

Research Article

Monodisperse Uniform CeO₂ Nanoparticles: Controlled Synthesis and Photocatalytic Property

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Ceria nanostructure-based catalysts have attracted much attention in recent years because of their unique physiochemical properties. Herein, we have presented a simple two-phase approach for the synthesis of ceria nanocrystals. Structural and morphological characterization by XRD and TEM showed that the as-synthesized monodisperse CeO_2 nanoparticles (NPs) had cubic fluorite crystal structure with average particle size about 6.75 nm. The effects of hydrothermal temperature, annealing time, and concentration of cerium nitrate on the nanostructures of the products were also investigated and discussed. In addition, the CeO_2 nanocrystals proved to be an effective catalyst for the photodegradation of blue methylene under UV illumination.

1. Introduction

Ceria, which is semiconducting, abundant, nontoxic, and inexpensive [1-5], is widely applied in heterogeneous catalytic reactions due to the high mobility of oxygen species and reversible transition between Ce4+ and Ce3+ oxidation states in CeO₂ crystal [6]. Recent researches have revealed that the size, morphology, surface structure, and synergistic interaction dramatically influence the catalytic performance of CeO₂. Wang et al. [7] found that the spindlelike CeO₂ exhibited the highest DMC yield, followed by nanorods, nanocubes, and nanooctahedrons, because the exposed active (111) planes, defect sites, and a large amount of acid-basic acids were active factors for dimethyl carbonate (DMC) formation. Zhou et al. [8] reported that the CeO_2 nanorod catalyst exhibited higher ethanol catalytic oxidation activity and CO₂ selectivity than the nanocube catalyst because the ceria nanorods had an amorphous structure, which yields more crystal defects. Liu et al. [9] presented that the CuO/CeO₂ catalysts nanorods showed the best activity for NO reduction by CO due to the strong synergetic interactions between copper(II) oxide and ceria nanorods and so forth. Thus, the development of facile approach for synthesis of nanostructured CeO_2 is of great importance to the investigation of its new physicochemical properties.

The synthesis of metal oxides nanostructures with various morphologies has drawn great attention. Two-phase route is a promising method to synthesize uniform nanocrystal with controlled particle size and shape. Compared to the singlephase approach, the two-phase strategy can obtain the products with good crystallinity under relative mild adopted conditions [10]. Brust et al. [11] first used a two-phase approach to synthesize gold nanocrystals, which holds a prominent position. Similarly, some noble metal nanostructures such as Ag [12], Pt [13], and Pd [14] have been fabricated by modifying Brust's method. Related progress using two-phase method was extended to the synthesis of varying nanostructured metal oxides. Pan et al. [15] used a hydrothermal two-phase route to synthesize monodisperse TiO₂ nanocrystals in a water-toluene mixture. The ZrO2 nanostructures with various shapes such as spheres and rodlike were also fabricated by this method [16]. Adschiri et al. modified this approach for

the fabrication of CeO₂ nanocubes using hydroxide precursor under supercritical water conditions. Nguyen and Do [10] developed two alternative two-phase approaches to prepare oxide nanocrystals of two groups of elements: rare earths, for example, Sm, Ce, Er, Gd, La, and Y, and transition metals, for example, Mn, Cr, Co, and Ni, in a water-toluene mixture using rare earth nitrate salts and rare earth-oleate complexes as starting precursors. Although some progress has been made in fabrication of nanomaterials, this method usually uses metal-surfactant complexes as precursor and through a complex experimental course. Furthermore, to the best of our knowledge, the controllable two-phase synthesis of CeO₂ nanostructures using cerium nitrate as starting precursor has rarely been reported. Thus it is essential to explore simple and inexpensive methods for the synthesis of uniform-sized ceria nanocrystals.

In this work, the novel two-phase approach for controllable synthesis of uniform CeO_2 NPs using metal salt instead of organometallic compounds is reported, which is an environmentally friendly and economical route with mild reaction condition. The results show that monodisperse CeO_2 NPs can be achieved by changing some synthesis conditions such as aging time, hydrothermal temperature, and cerium nitrate concentration. In addition, the enhanced catalytic activity of as-fabricated CeO_2 nanocrystals for photodegradation of methylene blue (MB) under UV illumination was also found.

2. Experimental

2.1. Materials. All chemicals were used as received without further purification. $Ce(NO_3)_3 \cdot 6H_2O$, $C_{17}H_{33}COOK$, tertbutylamine, and oleic acid were purchased from Merck. Methylene blue, toluene, and ethanol were purchased from Sigma-Aldrich.

2.2. CeO₂ Nanoparticles Preparation and Characterization. Here, the uniform CeO₂ NPs were synthesized based on the previous reported by Nguyen and Do [10] with significant modifications. For synthesis of CeO₂ nanocrystal, a homogeneous ethanol solution (10 mL) containing 3 g C₁₇H₃₃COOK was mixed with an organic solution of toluene (20 mL) and oleic acid (2 mL). Afterward, this organic phase was mixed with 20 mL of an aqueous solution containing cerium nitrate salt (0.08 M) and *tert*-butylamine (0.15 mL). The obtained two-phase mixture was transferred to a Teflonlined stainless steel autoclave and heated at 180°C for 24 h. The system was cooled to room temperature and then the nanocrystal solution was precipitated with the excess volume of ethanol. Finally, the as-synthesis CeO₂ NPs were recovered through filtering, washing, and drying at room temperature. The morphology and crystalline structure of products were characterized using transmission electron microscopy (TEM, Model JEO-3432, Japan) and an X-ray diffractometer (XRD, D8 Advance, Bruker, Germany), respectively. The particle size distribution analysis from TEM images was done by using the ImageJ program.

2.3. Photocatalytic Tests. The photocatalytic activity of CeO₂ nanocrystals was evaluated by the degradation of MB as model contaminant. The reactions were performed under UV light (20 W, 365 nm) at ambient temperature. In a photoreaction experiment, 50 mg of the catalyst was added in a conical flask containing 100 mL of varying concentrations of MB (4, 8, and 12 ppm). Prior to irradiation, the suspension was kept in the dark under stirring for 60 min to ensure the establishing of an adsorption/desorption equilibrium. At certain time intervals, about 5 mL suspensions were withdrawn and centrifuged and then filtered to remove the residual catalyst particulates for analysis. The filtrates were analyzed using UV-Visible spectrophotometer (Jasco V-550 UV-Vis). The concentration of the MB was determined by measuring the absorption intensity at its maximum absorbance wavelength (662 nm) of this dye, where C_0 is initial concentration of MB and C_t is the concentration of dye at any time of photocatalytic process.

3. Results and Discussion

3.1. Synthesis and Characterization of Uniform CeO₂ Nanoparticles

3.1.1. Influence of Reaction Temperature. The effect of reaction temperature on morphology of as-prepared CeO₂ nanocrystals was investigated. The TEM images in Figure 1 indicate that the morphology of the nanocrystal can be tuned through the controlling hydrothermal temperature. At low reaction temperatures (120 and 140°C), the products consist of irregular shapes. The CeO2 NPs fabricated at 160 and 180°C have homogenous morphologies with spherical shapes and regular dispersion. Corresponding to these TEM pictures, the CeO₂ NPs synthesized at 180°C have better dispersion and narrow particle size distribution than at 160°C. The average particle size slightly increases when the reaction temperature increases from 160 to 180°C (SI, Figure S1 in Supplementary Material available online at http://dx.doi.org/10.1155/2016/8682747), while the products obtained at 200°C are severe aggregates (SI, Figure S2). The formation of CeO₂ NPs involves two steps: nucleation and growth. The effect of reaction temperature on the formation mechanism of CeO₂ NPs can be explained as follows. At low temperatures, the nucleation rate was similar to the growth rate [17]. The particles initially formed act as the seeds and become larger as reaction proceeds. At the same time, other small NPs are formed. A moderately elevated temperature is conductive to the fast nucleation. When the nucleation rate is larger than growth rate, small particles with narrow size distribution can be easily obtained.

3.1.2. The Effect of Hydrothermal Time. In order to understand the particle formation, the effects of reaction time on size and shape of products were investigated. After 12 h of reaction, the average particle size was 5.73 nm (Figure 2(a)). The average size slightly increases (6.75 nm) for 24 h of reaction (Figure 2(b)). This means that larger particles are growing at the expense of smaller particles. It could be



FIGURE 1: TEM images of CeO2 NPs fabricated with different reaction temperatures: (a) 120, (b) 140, (c) 160, and (d) 180°C.

attributed to Ostwald ripening which is growth mechanism by dissolving and depositing of smaller particle on the more stable surface of the larger nanoparticles [18]. After 36 h, the size and morphology of the products do not change (Figure 2(c)), suggesting that the crystal growth reaches saturated state at 24 h.

3.1.3. Influence of Salt Concentration. The size evolution of CeO_2 NPs is found to be a function of cerium nitrate concentrations in the water solution (Figure 3). At a relatively low cerium nitrate concentration (C = 0.04 M), the CeO_2 NPs are formed with an average diameter of 5.43 nm. Their average particle size increases from 5.43 to 6.75 nm when cerium precursor concentration is 0.08 M (Figure 3(b)). By increasing the cerium ion concentration to 0.12 M, the morphology of the product obtained has irregular shape with large particle size distribution. Generally, the size and shape evolution of nanocrystals are strongly dependent on metal monomer concentrations. Low monomer concentrations favor anisotropic growth [19].

3.1.4. The Formation Mechanism of CeO_2 Nanoparticles. The phase purity and crystal structure of as-synthesized CeO_2 nanocrystals are characterized by XRD pattern (Figure 4). All the distinguishable peaks correspond to the (111), (200), (220), (311), (222), and (400) planes of a cubic fluorite structure (space group: *Fm3m*) of CeO₂ as identified using the standard

data JCPDS Card Number 34-0394. The average crystal size of synthesized NPs which is calculated from XRD data using the Debye-Scherrer equation is about 6.34 nm, which is similar to TEM result. The results suggest that the uniform CeO_2 NPs are a single crystal.

The formation mechanism of CeO_2 NPs can be explained in Figure 5. The Ce³⁺ ions are easily oxidized to the Ce⁴⁺ ion by the trace oxygen existing in the aqueous solution because the Ce⁴⁺ ions have stable empty 4f⁰ subshells [20]. The cerium hydroxide is formed under basic solution due to the hydrolysis of *tert*-butylamine in water to generate OH⁻ ions [10]. Upon hydrothermal treatment, cerium hydroxide is dehydrated to oxide nuclei at interfaces.

3.2. Photocatalytic Activity of CeO_2 Nanoparticles. The photocatalytic activity of as-synthesized CeO_2 NPs is studied by the degradation of MB solution under UV irradiation. The dye is an N-containing, heteroaromatic, cationic thiazine green colour organic dye with chemical formula $C_{16}H_{18}ClN_3S$ used as colouring agent in a variety of industries [21]. Figures 6(a)–6(c) show the UV-Vis absorption spectra of the photodegradation for varying MB dye concentrations versus irradiation time. It can be found that intensity of the absorption of MB decreases with time. The time needed for complete degradation of 4, 8, and 12 ppm of MB was 12, 15, and 27 min, respectively. The decomposition rate of MB decreases with the increase in the amount of MB in solution (Figure 6(d)). This phenomenon can be explained on two effects: (i) an increase in the number of dye molecules



FIGURE 2: TEM images of CeO₂ NPs synthesized at different reaction times and corresponding particle size distribution analysis: (a) 12 h, (b) 24 h, and (c) 36 h.



FIGURE 3: TEM images of CeO₂ NPs synthesized at different cerium nitrate concentrations and particles size distribution analysis, respectively: (a) 0.04, (b) 0.08, and (c) 0.12 M.

adsorbed on the surface of the catalyst leads to a decrease in the number of active sites that generate hydroxyl radicals [22]; (ii) the density of solution increases with the increase in the MB concentration in solution which restricts the penetration of the light into the solution [23, 24].

The mechanism of MB degradation by CeO_2 NPs under UV light can be explained on the basic of generation of electron/hole pairs. Under the UV light irradiation, the electrons from the valence band (O 2p) of CeO₂ get excited to an empty

conduction band (Ce 4f) which generates the positive holes and negative electrons (Ce^{4+(e⁻)} – O^{2-(h⁺)}) on the surface of the nanocrystal [25]. These electrons further react with the dissolved oxygen to generate the superoxide radical anions (O₂^{•-}), while h⁺ in valence band reacts with the adsorbed water and produces more OH[•] radicals [26]. These OH[•] and O₂^{•-} are reactive species which are mainly responsible for degradation of MB. The mechanism of photocatalysis can be summarized as Figure 7. Generally, the lifetime of



FIGURE 4: XRD patterns of CeO₂ NPs.



FIGURE 5: The scheme of the formation mechanism of uniform CeO₂ NPs from cerium nitrate.

photoexcited electrons is very much less and hence the transfer of e^- to longer distance is kinetically prohibited. Therefore, most photocatalysis happens in the near distance [27]. The nanostructured materials help to improve the adsorption of photons in the UV-Visible region. This could be improved for the fast response in the decomposition of dyes [28]. Thus, the monodisperse uniform CeO₂ NPs are promising photocatalyst for the wastewater treatment.

4. Conclusions

The monodisperse CeO_2 NPs were successfully synthesized by a simple, easier, and low cost two-phase approach. The possible mechanism could be described by Ostwald ripening process, and the formation of monodisperse CeO₂ nanocrystals strongly depends on synthesis conditions. The CeO₂ nanocrystals act as good catalyst for photodegradation of MB solution and completion of this dye (5 \cdot 10⁻⁶ M) at room temperature is achieved in about 27 min under UV illumination, which is critical for practical applications.

Competing Interests

The authors declare that there are no competing interests regarding the publication of this paper.



FIGURE 6: UV-Vis spectra (a) and photodegradation curves of MB versus time (b) under UV irradiation of CeO₂ nanocrystal catalysts.



FIGURE 7: Diagram for photocatalytic degradation process of MB by CeO₂ nanocrystals under UV light irradiation.

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References

- P. Periyat, F. Laffir, S. A. M. Tofail, and E. Magner, "A facile aqueous sol–gel method for high surface area nanocrystalline CeO₂," *RSC Advances*, vol. 1, no. 9, pp. 1794–1798, 2011.
- [2] D. Zhang, X. Du, L. Shi, and R. Gao, "Shape-controlled synthesis and catalytic application of ceria nanomaterials," *Dalton Transactions*, vol. 41, no. 48, pp. 14455–14475, 2012.
- [3] C. Sun, H. Li, and L. Chen, "Nanostructured ceria-based materials: synthesis, properties, and applications," *Energy and Environmental Science*, vol. 5, no. 9, pp. 8475–8505, 2012.
- [4] P. Pal, S. K. Pahari, A. Sinhamahapatra et al., "CeO₂ nanowires with high aspect ratio and excellent catalytic activity for selective oxidation of styrene by molecular oxygen," *RSC Advances*, vol. 3, no. 27, pp. 10837–10847, 2013.
- [5] Y. Su, Z. Tang, W. Han, P. Zhang, Y. Song, and G. Lu, "Influence of the pore structure of CeO₂ supports on the surface texture and catalytic activity for CO oxidation," *CrystEngComm*, vol. 16, no. 24, pp. 5189–5197, 2014.
- [6] M. Lin, Z. Y. Fu, H. R. Tan, J. P. Y. Tan, S. C. Ng, and E. Teo, "Hydrothermal synthesis of CeO₂ nanocrystals: ostwald ripening or oriented attachment?" *Crystal Growth and Design*, vol. 12, no. 6, pp. 3296–3303, 2012.
- [7] S. Wang, L. Zhao, W. Wang et al., "Morphology control of ceria nanocrystals for catalytic conversion of CO₂ with methanol," *Nanoscale*, vol. 5, no. 12, pp. 5582–5588, 2013.
- [8] G. Zhou, B. Gui, H. Xie et al., "Influence of CeO₂ morphology on the catalytic oxidation of ethanol in air," *Journal of Industrial and Engineering Chemistry*, vol. 20, no. 1, pp. 160–165, 2014.
- [9] L. Liu, Z. Yao, Y. Deng, F. Gao, B. Liu, and L. Dong, "Morphology and crystal-plane effects of nanoscale ceria on the activity of CuO/CeO₂ for NO reduction by CO," *ChemCatChem*, vol. 3, no. 6, pp. 978–989, 2011.
- [10] T.-D. Nguyen and T.-O. Do, "General two-phase routes to synthesize colloidal metal oxide nanocrystals: simple synthesis and ordered self-assembly structures," *Journal of Physical Chemistry C*, vol. 113, no. 26, pp. 11204–11214, 2009.
- [11] M. Brust, M. Walker, D. Bethell, D. J. Schiffrin, and R. Whyman, "Synthesis of thiol-derivatised gold nanoparticles in a twophase liquid-liquid system," *Journal of the Chemical Society, Chemical Communications*, no. 7, pp. 801–802, 1994.
- [12] S. Y. Kang and K. Kim, "Comparative study of dodecanethiolderivatized silver nanoparticles prepared in one-phase and twophase systems," *Langmuir*, vol. 14, no. 1, pp. 226–230, 1998.
- [13] S. L. Horswell, C. J. Kiely, I. A. O'Neil, and D. J. Schiffrin, "Alkyl isocyanide-derivatized platinum nanoparticles," *Journal of the American Chemical Society*, vol. 121, no. 23, pp. 5573–5574, 1999.
- [14] S. Chen, K. Huang, and J. A. Stearns, "Alkanethiolate-protected palladium nanoparticles," *Chemistry of Materials*, vol. 12, no. 2, pp. 540–547, 2000.
- [15] D. Pan, N. Zhao, Q. Wang, S. Jiang, X. Ji, and L. An, "Facile synthesis and characterization of luminescent TiO₂ nanocrystals," *Advanced Materials*, vol. 17, no. 16, pp. 1991–1995, 2005.
- [16] N. Zhao, D. Pan, W. Nie, and X. Ji, "Two-phase synthesis of shape-controlled colloidal zirconia nanocrystals and their

characterization," *Journal of the American Chemical Society*, vol. 128, no. 31, pp. 10118–10124, 2006.

- [17] Y.-F. Li, W.-P. Gan, J. Zhou, Z.-Q. Lu, C. Yang, and T.-T. Ge, "Hydrothermal synthesis of silver nanoparticles in Arabic gum aqueous solutions," *Transactions of Nonferrous Metals Society of China*, vol. 25, no. 6, pp. 2081–2086, 2015.
- [18] Z. Yang, J. Wei, H. Yang, L. Liu, H. Liang, and Y. Yang, "Mesoporous CeO₂ hollow spheres prepared by Ostwald ripening and their environmental applications," *European Journal of Inorganic Chemistry*, no. 21, pp. 3354–3359, 2010.
- [19] T.-D. Nguyen, C.-T. Dinh, D.-T. Nguyen, and T.-O. Do, "A novel approach for monodisperse samarium orthovanadate nanocrystals: controlled synthesis and characterization," *Journal of Physical Chemistry C*, vol. 113, no. 43, pp. 18584–18595, 2009.
- [20] L. Yan, R. Yu, J. Chen, and X. Xing, "Template-free hydrothermal synthesis of CeO₂ nano-octahedrons and nanorods: investigation of the morphology evolution," *Crystal Growth and Design*, vol. 8, no. 5, pp. 1474–1477, 2008.
- [21] R. Dhanabal, A. Chithambararaj, S. Velmathi, and A. C. Bose, "Visible light driven degradation of methylene blue dye using Ag₃PO₄," *Journal of Environmental Chemical Engineering*, vol. 3, no. 3, pp. 1872–1881, 2015.
- [22] H. R. Pouretedal and A. Kadkhodaie, "Synthetic CeO₂ nanoparticle catalysis of methylene blue photodegradation: kinetics and mechanism," *Chinese Journal of Catalysis*, vol. 31, no. 11, pp. 1328–1334, 2010.
- [23] L. B. Reutergådh and M. Iangphasuk, "Photocatalytic decolourization of reactive azo dye: a comparison between TiO₂ and us photocatalysis," *Chemosphere*, vol. 35, no. 3, pp. 585–596, 1997.
- [24] R. Kumar, J. Rashid, and M. A. Barakat, "Zero valent Ag deposited TiO₂ for the efficient photocatalysis of methylene blue under UV-C light irradiation," *Colloid and Interface Science Communications*, vol. 5, pp. 1–14, 2015.
- [25] Y. Li, Q. Sun, M. Kong et al., "Coupling oxygen ion conduction to photocatalysis in mesoporous nanorod-like ceria significantly improves photocatalytic efficiency," *Journal of Physical Chemistry C*, vol. 115, no. 29, pp. 14050–14057, 2011.
- [26] D. Channei, B. Inceesungvorn, N. Wetchakun et al., "Photocatalytic degradation of methyl orange by CeO₂ and Fe-doped CeO₂ films under visible light irradiation," *Scientific Reports*, vol. 4, article 5757, 2014.
- [27] R. Suresh, K. Giribabu, R. Manigandan et al., "Doping of Co into V_2O_5 nanoparticles enhances photodegradation of methylene blue," *Journal of Alloys and Compounds*, vol. 598, pp. 151–160, 2014.
- [28] N. S. Arul, D. Mangalaraj, T. W. Kim et al., "Synthesis of CeO₂ nanorods with improved photocatalytic activity: comparison between precipitation and hydrothermal process," *Journal of Materials Science: Materials in Electronics*, vol. 24, no. 5, pp. 1644–1650, 2013.







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