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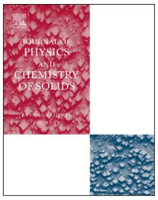

# ZIF-8 derived porous N-doped ZnO with enhanced visible light-driven photocatalytic activity

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## ABSTRACT

A facile and simple method was offered to synthesize porous N-doped ZnO via direct calcination of urea and ZIF-8 mixture. From XRD and XPS analysis, nitrogen has been successfully incorporated into ZnO lattices without introducing other N-containing or Zn-containing phases. Such nitrogen doping can enhance the visible-light harvesting ability and inhibit the recombination rate of electron-hole pairs; as a result, improved visible-light driven photocatalytic activity was achieved in N-doped porous ZnO and the photocatalytic activity of N-doped ZnO is 2.58 times higher than that of ZIF-derived pure ZnO.

## 1. Introduction

It is estimated that up to 20% of the total world dye production is lost during the dyeing process in textile industries. Dye wastewater can cause esthetic problems and cause great harm to the ecology of aquatic life due to reduction of sunlight penetration and inhibition of $O_2$ dissolution in water bodies [1,2]. Therefore, the treatment of dye wastewater has received increasing attention.

Among all the treatment of dye wastewater, photocatalysis is a promising and environmental-friendly technology. Besides traditional photocatalysts such as $TiO_2$ and ZnO or other composite materials, materials such as metal-organic frameworks (MOFs) or MOF-derived materials emerged and have been used as photocatalysts and their photocatalytic activity has been studied in recent years [3–6].

Zeolite imidazolate frameworks (ZIFs), a subclass of MOFs, consist of transition metal ions ($Zn^{2+}$, $Co^{2+}$) and imidazolate linkers that form 3D tetrahedral frameworks [7–9]. Such structure usually offers high surface areas, excellent thermal and chemical stabilities as well as good crystallinity. Moreover, ZIF-derived materials such as porous carbon or ZnO@C composites synthesized via direct carbonization of ZIFs also showed excellent properties such as high surface areas and unique pore structure; thus has attracted considerable attentions [10–12]. ZIFs and ZIF-derived materials can be directly used as photocatalysts [3–6,13]. For example, Jing et al. studied the photocatalytic activity of ZIF-8 to degrade methylene blue under UV light [14]. They found that ZIF-8 has the band gap of 5.16 eV; as a result, the photocatalytic activity of ZIF-8 is not satisfactory. In order to lower the band gap and achieve better photodegradation performance, Du et al. obtained porous ZnO via direct thermal treatment of ZIF-8 in air and they found that such ZIF-8 derived porous ZnO show improved photocatalytic activity compared to ZIF-8 [15].

Despite that ZIF-8 and ZIF-8 derived ZnO show certain photocatalytic activity, they all function under UV light, which only accounts for 5% of the natural light. Therefore, developing the band gap engineering of ZIF-8 or ZIF-8 derived ZnO into the visible-light active area is of interest and importance for their further visible-light-driven photocatalytic applications. Commonly, there are three ways to enhance the visible light harvesting ability of catalysts: (a) Metal-doping. Ag, AgCl, Cu or other metals are doped onto ZIFs to synthesize metal-doped materials [16,17]; (b) Non-metal doping (usually nitrogen-doping). The incorporation of nitrogen into the lattices of semiconductor oxides can not only enhance the light harvesting ability but also lower down the recombination rate of photo-generated electron-hole pairs [18–21]; and (c) Combining with other visible-light-driven materials such as $g\text{-}C_3N_4$ [22].

In this work, we present a simple and facile method to obtain N-doped porous ZnO via direct calcination of urea-ZIF-8 mixture. Photocatalytic activities of such N-doped porous ZnO was studied and compared with ZIF-8 derived pure ZnO and mechanism on how N-doping improves the photocatalytic activities was discussed in details.

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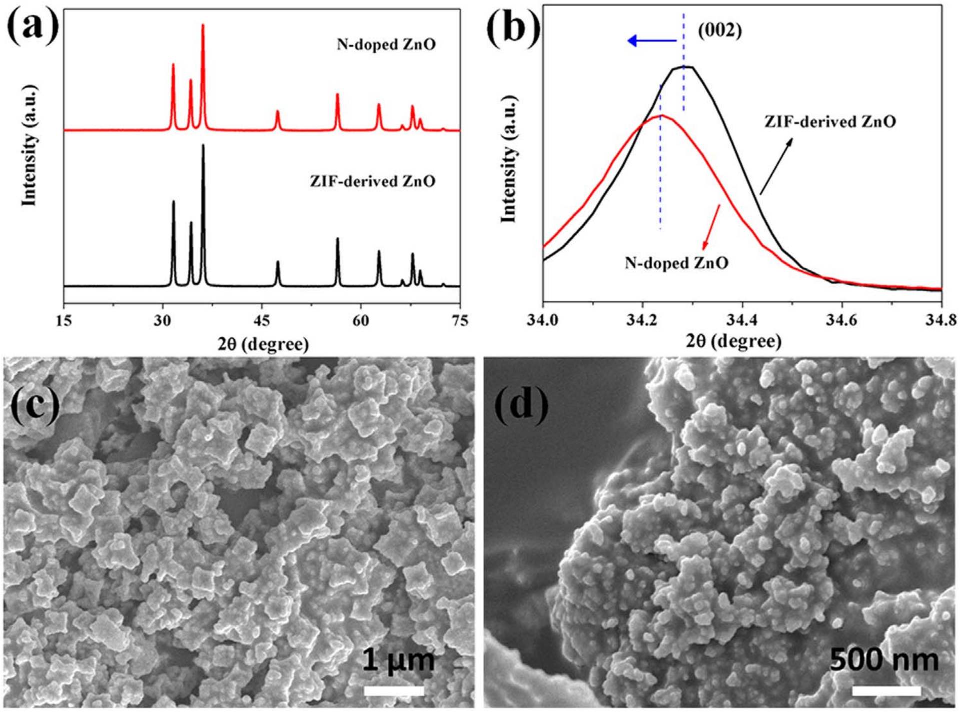

**Fig. 1.** XRD patterns of ZIF-8 derived pure ZnO and N-doped ZnO: (a) 2θ between 25° and 75° and (b) 2θ between 34.0° and 34.8°, and SEM images of (c) ZIF-8 derived pure ZnO and (d) N-doped ZnO.

## 2. Materials and methods

### *2.1. Chemicals*

Chemicals were used as received without a further purification process. They include zinc nitrate hexahydrate (≥99%, Tianjin Kemiou Chemical Reagent, China), 2-methylimidazole (Sinopham chemical reagent Co. Ltd., China), ammonium hydroxide solution ($NH_3$, 25–28%, Nanjing Chemical Reagent Co. Ltd., China), anhydrous ethanol (≥99.7%, Sinopham chemical reagent Co. Ltd., China), urea (Xilong huagong Co. Ltd., China) and Rhodamine B (RhB, Tianjin Chemical Reagent Research Institute, China).

### *2.2. Sample preparation*

ZIF-8 was synthesized according to previously reported studies [23]. In a typical synthesis, 2.97g of zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) was dissolved in 3g of deionized water; 1.64g of Hmim were added in 20.75 mL ammonium hydroxide solution; after that zinc nitrate and Hmim solutions were mixed together. The solution immediately turned into milk-like suspension, and stirred for 10 min at room temperature to complete the crystallization. The sample was collected by centrifugation and washed with deionized water three times until the final product had pH value of ~7, then dried at 60 °C overnight.

For the synthesis of mixture of urea and ZIF-8, 0.2 g ZIF-8 powders were first dispersed and ultrasonificated in 20 mL Deionization (DI) water followed by the addition of urea (2, 3, 4 g urea respectively to make the ratio of urea and ZIF-8 as 10:1, 15:1 and 20:1). After mixing and stirring, the urea and ZIF-8 mixture was dried at 110 °C to obtain solid powders.

ZIF-8 derived ZnO was obtained by direct calcination of ZIF-8 powder at 550 °C for 3 h with the heating rate of 10 °C/min whereas ZIF-8 derived N-doped ZnO was gained by calcination of ZIF-8 and urea mixture obtained above under the same calcination conditions.

### *2.3. Characterization*

X-ray diffraction (XRD) patterns of the samples were obtained on an Ultima IV diffractometer with Cu Kα radiation at a scan rate of 2° $min^{-1}$ with a step size of 0.02°. Scanning electron microscopy (SEM) images were taken with a JSM-7600F microscope operated at an accelerating voltage of 5.0 kV. Nitrogen adsorption-desorption isotherms were measured at liquid-nitrogen temperature (77 K) using a volumetric adsorption analyzer (Micromeritics ASAP 2020). Samples were degassed for 2 h at 110 °C. Surface areas were determined by the Brunauer-Emmett-Teller (BET) method. Diffuse reflectance UV–vis absorption spectroscopy was performed with a UV-2600 (Shimadzu, Japan) spectrophotometer with $BaSO_4$ as a reference. The chemical state of N dopant was verified by X-ray photoelectron spectroscopy (XPS) (AXIS UltraDLD, Japan). Room temperature photoluminescence (PL) spectra were recorded on a spectrofluorometer (FluoroMax-4, HORIBA Jobin Yvon) using a Xe lamp as the excitation source.

Rhodamine B (RhB) was used as a probe dye to evaluate the photocatalytic activity of ZIF-8 derived pure ZnO and N-doped ZnO under a 300 W xenon lamp at a light intensity of 70 $mW/cm^2$. During irradiation, a 400 nm cutoff lens was used to offer visible light with the wavelength higher than 400 nm. In a typical photo-degradation experiment, 40 mg photocatalyst was added into 40 mL dye solution (10 ppm RhB). Prior to visible light irradiation, the solution was kept stirring in dark for 60 min to reach the adsorption-desorption equilibrium on the photocatalyst. RhB concentration was measured via a UV-2600 (Shimadzu, Japan) spectrophotometer at the characteristic wavelength of 553 nm. The degradation kinetic was investigated via using the pseudo-first-order model by plotting $-\mathrm{Ln}(C/C_O)$ vs degradation time $t$ (C indicates the dye concentration at the time of t whereas $C_O$ is the initial dye concentration). The slope of $-\mathrm{Ln}(C/C_O)$ vs degradation time $t$ is the apparent rate constant. The photodegradation of phenol was carried out using the same method described above, where the initial phenol concentration was 5 ppm with a characteristic wavelength of 269.8 nm. To evaluate the cycling ability of N-doped ZnO, after each cycle of photo-degradation, photocatalyst was collected by centrifugation, washed with ethanol and then dried for the next