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# Synthesis of cobalt-doped ZnO/rGO nanoparticles with visible-light photocatalytic activity through a cobalt-induced electrochemical method☆

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ABSTRACT

ZnO is a semiconductor photocatalyst widely applied in photodegradation of organic pollutants and in photoelectric conversion. ZnO exhibits low photocatalytic activity due to poor absorption in the visible region. In this work, a novel cobalt-induced electrochemical growth method was developed to synthesize cobalt-doped ZnO/rGO nanoparticles in an aqueous solution at room temperature. Cobalt-doped ZnO/rGO nanoparticles exhibited wider visible-light absorption band ranging from 400 nm to 700 nm due to cobalt doping. The surface structure of ZnO formed by the cobalt-induced electrochemical method without other ions is suitable for photocatalytic reactions. The cobalt-doped ZnO/rGO nanoparticles were found to exhibit in photodegradation and photo-electrochemical measurements and exhibited enhanced photocatalytic activity under visible-light irradiation.



## 1. Introduction

Photocatalysis is a potential technology for addressing water pollution and energy issues. Many semiconductor photocatalysts that feature high stability, low cost, and low hazard have been widely developed and used for photodegradation, photo-electrochemistry, and photocatalytic hydrogen evolution [1–4]. ZnO, a photocatalyst with direct bandgap, is used for effective photodegradation of organic pollutants and photo-electrochemical water splitting [5–9]. However, ZnO with bandgap of 3.2 eV can only utilize UV light, which accounts for less than 5% of the solar spectra. This property of ZnO limits its application in photocatalytic treatments of pollutants. Doping with non-metal or metal elements can be used to improve the visible-light photocatalytic activity of semiconductor photocatalysts [10–14]. For example, $TiO_2$ doped with nitrogen, boron, or cobalt (Co) exhibits enhanced visible-light photocatalytic ability [12,14–17]. Co doping can be used to decorate the electron structure of metal oxides and achieve visible-light absorption [16,18–20]. In previous studies [11,21–27], metal ions were doped into ZnO to improve the photocatalytic activity of the oxide. However, the visible-light photocatalytic activity of ZnO is difficult to achieve through simple thermal doping in reductive atmosphere or through precursor ion doping. Thus, there is an urgent need to develop a simple method for preparing metal-doped ZnO with visible-light photocatalytic activity.

Noble metal-induced electrochemical growth techniques are a novel and effective strategy for synthesizing ZnO crystals from Zn powder in an aqueous solution at room temperature [28,29]. In our previous work [29], ZnO rods were prepared through a Pt-induced electrochemical method, with $Pt/H_2O/H_2$ as the cathode and ZnO/Zn served as the anode in an electrochemical cell. Pt, an inert electrode, can be replaced by other inert metals possessing lower electronegativity than Zn. Therefore, Co may be used as an inert electrode in the electrochemical growth of ZnO. Co ions can be potentially doped into ZnO crystals through a cobalt (Co)-induced electrochemical growth process. Co doping not only improves the visible-light absorption of ZnO but also alters the surface atomic state suitable for photocatalytic reactions.

Reduced graphene oxide (rGO) is a typical 2D material with high charge carrier transport rates and is widely used to prepare composite photocatalysts with increased surface carrier transport rate [30,31]. Meanwhile, graphene oxide (GO) contains a number of functional groups and displays strong oxidizing ability. Zn

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powder, which exhibits strong reduction ability, readily reacts with GO nanosheets to form a Zn–rGO composite. In a redox process, GO nanosheets are reduced and loaded onto the surface of Zn powder. rGO plays a key role in restraining the agglomeration of Zn powder.

In this study, a novel method for Co-induced electrochemical growth was developed to prepare Co-doped ZnO from Zn powder in aqueous solution at room temperature. rGO nanosheets were introduced into ZnO through a redox method to enhance surface carrier transport. Co-doped ZnO/rGO nanoparticles with a wider visible-light absorption band ranging from 400 nm to 750 nm exhibited enhanced photocatalytic activity under visible-light irradiation. The novel metal-induced electrochemical process represents a viable method to achieve nanomaterials and metal-doped catalysts.

## 2. Experimental

### 2.1. Synthesis of catalysts

Co-doped ZnO/rGO was synthesized in aqueous solution via a novel Co-induced electrochemical method at room temperature. First, graphene oxide (GO) solution was prepared by a modified Hummers method. In the typical preparation process, 1 g of zinc powder was dispersed in 30 mL of deionized water containing 10 mg of GO under continuous magnetic stirring for 30 min. Then, 20 mL of cobalt acetate aqueous solution was added dropwise to the above-mentioned solution with continuous magnetic stirring for 10 min. The mixture was transferred to a suction flask followed by a vacuum reaction at room temperature for 12 h. The production was labeled as Co-doped ZnO/rGO. The samples were collected and washed three times with deionized water and dried at 100 °C for 8 h. A series of Co-doped ZnO/rGO with different atomic ratios of Co were synthesized by adjusting the addition contents of cobalt acetate. The obtained products were thermally treated at different temperatures in an oven (200 °C) or a Muffle furnace (500 °C) for 2 h. The reference ZnO was prepared using zinc acetate and sodium hydroxide by the solution method at room temperature. The reference $Co_3O_4$ particles were prepared by a solid state reaction method. Cobalt acetate was calcined at 500 °C for 5 h.

### 2.2. Characterization of catalyst

X-ray diffraction (XRD) patterns were recorded by a Rigaku diffractometer using Cu $K_\alpha$ irradiation. Scanning electron microscopy (SEM) images and energy dispersive X-ray (EDX) spectroscopy profiles were obtained on a Nova SEM 200. Transmission electron microscope (TEM) images were obtained by a JEOL-2100. The Brunauer–Emmett–Teller (BET) specific surface area was analyzed on ASAP-2010M (Micrometritics). The UV–visible absorption spectra were measured with a UV–visible spectrophotometer (HITACHI U-4100). The chemical compositions of the samples were analyzed by using a monochromatic Al $K_\alpha$ X-ray photoelectron spectroscopy (XPS) source (Thermo Escalab 250). All binding energies were referenced to the C 1*s* peak (284.6 eV) produced by adventitious carbon.

### 2.3. Photocatalytic activity measurement

#### 2.3.1. Photodegradation of organic pollutants

The photocatalytic activity of prepared samples under visible-light irradiation was estimated toward the model molecule effluent methylene blue (MB). In the typical experiment, 100 mg of the photocatalyst prepared in this study was added to 100 mL of $2 \times 10^{-5}$ mol/L aqueous solution of MB. The mixed suspension was stirred in the dark for 30 min to reach adsorption equilibrium. Subsequently, the photocatalyst-suspended solution was irradiated under UV–visible light from a 300 W Xe lamp (light intensity: ca. 150 mW/cm$^2$), while still maintaining the stirring conditions. Consequently, 5 mL aliquots of the photocatalyst-suspended solution were sampled every 30 min, and the absorption spectra were recorded by using a UV–visible spectrophotometer (HITACHI U-4100). Long-pass filters were utilized to cut off the light.

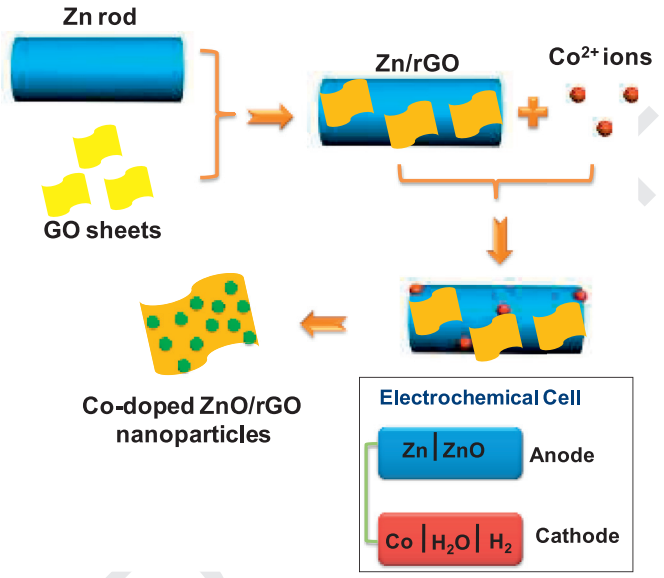


**Fig. 1.** Sketch map of Co-doped ZnO/rGO prepared by a two-step method concluding a redox reaction of GO nanosheets and Zn powders as well as Co-induced electrochemical growth process at room temperature.

#### 2.3.2. Photo-electrochemical measurement

A slurry consisted of 0.1 g resultant photocatalysts, 1 mL of deionized water, 5 drops of Triton X-100 and 2 drops of acetylacetone. The slurry was deposited on a FTO glass substrate by a doctor-blading method with adhesive type as a spacer. And then the film was dried at 200 °C for 2 h in an oven. Photoelectrochemical measurements were carried out in a quartz cell with a conventional three-electrode process. The samples loaded on FTO glass, Pt foil and Ag/AgCl electrode served as the working electrode, counter electrode and reference electrode, respectively. Electrolyte was 0.1 M of $Na_2SO_4$ aqueous solution. A sunlight simulator of 300 W Xe lamp was used as the excitation light source. Long-pass filters were utilized to cut off the light. The photoanode surface area illuminated was 1 cm$^2$, and the scanning rate was 5 mV/s.

## 3. Results and discussion

Co-doped ZnO/rGO nanoparticles were synthesized by a two-step method, which comprises redox reaction of GO nanosheets and Zn powder as well as Co-induced growth of ZnO (Fig. 1). In the first step, metal Zn powder, which features strong reductive ability, was reacted with GO nanosheets, which exhibits high oxidative ability, to form Zn/rGO composites [28]. In the redox process, the GO nanosheets were partially reduced to rGO nanosheets and used to prevent agglomeration of the metal Zn rods. Fig. 2(a) shows that the precursor Zn powder was unequal rod-like morphology with particle sizes less than 100 μm. A small quantity of ZnO was formed on the surface of the Zn rod employed due to natural oxidation. The high-resolution SEM image (Fig. 2) indicated that the surface of the Zn rods was very coarse and grew a number of protrusions. A number of rGO nanosheets were loaded onto the Zn rod surface (Fig. 3(c)), which confirmed that a redox reaction was feasible between the Zn rods and GO



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