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# The preparation, characterization and photocatalytic activity of radical-shaped $CeO_2$/ZnO microstructures

I-Tsan Liu[a], Min-Hsiung Hon[a], Lay Gaik Teoh[b],*

[a]Department of Materials Science and Engineering, National Cheng Kung University, Tainan 701, Taiwan
[b]Department of Mechanical Engineering, National Pingtung University of Science and Technology, Neipu, Pingtung 912, Taiwan

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## Abstract

This paper uses a wet-chemical precipitation route to prepare radical-shaped ZnO microprisms and to deposit Cerium oxide ($CeO_2$) on the surface of ZnO, to form $CeO_2$/ZnO microstructures. The samples are characterized using X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and UV–vis diffuse reflectance spectroscopy. Their catalytic activity is also evaluated using methylene blue (MB) as a detection reagent. $CeO_2$/ZnO systems exhibit higher UV absorption and transparency in the visible region. The experimental results show that the deposition of $CeO_2$ nanospecies is successful and that the radical-shaped microstructures of ZnO are well maintained. The $CeO_2$/ZnO microstructures exhibit a much greater intensity of UV-light absorptivity and much higher photocatalytic activity than those of radical-shaped ZnO microprisms.

*Keywords:* Radical-shaped ZnO microprisms; Radical-shaped $CeO_2$/ZnO; Methylene blue (MB); UV light absorption; Photocatalytic activity

## 1. Introduction

Nanocomposite materials have many special physical and chemical properties [1]. Not only do they have the nature of their constituents, but also they allow more efficient optical or electrical chemical reactions than do other composite materials. ZnO is a wide and direct band gap semiconductor and ZnO materials are used in many fields, because of their high catalytic efficiency, low cost and environmental sustainability. However, the reactivity of the ZnO surface depends significantly on the particle morphology [2,3]. Therefore, by controlling the ZnO particle morphology, it should be possible to develop a ZnO photocatalyst with high activity. However, ZnO particle morphologies are complex and diversified. ZnO particles with well-defined morphological characteristics, spherical, needle-like, prismatic and rod-like shapes, have been produced [4,5]. The preparation of ZnO aggregates that have a regular shape, such as intertwined ellipsoidal aggregates and flower- and tetrapod-like aggregates, has also been described [6].

$CeO_2$ is one of the most reactive rare earth metal oxides and it has a broad range of applications in various fields, because of its many special properties, such as its high refractive index, high optical transparency in the visible region and its high capacity to store oxygen and insert/extract charge density [7,8]. $CeO_2$/ZnO composites exhibit a unique ability to absorb UV, high stability at high temperatures, good hardness values and low activity as catalysts [9]. Different chemical methods are used for the synthesis of $CeO_2$/ZnO composites, such as atmospheric pressure metal-organic chemical vapor deposition (AP-MOCVD) [10], hydrothermal synthesis [11], the soft solution chemical route [12], the solid-stabilized emulsion route [13], the sol–gel method [14] and the precipitation technique [15]. The precipitation method has several advantages, in that it is simple, cost-efficient, allows the fabrication of products on a large industrial scale and it provides reproducible results. However, most of these procedures involve the precipitation of $Ce^{4+}$ and $Zn^{2+}$ ions and it is difficult to disperse Cerium species on the surface of ZnO to allow more active sites with smaller doses of Cerium. Its tendency to agglomerate into larger particles results in a reduction in their activity during the cycle of use.

This study uses a modified precipitation route, which has two steps, to prepare radical-shaped ZnO microprisms. $CeO_2$ is

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*Corresponding author. Tel.: +886 87703202x7527.
*E-mail address:* n5888107@mail.npust.edu.tw (L.G. Teoh).

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easily deposited on the surface of ZnO to form $CeO_2$/ZnO microstructures. The $CeO_2$/ZnO composites are characterized using XRD, SEM and UV–vis diffuse reflectance spectra measurement. Their catalytic and photocatalytic activities are also evaluated and compared with those of pure $CeO_2$ and pure ZnO samples.

## 2. Experimental procedure

For the synthesis of radical-shaped ZnO prisms, (0.01 M) $Zn(NO_3)_2.6H_2O$ and 1.5 ml ethylenediamine were dissolved in 100 ml of de-ionized water. Then, 10 g of hexamethylenetetramine (HMT) was added, while the mixture was stirred. The solution was then aged in a capped flask, at 90 °C for 24 h. The resulting precipitates were collected and washed, using de-ionized water and ethanol. All chemicals were of analytical grade. For the preparation of $CeO_2$/ZnO composite, the as-obtained ZnO product was dispersed in 250 ml of de-ionized water. (0.1 M) $Ce(NO_3)_3.6H_2O$, together with different reverse molar ratios (Ce/Zn)(100/0, 90/10, 50/50, 10/90, 0/100% v/v), was stirred for 2 h, after which 0.5 g poly-(vinyl pyrrolidone) (PVP) was added. The mixture was then stirred quickly for 2 h. The mixture was aged in a capped flask at 70 °C for 5 h. The resulting precipitates were collected and washed, using de-ionized water and ethanol. White powders of the $CeO_2$/ZnO components were obtained at the end of the experimental procedure.

The crystalline structure of the pure and component samples was identified using X-ray diffraction (XRD, Rigaku, Tokyo, Japan), in order to analyze and confirm the crystalline phase structure. The X-ray diffraction used CuKα radiation ($\lambda = 1.54178$ Å) and a Ni filter and operated at 30 kV, 20 mA, with a diffraction range of $2\theta = 25$–75° and a scanning speed of 2 °/min. The microstructure and morphology of the $CeO_2$/ZnO components and catalysts were characterized using scanning electron microscopy (SEM, JEOL JSM-6500FE). The absorption spectra of the samples were recorded using a (JASCO V-760 ultraviolet–visible) spectrophotometer in the range 250–800 nm. The diffuse reflectance spectra are directly measured by the JASCO instrument. The samples were dispersed in ethanol at a concentration of 10 mg/100 ml. In order to ensure that the $CeO_2$/ZnO composite was well dispersed and to guarantee the homogeneity of the final solution, an ultrasonic pool was used to vibrate the mixture for approximately 60 min, before the absorption spectra analysis. Photocatalytic degradation experiments using methylene blue (MB) (10 mg/1000 ml) were performed using a photoreactor, under UV-light irradiation. The light source for the photocatalysis was a mercury (Hg) tube lamp (Philips 18 W, $\lambda < 365$ nm). The volume of the initial MB solution was 100 ml. All powder concentrations in the MB aqueous solution were 10 mg/100 ml. The mixture was stirred in dark for 90 min, in order to ensure absorption/desorption equilibrium at room temperature before photoreaction. The suspension was then stirred magnetically, during irradiation. At regular intervals, samples were withdrawn and centrifuged, to separate solid particles for analysis. The concentration of aqueous MB was determined using a UV–vis spectrophotometer at 663 nm, by measuring its absorbance. The degradation rate was calculated as $(A_0 - A)/A_0 = (C_0 - C)/C_0$ [16], where $A_0$ is the initial maximum absorbance, $A$ is the absorbance after irradiation for a time, $t$, of maximum absorbance, $C$ is the concentration of MB at that time and $C_0$ is the concentration in the adsorption equilibrium, before irradiation. The photoactivity for MB in the presence of pure $CeO_2$ and pure ZnO, under UV-light irradiation, was also evaluated.

## 3. Results and discussion

X-ray diffraction (XRD) is usually used for the identification of crystal phase and the estimation of the crystallite size of each phase. Fig. 1 shows the XRD patterns for the different reverse molar ratios ($CeO_2$/ZnO) (100%/0%, 90%/10%, 50%/50%, 10%/90%, 0%/100% v/v) of the composites, after being calcined at 550 °C for 2 h, which gives a good insight into the crystallinity of the products. It is seen that there are two sets of diffraction peaks for the $CeO_2$/ZnO sample, which indicates that the as-synthesized samples are composite materials. The XRD peaks at $2\theta = 28.54°$, 33.07°, 47.47°, 56.33°, 59.07° and 69.40° are attributable to $CeO_2$, as shown in Fig. 1a. The pure $CeO_2$ has peaks of a weaker intensity than $CeO_2$90%/ZnO peaks (Fig. 1b). The diffraction lines also show a large narrowing of the peaks. This observation indicates that pure $CeO_2$ has crystallites of a larger than average size. Its lattice constant is $a = 5.412$ Å, so it belongs to the space group Fm-3m [225], while the characteristic peaks of the cubic phase $CeO_2$ gradually increase with as the $CeO_2$ content increases, as shown in Fig. 1c and d. These diffraction peaks are identified as that of pure $CeO_2$ with a cubic phase, which is consistent with JCPDS, No. 81-0792. The ZnO phase is clearly observed when the amount of ZnO is increased, while the intensity of $CeO_2$ decreases, correspondingly. The XRD peaks at $2\theta = 31.74°$, 34.38°, 36.01°, 47.48°, 56.54°, 62.78°, 66.30°, 67.87° and 69.01° are attributable to ZnO, as shown in Fig. 1e. Three peaks

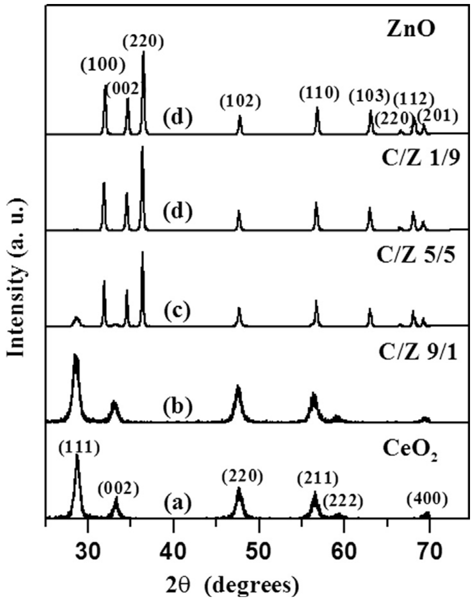

Fig. 1. The XRD patterns for (a) pure $CeO_2$, (b) $CeO_2$90%/ZnO, (c) $CeO_2$50%/ZnO, (d) $CeO_2$10%/ZnO and (e) pure ZnO, after calcination at 550 °C for 2 h.