Green and Chemical Synthesized CeO_2 Nanoparticles for Photocatalytic Indoor Air Pollutant Degradation

R. Magudieswaran,[a] Junki Ishii,[b] Krishna Chandar Nagamuthu Raja,[c] Chiaki Terashima,[c] R. Venkatachalam,[d] Akira Fujishima,[b] and Sudhagar Pitchaimuthu[e]

[a] *Department of Industrial Safety Engineering, K.S.Rangasamy College of Technology, Tiruchengode, Namakkal, Tamil Nadu, India.*
[b] *Photocatalysis International Research Center, Tokyo University of Science, 2351 Yamazaki, Nodhashi, Japan*
[c] *Department of Physics, School of Advanced Sciences, Vellore Institute of Technology, Vellore 632 014, India.*
[c] *Department of Automobile Engineering, Institute of Road and Transport Technology, Erode, Tamil Nadu. India*
[d] *Multi-functional Nanocatalyst & Coatings Group, SPECIFIC, College of Engineering, Swansea University (Bay Campus) Swansea SA1 8EN Wales, United Kingdom*

*Corresponding Authors: terashima@rs.tus.ac.jp (CT), S.Pitchaimuthu@swansea.ac.uk (SP)

Abstract

In this report, we demonstrate the advantage of *Jatropha curcus* plant extract as particle reducing agent in stabilizing cerium oxide (CeO_2) nanoparticles. The toxic-free, green *Jatropha curcus* extract mediated CeO_2 nanoparticles has tested in photocatalytic degradation of indoor gaseous pollutant acetaldehyde and compared with conventional chemically synthesized CeO_2 nanoparticles (NH_3 and NaOH). The results showed green synthesized CeO_2 nanoparticles are effectively reducing the particle size 3-5 nm and homogenous particle distribution compared to chemically synthesized CeO_2 (18-25 nm). As a result, it exhibits effective photocatalysis performance in acetaldehyde degradation.

Keywords: Nanoparticles; Semiconductors; Green Synthesis; Photocatalyst; CeO_2; Acetaldehyde degradation.

1. Introduction

Indoor air pollutants are considered as major threat to the environment which has considerable impact on human health, comfort and productivity [1]. Many researchers around the world are establishing the technologies to find simple and economic way of removing such pollutants from indoor air. On considering many technologies, photocatalytic oxidation using high surface area nanoscale semiconductor material could be an innovative and promising method [2-4]. In photocatalytic process, photocharge carriers (e^- and h^+) will be produced on the semiconductor surface under light illumination. These photocharge carriers can oxidize harmful organic volatile pollutant which turns into harm-free compounds. Recent reports concerned about the usage of cerium oxide (CeO_2) as effective catalyst [5]. Owing to many distinctive properties of CeO_2 such as Ce^{4+}/Ce^{3+} redox couple formation, high resistance to chemical and photocorrosion, and

excellent UV absorption ability which is considered as promising candidate for indoor based photocatalytic application.

Many wet chemical protocols including surfactant or particle stabilizing agent were devoted towards fabrication of semiconductor materials at nano regime, where most of the chemical components used in such methods are harmful to the environment. Hence synthesizing nanoscale semiconductor materials using microorganism or plant extracts can significantly eliminate such environmentally hazardous problems to the greater extent. The plant extracts not only acts as reducing agent but also effective on controlling the growth of the nanoparticles. The green synthesized nanomaterials are bio-compatible, reproducible and appreciable with size and shape distribution [6, 7]. In this work, the plant extract of *Jatropha curcas (J. curcas)* was chosen to fabricate green synthesized CeO_2 nanoparticles as *J. curcas* plant can be available in tropical and subtropical regions around the world. Importantly, *J. curcas* plant can grow in wastelands and cultivate on environment which considered as low-cost bio-surfactant for nanoparticle synthesis compared to chemical based surfactants [8, 9]. To the best of our knowledge, for the first time, we demonstrate the green synthesized metal oxide nanoparticle in photocatalytic indoor gaseous pollutant degradation.

2. Experimental

Synthesis of CeO_2 nanoparticles: The extract of the *Jatrobha curcus* leaves were obtained as follows; pre-dried leafs were boiled in double distilled water at 80°C under constant stir for 2 hr. The leaf extract was filtered through Whatmann (Number 1) filter paper and plant residues were removed. The known amount of cerium nitrate hexa hydrate was added in 100ml of filtered plant

extract and this solution kept in stirring for 2 hr under ambient condition. Followed that 80 ml of this solution was transferred to hydrothermal autoclave and kept at hot air oven for 150°C for 12hr. The dried precipitate was further annealed at 500°C for 2 hr in air. Finally, green synthesized CeO_2 powder has been collected from the furnace. In order to compare the chemical synthesis, 1 M NaOH or 1 M NH_3 was added in the above said reaction instead of plant extract.

Characterisation: The crystal structure of the as-synthesized CeO_2 powders were studied using an X-ray diffractometer (Rigaku Ultima IV). The morphology of CeO_2 synthesized at different stabilizers was studied through transmission electron microscope (TEM) (JEOL 2100). The UV-vis spectra of CeO_2 nanoparticles synthesized using different particle stabilizers are recorded using a V-670 JASCO UV-vis Spectrophotometer. During photocatalysis experiment, decrease in the acetaldehyde concentration and resultant CO_2 production were monitored using gas chromatography with nitrogen as a carrier (GC-2014, Shimadzu, equipped with a 2 m Porapak-Q column and a flame ionization detector).

3. Results and discussion

The X-ray diffraction profiles of CeO_2 nanoparticles synthesized using different particle stabilizers NH_3, NaOH and *J. curcas* plant extract are shown in **Figure 1 ((a), (c) and (e))**. The peaks are indexed towards cubic fluorite structure of CeO_2 which are consistent with the JCPDS Card no 34-0394. Though the three XRD profiles seem similar, the lattice strain attained by CeO_2 nanoparticles are different under the stabilizers NH_3, NaOH and JC plant extract. The broadening of XRD peaks was observed. This might ascribe to two effects ie. lattice strain and small crystallite size. These two effects can easily be distinguished by plotting a graph between $\beta \cos\theta$ in dependence of $4 \sin\theta$ (Williamson-Hall graph) [10]. From the WH graph (**Figure 1 (b),**

(d) and (f)), the lattice strain attained by the CeO_2 nanoparticles prepared from stabilizers NH_3, NaOH and JC plant extract are found to be 6.42 x 10^{-4}, 9.14 x 10^{-4} and 9.65 x 10^{-4}, respectively. The intercept of line profile determining the crystallite sizes are 25nm, 18nm and 5nm respectively.

The TEM and selected area diffraction images of CeO_2 are shown in **Figure 2 (a-f)**. From the **Figure 2 (a,b)** and **(c,d)**, NaOH, and NH_3 assisted CeO_2 showed anisotropy shape crystals and the particles are markedly larger (15-25 nm) than plant extract derived sample. In the case of *J. curcas* plant extract derived particles in **Figure 2 (e.f)**, they are small in size and uniform in shape. Importantly, the particles are monodispersing in shape with narrow size distribution of 2-5 nm which is consistent with XRD results (WH plots). The SAED patterns in the insets of **Figure 2 (b), (d)** and **(f)** show almost similar diffraction pattern which confirm the nanocrystalline nature of the particles.

The CeO_2 nanoparticles prepared from all the three stabilizers show strong optical absorption below 400 nm and they have distinct absorption around 340 to 360 nm (**Figure 3(a)**). The bandgap energy corresponding to this absorption are around 3.44 eV to 3.64 eV. The observed bandgap values are greater than the bulk bandgap of CeO_2 (3.19eV) [11]. This is attributed due to the quantum confinement effect exists in the system when the particles down to few nanometers.

The photocatalytic activity of the CeO_2 was evaluated in degradation of model indoor air pollutant acetaldehyde. **Figure 3(b)** shows results of the decrease in the concentration of acetaldehyde and the increase in the concentration of CO_2 products as a function of reaction time. The solid line plots indicate that the acetaldehyde concentration decreased as CO_2 formed by

photocatalysis process under irradiation of Xenon lamp (1 SUN intensity). The free radicals of O_2, and CH_3CHO formation at conduction band and valence band of CeO_2, respectively will mediate the chain reactions of acetaldehyde oxidation. Followed that acetaldehyde is transformed into CO_2 through multiple chemical reactions and Ce^{4+}/Ce^{3+} redox couple formation. The detailed mechanism of the photocatalysis based acetaldehyde degradation into harmless CO_2 and respective experimental details were explained in our previous report [12]. Under identical experimental conditions, the green synthesized CeO_2 showed comparative photocatalytic activity 99.6% of acetaldehyde degradation into CO_2 conversion with refers to NH_3 mediated CeO_2 (100%). The NaOH treated CeO_2 resulted relatively weaker photoactivity of 93.2%. The high surface area, and effective Ce^{4+}/Ce^{3+} redox formation at green synthesized CeO_2 is synergistically result high photocatalytic acetaldehyde degradation.

4 Conclusions

The green *J. curcas* extract based CeO_2 particles are successfully demonstrated which resulting homogenous spherical shape, and markedly reduced their size approximately 4 fold lesser than that of conventional chemical stablizers NaOH and NH_3. For the first time, these green synthesized CeO_2 nanoparticles have been evaluated in photocatalytic acetaldehyde degradation. The comparative photocatalysis performance of green synthesized CeO_2 nanoparticle strongly recommends to revisit the utilization of green synthesize route instead of chemically synthesis route for indoor photocatalysis based pollutant degradation applications. Owing to low dimensional nanoscale size, green synthesized CeO_2 will be value addition in diesel engine to promote the fuel conversion efficiency. Overall, removal of indoor gaseous pollutants through power-free photocatalysis technology using green synthesized nanoparticles will be promising in energy saving buildings.

Acknowledgment

C.T and S.P thanks Royal Society, UK (IEC\R3\170085- International Exchanges 2017 Cost Share) for partially supporting this project. S.P acknowledges Welsh Government and European Regional Development Fund (ERDF) for Sêr Cymru II-Rising Star Fellowship (80761-SU-102 (West)).

References

[1] D.G. Fullerton, N. Bruce, S.B. Gordon, Indoor air pollution from biomass fuel smoke is a major health concern in the developing world, Transactions of the Royal Society of Tropical Medicine and Hygiene 102(9) (2008) 843-851.

[2] I. Sopyan, M. Watanabe, S. Murasawa, K. Hashimoto, A. Fujishima, An efficient TiO2 thin-film photocatalyst: photocatalytic properties in gas-phase acetaldehyde degradation, Journal of Photochemistry and Photobiology A: Chemistry 98(1) (1996) 79-86.

[3] Y. Ohko, D.A. Tryk, K. Hashimoto, A. Fujishima, Autoxidation of Acetaldehyde Initiated by TiO2 Photocatalysis under Weak UV Illumination, The Journal of Physical Chemistry B 102(15) (1998) 2699-2704.

[4] Z. Shayegan, C.-S. Lee, F. Haghighat, TiO2 photocatalyst for removal of volatile organic compounds in gas phase – A review, Chemical Engineering Journal 334 (2018) 2408-2439.

[5] T. Montini, M. Melchionna, M. Monai, P. Fornasiero, Fundamentals and Catalytic Applications of CeO2-Based Materials, Chemical Reviews 116(10) (2016) 5987-6041.

[6] A.K. Mittal, Y. Chisti, U.C. Banerjee, Synthesis of metallic nanoparticles using plant extracts, Biotechnology Advances 31(2) (2013) 346-356.

[7] S. Jain, M.S. Mehata, Medicinal Plant Leaf Extract and Pure Flavonoid Mediated Green Synthesis of Silver Nanoparticles and their Enhanced Antibacterial Property, Scientific Reports 7(1) (2017) 15867.

[8] H. Bar, D.K. Bhui, G.P. Sahoo, P. Sarkar, S.P. De, A. Misra, Green synthesis of silver nanoparticles using latex of Jatropha curcas, Colloids and Surfaces A: Physicochemical and Engineering Aspects 339(1) (2009) 134-139.

[9] S. Joglekar, K. Kodam, M. Dhaygude, M. Hudlikar, Novel route for rapid biosynthesis of lead nanoparticles using aqueous extract of Jatropha curcas L. latex, Materials Letters 65(19) (2011) 3170-3172.

[10] N. Krishna Chandar, R. Jayavel, Synthesis and characterization of C14TAB passivated cerium oxide nanoparticles prepared by co-precipitation route, Physica E: Low-dimensional Systems and Nanostructures 58 (2014) 48-51.

[11] S. Tsunekawa, T. Fukuda, A. Kasuya, Blue shift in ultraviolet absorption spectra of monodisperse CeO2−x nanoparticles, Journal of Applied Physics 87(3) (2000) 1318-1321.

[12] S. Pitchaimuthu, K. Honda, S. Suzuki, A. Naito, N. Suzuki, K.-i. Katsumata, K. Nakata, N. Ishida, N. Kitamura, Y. Idemoto, T. Kondo, M. Yuasa, O. Takai, T. Ueno, N. Saito, A. Fujishima, C. Terashima, Solution Plasma Process-Derived Defect-Induced Heterophase Anatase/Brookite TiO2 Nanocrystals for Enhanced Gaseous Photocatalytic Performance, ACS Omega 3(1) (2018) 898-905.

Figure captions

Figure 1. XRD results of CeO_2 particles synthesized using different particle stabilizers (a) NaOH, (c) NH_3, and (e) *Jatropha curcus* plant extract. The W-H plots of CeO_2 particles synthesized using different particle stabilizers (b) NaOH, (d) NH_3, and (f) *Jatropha* C*curcus* plant extract.

Figure 2. HRTEM images of CeO_2 synthesized using (a) NH_3 and (c) NaOH and (e) *J. curcas* plant extract. The high magnification HRTEM images (at 20 nm scale) of Figure 2 (a), (c) and (e) were presented in (b), (d) and (f), respectively (note that SAED pattern were presented in the inset).

Figure 3. Optical absorption spectra of CeO_2 synthesized using (i) NH_3 and (ii) NaOH and (iii) *J. curcas* plant extract; (b) Acetaldehyde pollutant degradation into CO_2 using (i) NH_3 and (ii) NaOH and (iii) *J. curcas* plant extract mediated CeO_2 nanoparticles.

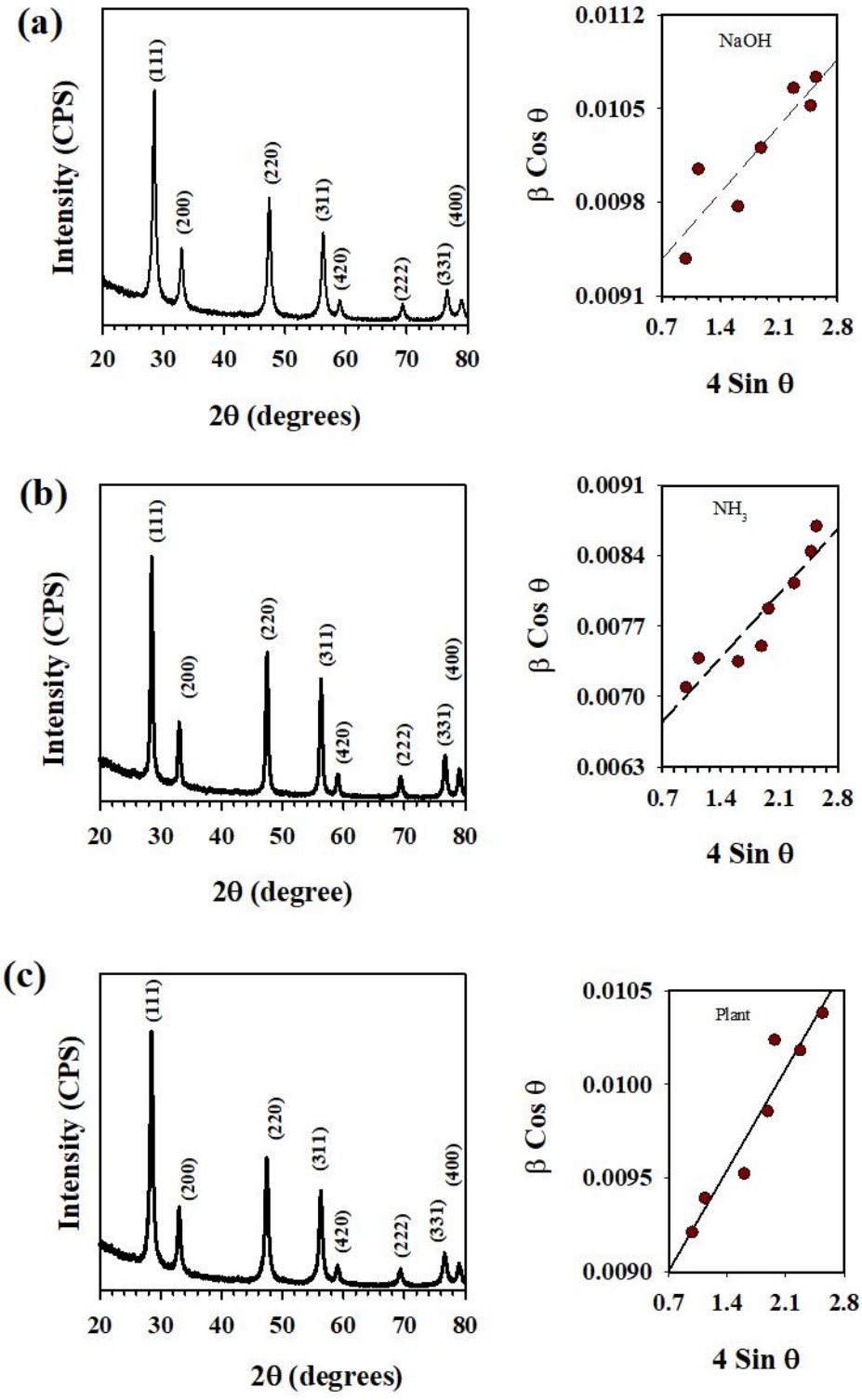
(a)
Intensity (CPS)
(111)
(200)
(220)
(311)
(420)
(222)
(331)
(400)
20 30 40 50 60 70 80
2θ (degrees)
NaOH
β Cos θ
0.0112
0.0105
0.0098
0.0091
0.7 1.4 2.1 2.8
4 Sin θ
(b)
Intensity (CPS)
(111)
(200)
(220)
(311)
(420)
(222)
(331)
(400)
20 30 40 50 60 70 80
2θ (degree)
NH3
β Cos θ
0.0091
0.0084
0.0077
0.0070
0.0063
0.7 1.4 2.1 2.8
4 Sin θ
(c)
Intensity (CPS)
(111)
(200)
(220)
(311)
(420)
(222)
(331)
(400)
20 30 40 50 60 70 80
2θ (degrees)
Plant
β Cos θ
0.0105
0.0100
0.0095
0.0090
0.7 1.4 2.1 2.8
4 Sin θ

Figure 1

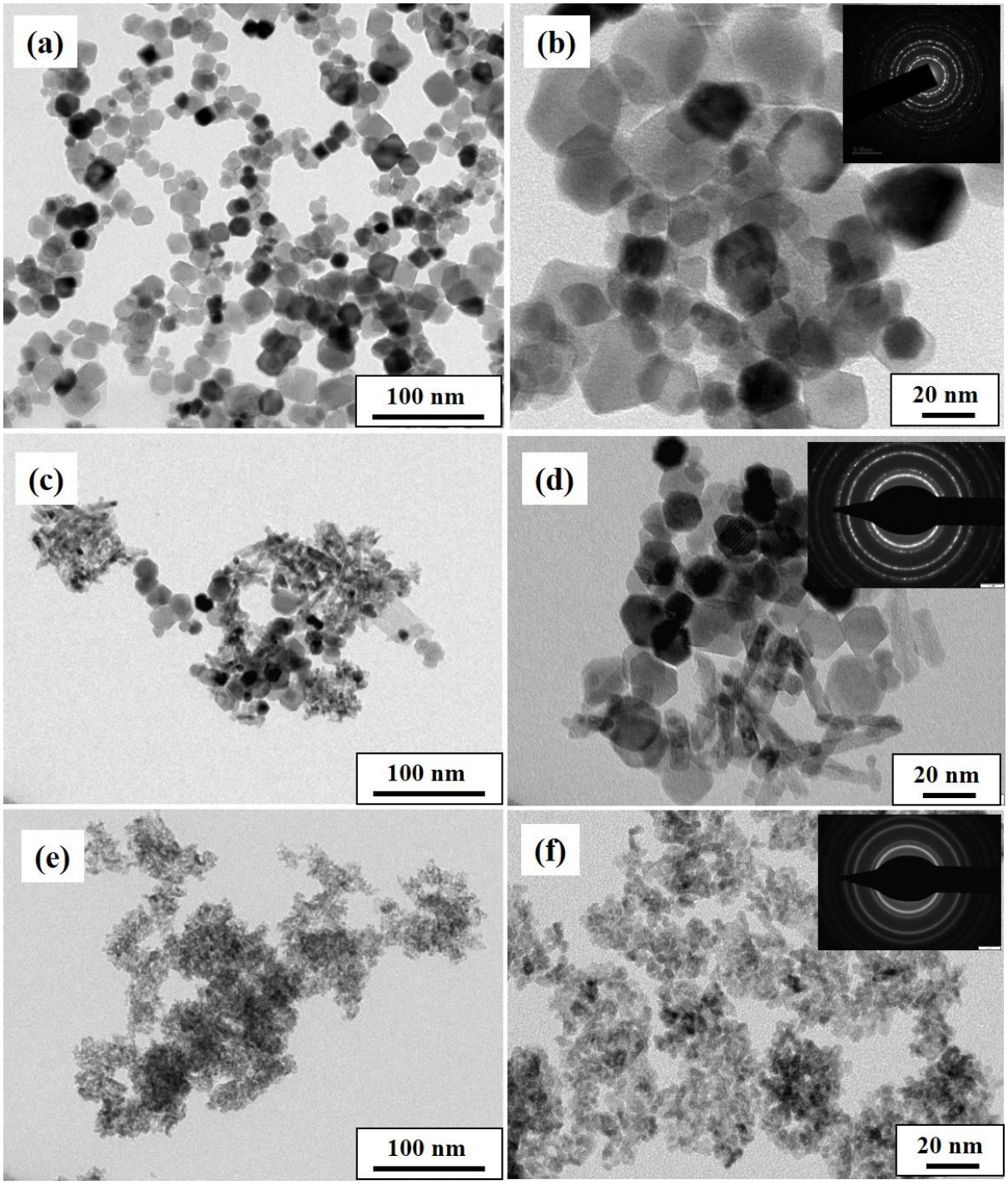

Figure 2

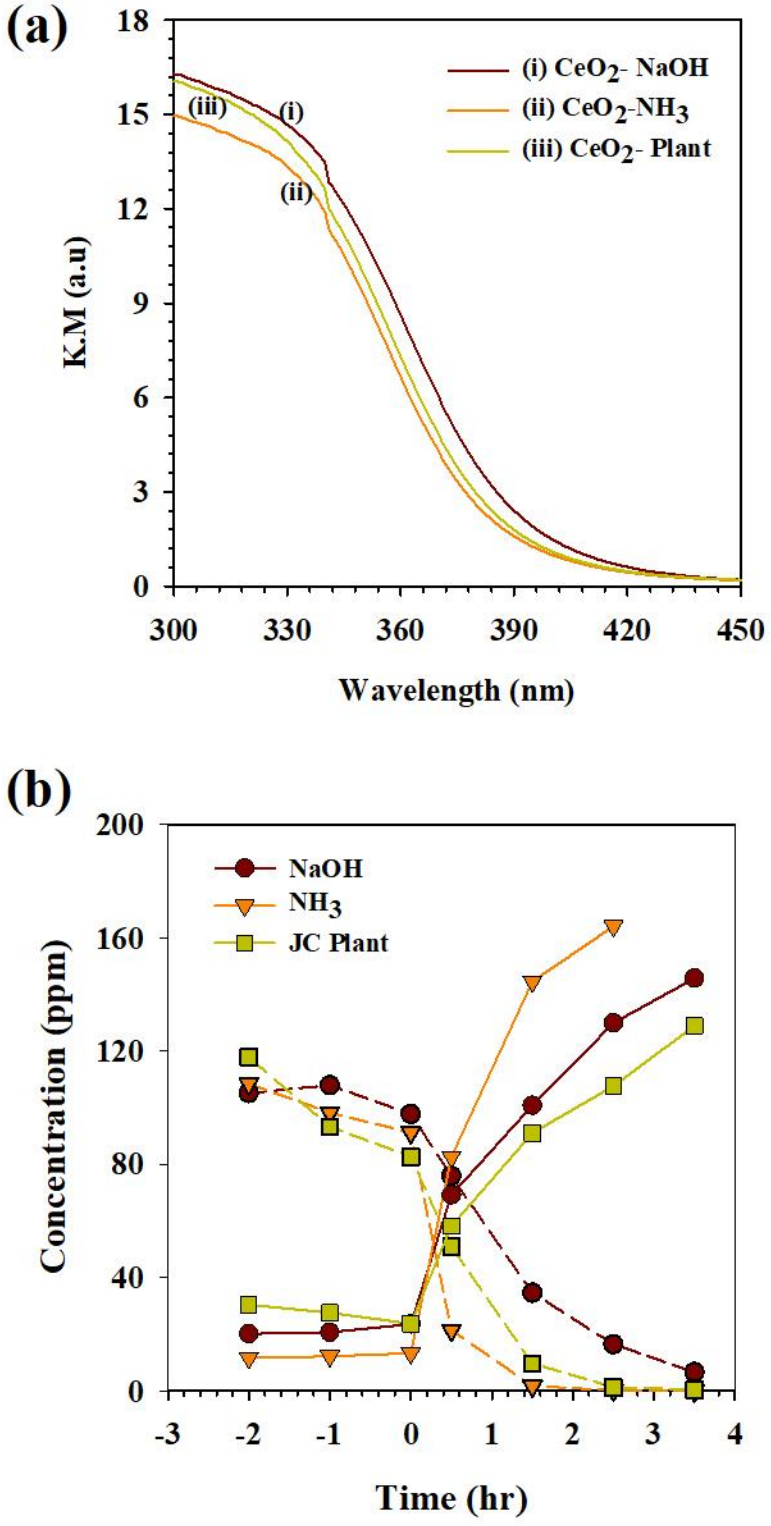
(a)
(i) CeO_2- NaOH
(ii) CeO_2-NH_3
(iii) CeO_2- Plant
(i)
(ii)
(iii)
K.M (a.u)
Wavelength (nm)
(b)
NaOH
NH_3
JC Plant
Concentration (ppm)
Time (hr)

Figure 3