



Effect of Ni coupling on the photoluminescence property and photocatalytic activity of ZnO nanorods



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ABSTRACT

ZnO nanoparticles are promising UV light driven photocatalyst for the degradation of organic dyes. In this work, we demonstrated that the photocatalytic activity of ZnO nanoparticles could be improved by coupling with Ni particles. The Ni coupled ZnO nanorods were synthesized by two steps solution precipitation method. The surface plasmon resonance stimulated by the defect transition experienced by Ni coupled ZnO nanorods caused quenching of visible emission but enhancing of UV emission in RTPL analysis. The photodegradation of RhB solution in the presence of Ni coupled ZnO nanorods under UV irradiation followed first-order kinetic. The best photodegradation efficiency, i.e. 64% of RhB removal after 90 min UV irradiation with rate constant of 0.0119 min^{-1} , was achieved when ZnO nanorods coupled with Ni nanoparticles prepared at 0.03 M nickel nitrate were used. The Ni nanoparticles acted as electron traps, pro-longing the charge separation duration. The scavenger test shows that holes and hydroxyl free radical were the dominant reactive species in the photocatalytic degradation of RhB dye by Ni coupled ZnO nanorods under UV irradiation. A refined photodegradation mechanism of RhB dye by Ni coupled ZnO nanorods is proposed based on these findings.

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1. Introduction

A large quantities of synthetic dyes used in the textile industry are lost to the effluents during the manufacturing yearly [1]. These synthetic dyes, consist of one or more azo groups which bound to aromatic rings, are widely used to produce textile, paint and plastics. These azo-based dyes are commonly used in the industry attributed to their good chemical stability during washing process and their simple dyeing steps. However, these colored dyes create series of environmental pollution problems by releasing toxic and potential carcinogenic substances into the aqueous systems. There are several treatment methods ranging from physical, chemical and biological methods or suitable combinations of them are available for the treatment of colored dyes. However, some of them such as coagulation, filtration and absorption by activated carbon only transfer the organic pollutants from one phase to another causing secondary pollutant to the environment [2].

Semiconductor photocatalysts based on advanced oxidation processes (AOPs) have been given attention to remove colored dyes

from wastewater due to their high efficiency, commercial availability and high chemical stability [3]. It is noted that most of the wide bandgap semiconductors can be used as photocatalysts. Among them, ZnO [4] and TiO₂ [5] nanoparticles were commonly studied for photodegradation of organic pollutants into less harmful byproducts such as water and carbon dioxide under sunlight. ZnO and TiO₂ have similar band gaps around 3.2–3.4 eV [6,7]. Indeed, a higher catalytic efficiency for some reactive dyes in aqueous solutions has been reported for ZnO as compared to TiO₂ [8–10]. The photocatalytic activities of ZnO nanostructures such as nanodisks [11], nanorices [12], nanoflakes [13], nanospheres [14] and nanorods [15], in removal of organic dyes have been investigated by researchers. In particular, ZnO nanorods demonstrated good photocatalytic performance among these nanostructures attributed to a large number of photogenerated electron and hole pair could exist on the active sites of the surface of ZnO nanorods [16].

To enhance the photocatalytic activity of ZnO nanorods, many efforts have been done to improve charge separation duration. This includes deposition of noble metal such as Au [17], non-metallic elements doping (e.g. C, N, S) [18–20], rare-earth ion doping (e.g. Ce, La) [21,22], transitional metal doping (e.g. Ni, Co, Mn, Fe, Cu) [23–27] and coupling of oxide semiconductor [28]. In this work, we

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demonstrated that photodegradation efficiency of ZnO nanorods could be improved by depositing with an optimum amount of Ni particles onto their surface. The Ni particles experienced surface plasmon resonance during UV irradiation and became the traps of electrons. As a result, it prolonged the charge separation, allowing more free radicals to be generated for degrading the RhB dye. A refined photodegradation mechanism of RhB by Ni coupled ZnO nanorods was proposed based on the correlation finding between RTPPL and photodegradation efficiency of RhB dye.

2. Experimental procedure

2.1. Synthesis of ZnO nanorods

ZnO nanorods were synthesized by solution precipitation method as reported in our previous paper [15]. In this method, precursor solutions of 12 mmol of zinc nitrate tetrahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) in 100 ml of de-ionized water, 12 mmol of 1,3-hexamethylenetetramine (HMTA, $\text{C}_6\text{H}_{12}\text{N}_4$) in 100 ml of de-ionized water and 0.4 g of polyvinyl pyrrolidone (PVP) in 100 ml of de-ionized water were prepared separately. The solutions were stirred for 30 min at 90 °C. Subsequently, these solutions were mixed together under constant stirring rate at 90 °C. The mixture of solution was heated to 90 °C in a water bath, producing white precipitate. Thus, centrifugation was carried out at 3000 rpm for 20 min in order to separate the precipitate from the solution. The precipitate was washed by de-ionized water for several times until the pH of the washed water became 7. The precipitate was dried in the oven for 8 h at 100 °C.

2.2. Synthesis of Ni coupled ZnO nanorods

Ni coupled ZnO nanorods were synthesized by immersing the as-prepared ZnO nanorods into various concentration of nickel nitrate ($\text{Ni}(\text{NO}_3)_2$) solutions, *i.e.* 0.02 M, 0.03 M, 0.07 M and 0.14 M, respectively. The mixture was stirred at room temperature for 24 h to allow deposition of Ni particles onto the surface of ZnO nanorods. The mixture was filtered and dried in the oven for 12 h at 120 °C. The resultant products, including ZnO nanorods, were annealed at 500 °C for 1 h and reduced at 500 °C for 2 h under hydrogen atmosphere. The samples were designated as ZnO, 0.02NZ, 0.03NZ, 0.07NZ and 0.14NZ according to the concentration of nickel nitrate solution respectively.

2.3. Characterization

The crystal structure of Ni coupled ZnO nanorods was analyzed by XRD (Rigaku, $\text{Cu K}\alpha$ with $\lambda = 0.154$ nm at 40 kV and 30 mA). The morphology of the particles was examined using scanning electron microscope (SEM, Zeiss Supra 35 VP) and transmission electron microscope (TEM, Tecnai G2 20 S-Twin). The optical band gap of the particles was measured using UV–vis spectrometer (Cary 500 Scan). The photoluminescence (PL) spectra of the particles were characterized at room temperature using He–Cd laser with excitation wavelength of 325 nm (Jobin-Yvon HR800uV).

Photocatalytic activity of particles in removal of Rhodamine B (RhB) dye under UV irradiation was studied. The RhB is one of the most common xanthenes dyes uses for textile industry. It is highly soluble in water and organic solvent, and its color is fluorescent bluish-red. The RhB aqueous solution with initial concentration of 1×10^{-5} M was prepared using magnetic stirrer in the dark room to avoid pre-mature decomposition of RhB dye solution. Subsequently, the RhB solution with Ni coupled ZnO nanorods as photocatalyst was UV irradiated (352 nm). The photodegradation of RhB solutions using ZnO and Ni coupled ZnO nanorods as photocatalysts was determined by monitoring the absorbance peak of

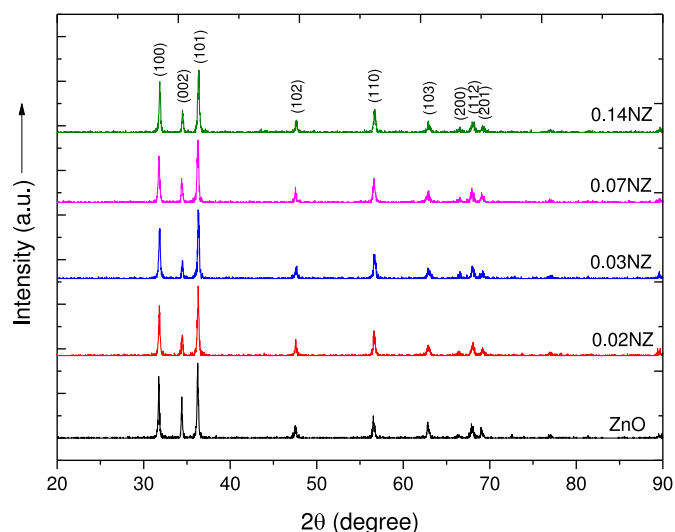


Fig. 1. XRD patterns of ZnO nanorods and Ni coupled ZnO nanorods prepared at different nickel nitrate concentration.

RhB, *i.e.* at 553 nm from the solution sampled at different time interval.

3. Results and discussion

3.1. Structural and optical properties of Ni coupled ZnO nanorods

The crystal structure of ZnO nanorods and Ni coupled ZnO nanorods was characterized by X-ray diffraction as seen in Fig. 1. All of the diffraction peaks in Fig. 1 could be indexed to hexagonal wurtzite ZnO (JCPDS No. 01-079-2205) with lattice constant of $a = 3.250$ Å and $c = 5.207$ Å. There is no change in crystal structure of Ni coupled ZnO nanorods as compared to ZnO nanorods. The diffraction peaks at 31.74° , 34.40° , 36.26° , 47.52° , 56.54° , 62.84° , 66.26° , 67.92° and 68.98° are corresponded to (100), (002), (101), (102), (110), (103), (200), (112) and (201) crystal planes of hexagonal ZnO respectively. Their strong and sharp diffraction peaks suggest that the particles were well crystalline. No XRD pattern of Ni could be found in the analysis, suggesting that the Ni presented in a very low concentration on the surface of ZnO nanorods [29–31], which beyond the detection sensitivity of XRD.

Fig. 2a shows the field emission scanning electron microscopy (FESEM) image of as-synthesized ZnO nanorods. It could be clearly seen that the nanorods poses hexagonal tips. Interfaces are found mainly in the middle of the ZnO nanorods, indicating that each particle at least consists of two nanorods that joined in their (002) polar surfaces. Generally, the morphology of Ni coupled ZnO nanorods did not change with increasing of nickel nitrate concentration. However, as shown in inset of Fig. 2c–e, small particles could be found on the surface of ZnO nanorods. These particles were homogeneously distributed on the surface of ZnO nanorods. The EDX elemental analysis was performed on the Ni coupled ZnO nanorods as shown in Fig. 3a. The results show that the nanorods composed of Zn, O and Ni elements. The EDX analysis indicates that Zn-rich ZnO nanorods were synthesized in this work. This is explainable as a result of slow forming of NH_3 from HMTA, which subsequently hydrolyzes to form OH^- ions [32–34]. Thus, lacking of OH^- ions in the solution caused the formation of Zn-rich ZnO nanorods in our work. It is also noted that the Ni atom percentage increases with the increase of nickel nitrate concentration as shown in Fig. 3b.

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