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# The effect of $Ce^{4+}$ incorporation on structural, morphological and photocatalytic characters of ZnO nanoparticles

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ABSTRACT

We report a simple chemical precipitation method for the preparation of undoped and cerium doped ZnO nanocrystals. The concentration of cerium in the products can be controlled in the range of 0.025–0.125 mol. The structure and chemical compositions of the products were characterized by X-ray diffraction, X-ray photoelectron spectroscopy; energy dispersive spectrum and Fourier transform infrared spectroscopy. The results demonstrate that $Ce^{4+}$ ions were successfully incorporated into the lattice position of $Zn^{2+}$ ions in ZnO. The morphology of the products was analyzed by field emission scanning electron microscopy and confirmed by high resolution transmission electron microscope analysis. The optical properties of the products were studied by ultraviolet–visible and room temperature photoluminescence measurements. The photoluminescence emission spectra of Ce-doped ZnO showed enhanced visible emissions as a result of 5d → 4f transition of cerium. In particular, a novel photocatalytic activity of the products was assessed using methylene blue. The obtained result reveals that Ce-doped products show higher reduction efficiency for methylene blue than the undoped ZnO.

## 1. Introduction

Semiconductor materials in nanodimensions have fascinated the scientific community in the recent past owing to their peculiar physical and chemical properties [1]. Among the semiconductor materials ZnO an important II–VI semiconductor material with a wide band gap of 3.37 eV and a large excitation binding energy of 60 MeV, has been studied extensively because of its potential applications in ultraviolet light-emitting diodes and laser diodes [2], field emission displays [3], solar cells [4], sensors [5,6], varistors [7], and catalysis [8]. Bhargava and Gallagher reported that doped nanocrystals of semiconductors can yield both higher luminescence efficiencies and lifetime shortening from microseconds to nanoseconds at the same time [9]. Photocatalysis is one promising approach to protecting the aquatic environment, based on its ability to oxidize low concentration of organic pollutants in water [10]. Among the different photocatalysts, ZnO has a vital role due to its high semiconducting nature. To enhance the photocatalytic efficiency, it is essential to retard the recombination of the excitons [11]. Doping is an effective way to inhibit the recombination of excitons in semiconductor photocatalyst [12]. Few earlier reports have discussed the photocatalytic activity of metal ions doped ZnO nanoparticles [13,14]. Nanoparticles of ZnO are often doped with rare earth ions such as $Eu^{2+}$ and $Ce^{3+}$ to improve their luminescent properties. It has been reported that the photocatalytic activity of semiconductor photocatalyst can be enhanced by doping rare earth ions [15] which can play a major role in the inhibition of electron–hole recombination [16]. The change in photocatalytic activities of Ce-doped ZnO when it undergoes thermal treatments was studied in detail by Rezaei et al., who calcined the product at temperatures from 200 to 500 °C. They showed that the photocatalytic activity increases with calcination temperature up to 400 °C and then decreases [17]. Unlike their previous work [17], in the microwave assisted preparation of Ce-doped ZnO nanostructures, Rezaei et al. found the deteriorated photocatalytic activity on annealing [18]. In a report by Chi-Jung Chang et al., they showed that the photocatalytic activity of Ce-doped ZnO nanorods was reduced on too much dopant addition [19]. As per the available literature, various methods are available for the preparation of ZnO nanostructures such as sol–gel method [20], pulsed laser deposition [21], spray pyrolysis [22] and hydrothermal method [23–25]. However, many of the aforementioned methods that have been reported require more complex devices, multiple steps and a careful execution. Therefore, it is quite challenging to adopt a simple and convenient method for the preparation of semiconductor nanoparticles. Chemical precipitation method is one among the effective approaches to synthesize the ZnO nanostructures since this method is simple and cost effective. In the best of our knowledge, there is only limited report about the preparation of Ce-doped ZnO nanostructures using a simple chemical precipitation method and investigation of their photocatalytic activity with natural sunlight. Previously, we have reported the effect of $Ce^{3+}$ incorporation in ZnS nanocrystals [26]. In this work a simple chemical precipitation method was adopted for the preparation of ZnO and different mole percentages of cerium (Ce) doped ZnO nanocrystals. To prove cerium doped ZnO as a suitable candidate for photocatalytic application, we have evaluated the photocatalytic

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performance of undoped and doped products by the photodegradation of methylene blue (MB) under solar-light irradiation.

## 2. Materials and Methods

All the chemicals used in this study are of AR grade with 99% purity (Merck and SD Fine Chemicals) and used without further purification. Sample preparation and dilutions were made of ultrapure water. Zinc acetate dihydrate [$Zn\ (CH_3COO)_2 \cdot 2H_2O$], cerium (III) chloride hepta hydrate [$(CeCl_3) \cdot 7H_2O$] and ammonium carbonate [$(NH_4)_2CO_3$] were used as precursors.

For the synthesis of Ce-doped ZnO, 5.49 g (0.5 mol) of zinc acetate dissolved in 50 ml of deionized water was stirred vigorously by a magnetic stirrer and cerium (III) chloride hepta hydrate with different mole percentages (0.025, 0.05, 0.075, 0.1 and 0.125 mol) prepared in 20 ml aqueous were mixed drop by drop. Then, 5.63 g (1 mol) of ammonium carbonate in 50 ml of deionized water was added drop by drop to the above mixture. The entire was stirred magnetically at 60 °C until a white precipitate was formed. The obtained dispersions were purified by dialysis against de-ionized water and ethanol several times to remove impurities [27]. The yield products were dried in a hot air oven at 100 °C for 6 h to evaporate water and organic material to the maximum extent. Finally, the product was annealed in a muffle furnace at 500 °C for 2 h. The annealed powders were pulverized to fine powders using agate mortar for further characterizations. A similar method of preparation without the addition of cerium was used to synthesize undoped ZnO nanocrystals.

For the purpose of studying the photocatalytic activity of ZnO, 0.2 g of ZnO was added to a quartz photoreactor containing 100 ml of a 1 mg/l MB aqueous solution. After stirring for 30 min in the dark in order to reach the absorption equilibrium, the mixture was irradiated with sunlight with intensity fluctuation of $950 \pm 25\ W\ m^{-2}$. The residual MB in the aqueous solution was analyzed by checking the absorbance at 664 nm in the UV–Vis absorption spectra. To determine the percentage of degradation of MB, the samples were collected at regular intervals (for every 15 min), filtered and centrifuged to remove the nanophotocatalyst particles that exist as undissolved particles in the sample and studied using UV–Vis absorption. Photodegradation studies were performed by monitoring the absorbance of the dye solution at a wavelength of 664 nm. The degradation percentage of the dye in the presence and absence of ZnO nanoparticles can be calculated from the following equation [28].

$$\%D = \frac{C_0 - C_t}{C_0} \times 100 \qquad (1)$$

where $C_0$ is the initial concentration of the dye and $C_t$ is the concentration of dye after irradiation in selected time interval. The same procedure was adopted for cerium doped ZnO nanoparticles.

The crystalline phase and particle size of pure and Ce-doped ZnO nanoparticles were analyzed by X-ray diffraction (XRD) measurement which was carried out at room temperature by using the X'PERT-PRO diffractometer system (scan step of 0.05° (2θ), counting time of 10.16 s per data point) equipped with a Cu tube for generating Cu $K\alpha$ radiation ($k = 1.5406$ Å); as an incident beam in the 2-theta mode over the range of 10°–80°, operated at 40 kV and 30 mA. X-ray photoelectron spectra, arising during photoemission of electrons from the sample surface, were obtained under vacuum $1.3 \times 10^{-7}$ Pa at room temperature with electrostatic spectrometer HP 5950A Hewlett-Packard firm using monochromatized $AlK_{\alpha 1,2}$ ($h\nu = 1486.6$ eV) X-ray excitation and the gun of low-energy electrons for compensation of electrostatic charging of samples. The spectrometer resolution measured full width at the half-maximum of $Au4f_{7/2}$-electron line was 0.8 eV. The values of binding energies $E_b$ (eV) were taken relative to the binding energy of C 1s-electrons of hydrocarbonates on the sample surface, which is accepted to be equal to 285.0 eV. On the golden substrate $E_b$ (C 1s) = 284.7 eV and $E_b$ ($Au4f_{7/2}$) = 83.8 eV. The widths of lines Γ (eV), measured at half their maximum, are brought relatively to the width of C 1s-electron line of hydrocarbonates, which is accepted to be equal to 1.3 eV. The error in determination of electron binding energy values and of line widths did not exceed 0.1 eV and that of relative intensities of lines was less than 10%. The band-gap energy was measured at wavelengths in the range of 200–800 nm by UV–Vis–NIR spectrophotometer (Varian/Carry 5000) equipped with an integrating sphere and the baseline correction was performed using a calibrated reference sample of powdered barium sulfate ($BaSO_4$). The photoluminescence (PL) emission spectra of the samples were recorded with a spectrofluorometer (Jobin Yvon, FLUOROLOG-FL3-11). The functional groups were determined by a SHIMADZU-8400 Fourier-transform infrared spectrometer in which the IR spectra were recorded by diluting the milled powders in KBr and the wavelength between 4000 and 400 $cm^{-1}$ was used to assess the presence of functional groups in pure and Ce— doped ZnO. The morphological analysis was performed by a HITACHI S-4700 field emission scanning electron microscope (FESEM), and confirmed by JEOL 3010 high resolution transmission electron microscopy (HRTEM). Energy-dispersive spectrum (EDS) analysis of the products was performed during FESEM measurements. The UV–visible absorption measurements of the products during photocatalytic measurements were recorded in the wavelength range of 400–800 nm using a LAMBDA 25 PERKIN ELMER spectrometer.

## 3. Results and Discussion

The phase characteristics of the products were examined by powder X-ray diffraction. Fig. 1a shows the XRD patterns of ZnO and ZnO doped with different levels of cerium ions, respectively. All of the diffraction peaks can be indexed as wurtzite phase ZnO with lattice parameters comparable to that of the JCPDS card (36-1451). The relatively broad XRD peaks reveal the smaller size of the ZnO nanocrystals (Fig. 1b). It is noticed that for a lower concentration of Ce-doping no other crystalline impurities were detected by XRD, suggesting that the doping limit of Ce in ZnO matrix is ≥0.075 mol. However, on higher levels of Ce-doping (0.1 and 0.125 mol), a small peak positioned at $2\theta = 28.6°$ related to (111) reflection plane of $CeO_2$ is noted [29]. Similar behavior was reported by Faisal et al. on higher concentration of cerium doped ZnO nanocrystals [30].

The average crystalline sizes of the synthesized samples were calculated using the Debye–Scherer formula [26]

$$D = \frac{0.9\lambda}{\beta \cos\theta} \qquad (2)$$

where λ is the wavelength for the $K\alpha$ component of the employed copper radiation (1.54056 Å), β is the corrected full width at half maximum (FWHM) and θ is the Bragg's angle. The lattice constants *a* and *c* were calculated using the following formula used for hexagonal systems [31]:

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2} \qquad (3)$$

where *d* is the lattice spacing, *a* and *c* are the lattice constants, *h*, *k*, and *l* are the miller indices, θ is the angle of corresponding peak and λ is the wavelength of X-ray used (1.5406 Å). The unit cell volume of the products is given by the formula $V = (0.866)\ a^2c$ [32].

The results of the calculation of particle size, unit-cell parameters and unit-cell volume are given in Table 1. As shown in the table the lattice parameters of cerium doped ZnO are found to be slightly larger than those of pure ZnO for all the concentration of doping. This is due to larger ionic radius of $Ce^{4+}$ (1.01 Å) than that of $Zn^{2+}$ (0.74 Å) [33]. From Table 1, it can be observed that the average grain size of ZnO is around 24 nm. After doping with cerium, the grain size reduced to 15, 16, 11,