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# Narcis-like zinc oxide: Chiral ionic liquid assisted synthesis, photoluminescence and photocatalytic activity

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ABSTRACT

In this paper, growth and assembly of the narcis-like zinc oxide is performed using microwave assisted chiral ionic liquid $(2[N\text{-}(n\text{-}But)_4]^+[C_2H_4(OH)_2(CO_2)_2]^{2-})$, as a templating agent. The effect of different parameters such as concentration of the chiral ionic liquid and microwave output power was studied. X-ray diffraction (XRD), scanning electron microscopy (SEM), and photoluminescence (PL) spectra were employed for characterization of the as synthesized zinc oxide. Furthermore, the results indicate that concentration of chiral ionic liquid and microwave output power are effective in controlling the shape and luminescence properties of the prepared zinc oxide samples.



## 1. Introduction

Zinc oxide is one of the most promising semiconductors for the fabrication of optoelectronic devices and gas sensing applications. It is well known that the novel properties of materials are obviously dependent on size, crystallographic orientation and morphology. Therefore, developments of morphologically controllable synthesis of zinc oxide are important. Until now, most techniques have been adopted to fabricate ZnO structures. Various flower-like ZnO structures have been found in different preparing methods [1–5]. In our previous research, flower-shaped ZnO structures were prepared by hydrothermal route [6,7]. The application of ionic liquid (IL) in inorganic material synthesis has received increasing attention in recent years [6–8]. Microwave assisted ionic liquid is a special heat-treatment method, and under the condition, reaction time can be greatly reduced, and it has been used to synthesize various materials [9–11]. Industrial wastewaters containing toxic organic dyes are serious problems to the environment. About 1–20% of the total world production of dyes is lost during the dying process and released into the environment as textile effluents. Zinc oxide has been widely used as a photocatalyst [12–14]. Obviously, fabrication of zinc oxide structures with simple approach under mild conditions and further exploring their novel properties continues to be a challenge. In this work, we report tailoring of the narcis-like zinc oxide by employing microwave-assisted chiral ionic liquid. X-ray diffraction (XRD), scanning electron microscopy (SEM), and photoluminescence (PL) spectra have been employed for characterization of the as-synthesized ZnO samples. The photocatalytic performance of narcis-like zinc oxide was evaluated by decolorization of congo red dye solution under (UV-C) irradiation.

## 2. Experimental

### 2.1. Synthesis and characterization

The chiral ionic liquid (CIL) used in this research was synthesized according to the procedures reported in the literature [15]. Fig. 1 shows the structure of the CIL used in this research.

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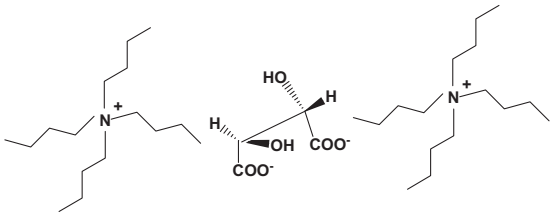


**Fig. 1.** Structure of the CIL.

Zinc acetate dihydrate and sodium hydroxide were purchased from Aldrich. Zinc acetate dihydrate was dissolved in 50 ml double distilled water under vigorous stirring and, NaOH solution (mole ratio of the $OH^-/Zn^{2+}=15:1$) was added drop wise until the solution became transparent. Then, 0.1–0.3 g, CIL was added to the first solution and stirred for about 5 min. Finally, 10 ml of the mixture was loaded into a 50 ml capacity pyrex bottle. The reaction vessel was placed in a microwave oven (Daewo, KOR-63A5, 800 w) and 25–100% of the microwave output power was used to irradiate the mixture for 2 min (on for 30 s, off for 7 s). The product was separated by decantation, washed with double distilled water several times and dried. The structure and morphology of the product were characterized by using XRD (Holland Philips Xpert X-ray diffractometer with Cu-Kα radiation) and SEM (Holland Philips XL30 microscope with an accelerating voltage of 25 kV). The PL spectra were recorded on a Varian Cary-Eclipse spectrometer.

### 2.2. Photocatalytic performance

A UV lamp (30 w, UV-C, $\lambda=253.7$ nm, photon provides 4.89 eV, manufactured by Philips, Holland), was used as the UV–vis source. The radiation source, was irradiated perpendicularly to the surface of the solution, and the distance between the light source and vessel containing the reaction mixture was fixed at 15 cm. Air was blown into the reaction by an air pump to keep the solution saturated with oxygen during the course of the reaction. In order to study the photocatalytic properties of the prepared zinc oxide, 5 ppm congo red (C.R.) azo dye solution (C.I. Direct Red 28, MW=696.67 g/mol $C_{32}H_{24}N_6O_6S_2\cdot 2Na$) was utilized as environmental pollutant. During the whole experiment, photocatalyst amount was 0.5 g/l. During irradiation, agitation was maintained by a magnetic stirrer to keep the suspension homogeneous. The suspension was sampled at regular intervals and immediately centrifuged to completely remove catalyst particles. Absorption peaks corresponding to congo red appeared at 497, 347 and 237 nm. Photodecolorization of the congo red solution was obtained measuring the optical absorbance at $\lambda=497$ nm. This is accompanied by a parallel decrease of the intensities of the band at 497 nm, attributed to the destruction of chromophoric structure. Then, the degree of photodedecolorization ($X$), as a function of time, is given by $X=(C_0-C)/C_0$ where $C_0$ is the initial concentration of dye, and $C$ the concentration of dye at time $t$. The progress of photocatalytic decolorization was measured by a UV–vis spectrophotometer (Shimadzu UV 2100).

## 3. Results and discussion

The crystallinity and phase characteristics of products were determined by using XRD pattern of the samples. A typical example is shown in Fig. 2. All the diffraction peaks are in agreement with the JCPDS file (JCPDS no. 36-1451, $a=3.249$ Å, $c=5.206$ Å and $c/a=1.60$), which can be indexed as a hexagonal phase of zinc oxide. The sharp diffraction peaks manifest in the high crystallinity of the sample. The crystallite size ($D$) of the zinc oxide samples was estimated using Scherrer's equation as follows [16]:

$$D=\frac{(0.9)\lambda}{\beta\cos\theta} \quad (1)$$

where $\lambda$, $\theta$, and $\beta$ are the X-ray wavelength (0.154056 nm for Cu-Kα), the Bragg diffraction angle, and the full width at half maximum of the diffraction peak (FWHM), respectively. In this calculation we took the highest intensity peak (101). Table 1 shows the crystallite size of the ZnO samples as estimated using Scherrer's equation. At the highest microwave output power, the sample (c), with smaller crystallite size (21.9 nm), was synthesized. Furthermore, there is no significant change in crystallite size with increasing amount of the CIL. For the prepared zinc oxide in absence of the CIL according Ref. [16], the increase in crystallite size is observed.

### 3.1. Effect of microwave output power on the morphology

In these experiments amount of 0.1 g chiral ionic liquid mole ratio of $OH^-/Zn^{2+}=15:1$ and microwave output power 200 W (sample (a)), 400 W (sample (b)) and 800 W (sample (c)) were used. The SEM images show that, narcis-like ZnO is obtained under microwave irradiation with 800 W output power. Results suggest that

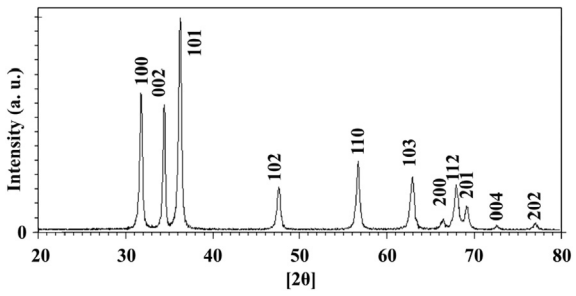


**Fig. 2.** Typical XRD pattern of the as-synthesized zinc oxide.

**Table 1**
The crystallite size of zinc oxide samples as estimated using Scherrer's equation.

| Sample | CIL amount (g) | Microwave output power (W) | Crystallite size (nm) |
|---|---|---|---|
| (a) | 0.1 | 200 | 23.0 |
| (b) | 0.1 | 400 | 22.9 |
| (c) | 0.1 | 800 | 21.9 |
| (d) | 0.2 | 200 | 22.3 |
| (e) | 0.3 | 200 | 22.2 |
| Ref. [16] | In absence CIL | 400 | 25.7 |