubes>
 35. A. Merkoci, *Microchim Acta*, 2006, **152**, 157–174.
 36. M. Endo, Y. A. Kim, T. Hayashi, Y. Fukai, K. Oshida, M. Terrones, T. Yanagisawa, S. Higaki, and M. S. Dresselhaus, *Appl. Phys. Lett.*, 2002, **80**, 1267-1269.
 37. W. A. Solomonsz , G. A. Rance , M. Suyetin , A. La Torre , E. Bichoutskaia , A. N. Khlobystov , *Chem. Eur. J.*, 2012, **18** , 13180-13187.
 38. G. A. Rance , W. A. Solomonsz , A. N. Khlobystov , *Chem. Commun.*, 2013, **49**, 1067-1069.
 39. W. A. Solomonsz , G. A. Rance and A. N. Khlobystov, *Small*, 2014, **10**, 1866–1872.
 40. M. d. C. Gimenez-Lopez, A. Kurtoglu, D. A. Walsh and A. N. Khlobystov, *Adv. Mater.*, 2016, **28**, 9103-9108.
 41. M. A. Lebedeva, T. W. Chamberlain, A. Thomas, B. E. Thomas, C. T. Stoppiello, E. Volkova, M. Suyetind and A. N. Khlobystov, *Nanoscale*, 2016, **8**, 11727–11737.
 42. <https://www.britannica.com/science/rare-earth-element>
 43. H. C. Aspinall, *Chemistry of the f –Block Elements*, Gordon & Breach Science Publishers, Canada, 2001.
 44. (a) M. Yada, H. Kitamura, A. Ichinose, M. Machida and T. Kijima, *Angew. Chem. Int. Ed.*, 1999, **38**, 3504-3506., (b) J. W. Stouwdam and F. C. J. M. van Veggel, *Nano Lett.*, 2002, **2**, 733-737., (c) K. Kompe, H. Borchert, J. Storz, A. Lobo, S. Adam, T. Moller and M. Haase, *Angew. Chem., Int. Ed.*, 2003, **42**, 5513-5516., (d) R. S. Meltzer, S. P. Feofilov, B. Tissue and H. B. Yuan, *Phys. Rev. B.*, 1999, **60**, R14012-

-
- R14015.,(e) A. B. Panda, G. Glaspell and M. S. El-Shall, *J. Phys. Chem. C*,2007, **111**, 1861-1864.
45. J.C. G. Bünzli, S. Comby, A.-S. Chauvin and C. D. B. Vandevyver, *J. Rare Earths*, 2007, **25**, 257–274., (b) T. Jüstel, H. Nikol and C. Ronda, *Angew. Chem. Int. Ed.*, 1998,**37**, 3084–3103.
46. J.B. Hedrick, *Rare Earths. Minerals Yearbook. Vol I. Metals and Minerals*; US Geological Survey, US Department of the Interior: Reston, VA, USA, 2004.
47. (a)C. T. Campbell and C. H. F. Peden, *Science*, 2005, **309**, 713-714., (b) J. Guzman, S. Carrettin, J. C. Fierro-Gonzalez, Y. L. Hao, B. C. Gates, A. Corma, *Angew.Chem. Int. Ed.*, 2005, **44**, 4778-4781., (c) S. Carrettin, J. Guzman and A. Corma, *Angew. Chem. Int. Ed.*, 2005, **44**, 2242-2245.
48. A. B. Stambouli and E. Traversa, *Renew. Sust. Energ. Rev.*,2002, **6**,433-455.
49. A. Corma, P. Atienzar, H. Garcia and J. Y. Chane-Ching, *Nat. Mater.*,2004,**3**,394-397.
50. S. Patil, S. C. Kuiry, S. Seal, R. Vanfleet, *J. Nanopart. Res.*,2002,**4**,433-438.
51. M.Das, S. Patil, N. Bhargava, J. F. Kang, L. M. Riedel, S. Seal and J. J. Hickman, *Biomaterials*, 2007, **28**, 1918-1925.
52. I.Celardo, J. Z. Pedersen, E. Traversa and L. Ghibelli, *Nanoscale*,2011,**3**,1411-1420.
53. A. Trovarelli, *Ceria and Related Materials (Ed.: A. Trovarelli)*, Imperial College Press, London, 2002.
54. M. Tamura and K. Tomishige, *Angew. Chem. Int. Ed.*, 2015, **54**, 864-867.
55. P.Zhang, H. Lu, Y. Zhou, L. Zhang, Z. Wu, S. Yang, H. Shi, Q. Zhu, Y. Chen and S. Dai, *Nat. Commun.*, 2015, **6**,8446, 1-10.
56. X. Yang, S. Kattel, S. D. Senanayake, J. A. Boscoboinik, X. Nie, J. Graciani, J.A.

-
- Rodriguez, P. Liu, D. J. Stacchiola and J. G. Chen, *J. Am. Chem. Soc.*, 2015, **137**, 10104–10107.
57. T. Alammar, H. Noei, Y. Wang, W. Grünert and A.V. Mudring, *ACS Sustainable Chem. Eng.*, 2015, **3**, 42–54.
58. G. Chen, C. Xu, X. Song, W. Zhao, Y. Ding and S. Sun, *Inorg. Chem.*, 2008, **47**, 723–728.
59. H. Li, G. Lu, Q. Dai, Y. Wang, Y. Guo and Y. Guo, *ACS Appl. Mater. Interfaces*, 2010, **2**, 838–846.
60. S. Carrettin, P. Concepcion, A. Corma, J. M. L. Nieto and V. F. Puentes, *Angew. Chem. Int. Ed.*, 2004, **43**, 2538–2540.
61. J. Guzman, S. Carrettin and A. Corma, *J. Am. Chem. Soc.*, 2005, **127**, 3286–3287.
62. S. Phokha, S. Pinitsoontorn, P. Chirawatkul, Y. Poo-arporn and S Maensiri, *Nanoscale Res. Lett.*, 2012, **7**, 425, 1–13.
63. B. Choudhury, P. Chetri and A. Choudhury, *RSC Adv.*, 2014, **4**, 4663–4671.
64. C. Sun and L. Chen, *Eur. J. Inorg. Chem.*, 2009, **26**, 3883–3887.
65. Z. Sun, H. Zhang, G. An, G. Yang and Z. Liu, *J. Mater. Chem.*, 2010, **20**, 1947–1952.
66. H. X. Mai, L. D. Sun, Y. W. Zhang, R. Si, W. Feng, H. P. Zhang, H. C. Liu, C. H. Yan, *J. Phys. Chem. B*, 2005, **109**, 24380–24385.
67. C. Ho, C. J. Yu, T. Kwong, A. C. Mak and S. Lai, *Chem. Mater.*, 2005, **17**, 4514–4522.
68. C. L. Robert, J. W. Long, E. M. Lucas, K. A. Pettigrew, R. M. Stroud, M. S. Doescher, and D. R. Rolison, *Chem. Mater.*, 2006, **18**, 50–58.
69. H. Xiao, Z. Ai and L. Zhang, *J. Phys. Chem. C*, 2009, **113**, 16625–16630.
70. T. Sakata and H. Mori, *Chem. Mater.*, 1997, **9**, 2197–2204.

-
71. M. D. Hernandez-Alonso, A. B. Hungria, A. Martinez-Arias, J. M. Coronado, J. C. Conesa, J. Soria, M. Fernandez-Garcia, *Phys. Chem. Chem. Phys.*, 2004, **6**, 3524-3529.
72. L. Madler, W.J. Stark, and S.E. Pratsinis, *J. Mater. Res.*, 2002, **17**, 1356-1362.
73. A. Bruix, J. A. Rodriguez, P. J. Ramirez, S. D. Senanayake, J. Evans, J. B. Park, D. Stacchiola, P. Liu, J. Hrbek and F. Illas, *J. Am. Chem. Soc.*, 2012, **134**, 8968-8974.
74. J. Graciani, K. Mudiyanse, F. Xu, A. E. Baber, J. Evans, S. D. Senanayake, D. J. Stacchiola, P. Liu, J. Hrbek, J. F. Sanz and J. A. Rodriguez, *Science*, 2014, **345**, 6196, 546-550.
75. J. A. Rodriguez, P. Liu, D. J. Stacchiola, S. D. Senanayake, M. G. White and J. G. Chen, *ACS Catal.*, 2015, **5**, 6696-6706.
76. F. Fajardie, J. F. Tempère, G. D. Mariadassou, and G. Blanchard, *J. Catal.*, 1996, **163**, 77-86.
77. A. S. Escibano, F. Coloma, and F. R. Reinoso, *J. Catal.*, 1998, **178**, 649-657.
78. Z. A. Reddam, R. E. Mail, F. Colomaa, A. S. Escibano, *Catal. Today*, 2015, **249**, 109-116.
79. H. H. Liu, Y. Wang, A. P. Jia, S. Y. Wang, M. F. Luo, J. Q. Lu, *Appl. Surf. Sci.*, 2014, **314**, 725-734.
80. H. Wang, K. An, A. Sapi, F. Liu, G. A. Somorjai, *Catal Lett.*, 2014, **144**, 1930-1938.
81. G. N. Vayssilov, Y. Lykhach, A. Migani, T. Staud, G. P. Petroval, N. Tsud, T. Skala, A. Bruix, F. Illas, K. C. Prince, V. Matolín, K. M. Neyman and J. Libuda, *Nat. Mater.*, 2011, **10**, 310-315.
82. A. Migani, G. N. Vayssilov, S. T. Bromley, F. Illas and K. M. Neyman, *Chem.*

-
- Commun.*, 2010, **46**,5936–5938.
83. X. Yang, Y. Mueanngern, Q. A. Baker and L. R. Bake, *Catal. Sci. Technol.*, 2016, **6**, 6824-6835.
 84. A. Shukla, R. K.Singha, T.Sasaki and R. Bal, *Green Chem.*, 2015, **17**, 785-790.
 85. C. R. Kim, T. Uemura and S. Kitagawa, *Chem. Lett.*, 2014, **43**, 1749–1751.
 86. X. Zhao, H. Li, J. Zhang, L. Shi and D. Zhang, *I n t. J. Hydrogen Energy*, 2016, **41**, 2 4 4 7-2 4 5 6.
 87. H. Wang, X. Chen, X. Weng, Y. Liu, S. Gao, Z. Wu, *Catal. Commun.*,2011, **12**, 1042–1045.
 88. V. Shanmugam, R. Zapf, S. Neuberg, V. Hessel, G. Kolb, *Appl. Catal. B Environ*, 2017, **203**, 859-869.
 89. R. Raoa, Q. Zhanga, H. Liua, H. Yanga, Q. Linga, M. Yanga, A. Zhanga and W. Chen, *J. Mol. Catal. A: Chemical*, 2012, **363–364**, 283–290.
 90. (a)J. Liu, A. G. Rinzler, H. Dai, J. H. Hafner, R. K. Bradley, P. J. Boul, A. Lu, T. Iverson, K. Shelimov, C. B. Huffman, F. Rodriguez-Macias, Y. S. Shon, T. R. Lee, D. T. Colbert and R. E. Smalley, *Science*,1998, **280**, 1253-1256., (b) S.C.Tsang, Y.K.Chen, P.F.J.Harris and M.L.H.Green, *Nature*,1994,**372**,159-162.
 91. T.Saitoa, K.Matsushigeb and K.Tanaka, *Physica B*, 2002, **323**,280–283.
 92. T. J. Aitchison, M. Ginic-Markovic, J. G. Matisons, G. P. Simon, and P. M. Fredericks, *J. Phys. Chem. C*, 2007, **111**, 2440-2446.
 93. X. X. Wang, J. N. Wang, L. F. Su and J. J. Niu, *J. Mater. Chem.*, 2006, **16**, 4231–4234.

-
94. C. Wang, S. Guo, X. Pan, W. Chen and X. Bao, *J. Mater. Chem.*, 2008, **18**, 5782–5786.
95. A. L. Torre, G. A. Rance, a J. E. Harfi, J. Li, D. J. Irvine, P. D. Brown and A. N. Khlobystov, *Nanoscale*, 2010, **2**, 1006–1010.
96. W. A. Solomonsz, G. A. Rance, B. J. Harrisa and A. N. Khlobystov, *Nanoscale*, 2013, **5**, 12200–12205.
97. A. N. Khlobystov and D. A. Britz, *Chem. Soc. Rev.*, 2006, **35**, 637–659.
98. A. Beltram, M. Melchionna, T. Montini, L. Nasi, R. J. Gorte, M. Prato, P. Fornasiero, *Catal. Today*, 2015, **253**, 142–148.
99. M. Cargnello, M. Grzelczak, B. R. González, Z. Syrgiannis, K. Bakhmutsky, V. L. Parola, L. M. Liz-Marzan, R. J. Gorte, M. Prato and P. Fornasiero, *J. Am. Chem. Soc.*, 2012, **134**, 11760–11766.
100. Y. Gao, K. Xie, W. Wang, S. Mi, N. Liu, G. Pan and W. Huang, *Catal. Sci. Technol.*, 2015, **5**, 1568–1579.
101. A. L. Torre, G A Rance, S A Miners, C H. Lucas, E F Smith, M W Fay, T Zoberbier, M. C. G. López, U Kaiser, P D Brown and A N Khlobystov, *Nanotechnology*, 2016, **27**, 175604.
102. O. Zhou, R.M. Fleming, D.W. Murphy, C.H. Chen, R.C. Haddon, A.P. Ramirez, S.H. Glarum, *Science*, 1994, **263**, 1744–1747.
103. J.D. Qiu, S. G. Cui and R. P. Liang, *Microchim Acta*, 2010, **171**, 333–339.
104. B. D. Cullity and S. R. Stock, *Elements of X-ray Diffraction* (Prentice Hall, Upper Saddle River, NJ, 2001) 3rd ed.
105. P. Azadi, R. Farnood and E. Meier, *J. Phys. Chem. A*, 2010, **114**, 3962–3968.

-
106. V. Halka, R. Tsekov, W. Freyland, *Phys. Chem. Chem. Phys.*, 2005, **7**, 2038-2043.
107. S. Chen, G. Wu, M. Sha and S. Huang, *J. Am. Chem. Soc.* 2007, **129**, 2416-2417.
108. E. K. Goharshadi, S. Samiee, P. Nancarrow, *J. Colloid Interf. Sci.*, 2011, **356**, 473-480.
109. W. Zhang, T. Yang, X. Zhuang, Z. Guo, K. Jiao, *Biosens. Bioelectron.*, 2009, **24**, 2417-2422.
110. K. P. Esko, T. Wehner, P. S. Schulz, F. W. Heinemann, K. M. Buschbaum, and P. Wasserscheid, *Eur. J. Inorg. Chem.*, 2016, **9**, 1333-1339.
111. C. Liu, H. Liang, X. Kuang, J. Zhong, S. Sun, and Y. Tao, *Inorg. Chem.*, 2012, **51**, 8802-8809.
112. S. Banerjee, M. G. C. Kahn, and S. S. Wong, *Chem. Eur. J.*, 2003, **9**, 1898-1908.
113. Y. Li, J. Ding, J. Chen, C. Xu, B. Wei, J. Liang, D. Wu, *Mater. Res. Bull.*, 2002, **37**, 313-318.
114. S. Vijayakumar, S. Nagamuthu and G. Muralidharan, *ACS Sustainable Chem. Eng.*, 2013, **1**, 1110-1118.
115. E. A. Anumol, P. Kundu, P. A. Deshpande, G. Madras, and N. Ravishankar, *ACS Nano*, 2011, **5**, 8049-8061.
116. S. Bellayer, J.W.Gilman, N. Eidelman, S.Bourbigot, X.Flambar, D.M.Fox, H.C.D.long and P.C.Trulove, *Adv. Funct. Mater.*, 2005, **15**, 910-916.
117. Y. Huang, Y. Xiao, H. Huang, Z. Liu, D. Liu, Q. Yang and C. Zhong, *Chem. Commun.*, 2015, **51**, 17281-17284.
118. T. Fukushima, A. Kosaka, Y. Ishimura, T. Yamamoto, T. Takigawa, N. Ishii, T. Aida, *Science*, 2003, **300**, 2072-2074.

-
119. J. C. Ma and D. A. Dougherty, *Chem. Rev.*, 1997, **97**, 1303-1324.
120. B. Yu, F. Zhou, G. Liu, Y. Liang, W. T. S. Huck and W. Liu, *Chem. Commun.*, 2006, 2356-2358.
121. M. J. Park, J. K. Lee, B. S. Lee, Y. W. Lee, I. S. Choi, and S. Lee, *Chem. Mater.*, 2006, **18**, 1546-1551.
122. T. Fukushima and T. Aida, *Chem. Eur. J.*, 2007, **13**, 5048 - 5058.
123. X. Zhou, T. Wu, K. Ding, B. Hu, M. Hou and B. Han, *Chem. Commun.*, 2009, 1897-1899.
124. L. R. Perez, E. Teuma, A. Falqui, M. Gomez and P. Serp, *Chem. Commun.*, 2008, 4201-4203.
125. M. Matsumoto, Y. Saito, C. Park, T. Fukushima and T. Aida, *Nat. Chem.*, 2015, **7**, 730-736.
126. A. Elbourne, B. M. Lean, K. Voitchovsky, G. G. Warr and R. Atkin, *J. Phys. Chem. Lett.*, 2016, **7**, 3118-3122.
127. N. Liu, F. Luo, H. Wu, Y. Liu, C. Zhang and J. Chen, *Adv. Funct. Mater.*, 2008, **18**, 1518-1525.
128. Y. Yu, Z. Han, Y. Zhang, B. Dong, A. Kong, and Y. Shan, *New J. Chem.*, 2016, **40**, 3147-3154.
129. X. Wang, P. F. Fulvio, G. A. Baker, G. M. Veith, R. R. Unocic, S. M. Mahurin, M. Chi, and S. Dai, *Chem. Commun.*, 2010, **46**, 4487-4489.
130. W. Ye, X. Li, H. Zhu, X. Wang, S. Wang, H. Wang, R. Sun, *Chemical Engineering Journal*, 2016, **299**, 45-55.
131. J. Hao, X. Jiao, L. Han, Q. Suo, A. Ma, J. Liu, X. Lian and L. Zhang, *RSC Adv.*, 2015, **5**, 13809-13817.

-
132. N. Ameur, S. Bedrane, R. Bachir and A. C. Braham, *J. Mol. Catal. A: Chemical*, 2013, **374– 375**, 1– 6.
133. Y. Cao, H. Yu, F. Peng and H. Wang, *ACS Catal.*, 2014, **4**, 1617–162.
134. B. McAteer, N. Beattie, D. T. Richens, *Inorganic Chemistry Communications*, 2013, **35**, 284–289.
135. R. Zhang and R. Tang, *J Mater Sci.*, 2016, **51**, 5802–5810.
136. S. Ganji, P. Bukya, V. Vakati, K. S. R. Rao and D, R. Burri, *Catal. Sci. Technol.*, 2013, **3**, 409–414.
137. H. Weiner, A. Trovarelli, R. G. Finke, *J. Mol. Catal. A: Chemical*, 2003, **191**, 217–252.
138. S. Song, H. Yang, R. Rao, H. Liu, A. Zhang, *Catal. Commun.*, 2010, **11**, 783–787.
139. S. El-Korso, S. Bedrane, A. C. Braham and R. Bachir, *RSC Adv.*, 2015, **5**, 63382–63392.
140. K. Leus, I. Muylaert, M. Vandichel, G. B. Marin, M. Waroquier, V. V. Speybroeck and P. V. D. Voort, *Chem. Commun.*, 2010, **46**, 5085–5087.
141. A. G. Macedo, S. E. M. Fernandes, A. A. Valente, R. A. S. Ferreira, L. D. Carlos, and J. Rocha, *Molecules*, 2010, **15**, 747–765.
142. N. Sutradhar, A. Sinhamahapatra, S. Pahari, M. Jayachandran, B. Subramanian, H. C. Bajaj, and A. B. Panda, *J. Phys. Chem. C*, 2011, **115**, 7628–7637.
143. T. Kiyonaga, Q. Jin, H. Kobayashi and H. Tada, *Chem. Phys. Chem.*, 2009, **10**, 2935–2938.
144. Y. Liu, H. Tsunoyama, T. Akita, S. Xie and T. Tsukuda, *ACS Catal.*, 2010, **1**, 2–6.
145. R. Hiatt, T. Mill, and F. R. Mayo, *J. Org. Chemisty*, 1968, **33**, 1416–1420.
146. P. Cancino, V. Paredes-García, P. Aguirre and E. Spodine, *Catal. Sci. Technol.*, 2014, **4**, 2599–2607.

-
147. A. L. G.Cabeza, R. M.Barrios, F. J. M. Dorado, María J. Ortega,G. M. Massanet, and F. M. Guerra, *Org. Lett.*, 2014, **16**, 1598–1601.
148. P. Yu, Y. Zhou, Y. Yang and R. Tang, *RSC Adv.*, 2016, **6**, 65403–65411.
149. Z. Chen and R. L. Luck, *Green Chem.*, 2016, **18**, 3354–3359.
- 150.M.Zarghani and B. Akhlaghinia, *RSC Adv.*, 2016, **6**, 38592–38601.
151. L. Bai, L. Yao, Y. Yang and J. M. Lee, *Chem. Commun.*, 2015, **51**, 4259–4262.
152. S. Bawaked, N F. Dummer, D. Bethell, D. W. Knight and G. J. Hutchings, *Green Chem.*, 2011, **13**, 127–134.
153. J.M. Vincent, A. Rabion, V. K. Yachandra and R. H. Fish, *Angew. Chem. Int. Ed.*, 1997, **36**,2346-2349.
154. R. A. Sheldon, M. Wallau, I. W. C. E. Arends, and U. Schuchardt, *Acc. Chem. Res.*,1998, **31**, 485-493.
155. Y L Hu, H.Jiang and M. Lu, *Green Chem.*, 2011, **13**, 3079–3087.
156. J. Wang, S. Yu, J. Xi, L. Chen, W. Zhu, and X.Qiu, *Electrochem. Solid-State Lett.*, 2007,**10**, 7,B114-B118.
157. S. Torbrügge, M. Cranney and M. Reichling, *Appl. Phys. Lett.*, 2008, **93**, 073112.
158. Y. Lykhach, T. Staudt, M. P. A. Lorenz, R. Streber, A. Bayer, H.P. Steinrck, and J. Libuda, *Chem.Phys.Chem.*, 2010, **11**, 1496 – 1504.
159. K. Cheng, W. Song, Y. Cheng, J. Liu, Z. Zhao and Y. Wei, *Catal. Sci. Technol.*, 2016,**6**, 4478-4490.
160. M. Tamura, T. Kitanaka, Y. Nakagawa and K. Tomishige, *ACS Catal.* 2016,**6**, 376–380.
161. S. Banerjee, *NewJ.Chem.*, 2015,**39**,5350-5353.
162. D. He, G. Wan, H. Hao, D. Chen, J. Lu, L. Zhang, F. Liu, L. Zhong, S. He and Y. Luo, *Chemical Engineering Journal*, 2016,**289**,161–169.

-
163. X. Wang, C. Yang, T. M. Wang and P. Liu, *Electrochim.Acta*, 2011, **58**, 193-202.
164. K. Asami, K-I Kusakabe, N. Ashi, Y. Ohtsuka, *Applied Catalysis A: General*, 1997,**156**, 43-56.
165. Y. Borchert, P. Sonström, M. Wilhelm, H. Borchert and M. Bäumer, *J. Phys. Chem. C*, 2008, **112 (8)**, 3054–3063.

Appendix-I

