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Room-temperature solid state synthesis of Co_3O_4/ZnO p–n heterostructure and its photocatalytic activity

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ABSTRACT

A facile solid state reaction route was employed to synthesize the Co_3O_4/ZnO p-n heterostructure by grinding zinc acetate, Co_3O_4 and sodium hydroxide with appropriate molar ratios together at room temperature without any surfactant or template. The as-obtained samples were characterized for the surface structure, chemical state, phase structure using field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), photoluminescence spectroscopy (PL), Brunauer–Emmett–Teller (BET) analysis. The photodegradation of Rhodamine B (RhB) dye clearly revealed that the photocatalytic activity of the prepared Co_3O_4/ZnO p-n heterostructure was higher than that of pure ZnO nanostructure and 7% Co_3O_4 loaded Co_3O_4/ZnO photocatalyst exhibited the maximum photocatalytic activity. Under UV light it was also found to be more than five times that of pure ZnO. The photoluminescence (PL) emission spectroscopy confirmed the high separation efficiency of the photogenerated electrons-holes in the Co_3O_4/ZnO heterostructure which led to the high photocatalytic activity of the material.

1. Introduction

During the last decades, considerable interest has been focused on environmental problems such as organic pollutants and toxic water pollutants produced by some industries eg. plastics, paint, textile and paper [1–5]. These industries and especially textile industries use huge quantities of dyes in their fabrication process and discharge colored wastewater into the effluent. This not only harms the environment but also human beings; the high concentration of dyes is known to cause ulceration of skin, and mucous membrane, dermatitis, perforation of nasal septum, severe irritation of respiratory tract and on ingestion may cause vomiting, pain, and sharp diarrhea [6]. Many of these dyes are toxic, carcinogenic or mutagenic to life forms mainly because of carcinogens, like benzidine, naphthalene and other aromatic compounds [5]. Even very low concentrations of dyes in the effluents are highly visible and undesirable; they reduce the light penetration resulting in inhibition of photosynthesis and the ultimate destruction of the aquatic life [7]. That is why these dyes must be removed from industrial effluents before the water is returned to the environment. Dyes usually have complex aromatic molecular structures which make them more stable and difficult to biodegrade. Without adequate treatment these dyes can remain in the environment for a long period of time [5]. Several physical and chemical techniques such as adsorption, ozonization, membrane filtration, electrolysis; oxidation, bio-degradation etc. have been widely used for the removal of dyes from wastewater [7,8]. However these techniques have some limitations: low removal efficiency, costly, energy demanding, ineffective for the complete mineralization of dyes [9,10].

Recent studies have been devoted to the use of photocatalysis in the removal of dyes from wastewaters, particularly, because of the ability of this method to completely mineralize pollutants [10]. Nanostructured semiconductor metal oxides, ZnO [11], TiO_2 [12], Fe_2O_3 [13], Co_3O_4 [14], have been assessed to be applied in photocatalysis degradation of dyes. Ge et al. reported the heterojunction photocatalyst of Co_3O_4/g-C_3N_4 exhibited a significantly enhanced photocatalytic activity in degrading methyl orange [14]. And Xu et al. also reported ZnO coupled with versatile carbon can effectively improve the photocatalytic performance of semiconductor ZnO [11]. Therefore, the photocatalytic activity of Co_3O_4/ZnO heterojunction should be revealed, especially the photocatalytic mechanism of Co_3O_4/ZnO p-n heterojunction. Photocatalysis, in general, occurs based on the reaction between adsorbed molecules (oxygen, surface hydroxyl groups) or water and photogenerated electron/hole pairs excited by photons with equal or higher energy

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than the band gap of the semiconductor [15]. However, the fast recombination of the photogenerated electron-hole pairs hinders the industrial application of photocatalytic techniques in the degradation of contaminants in water.

So far, there have been several investigations on improvement of photocatalytic efficiency of semiconductors, such as depositing noble metals [16], combination with carbon based materials such as carbon nanotube [17], graphene [18] graphene oxide (GO) [19,20] and reduced graphene oxide (rGO) [21,22] materials, formation of hierarchical structures and/or porous surface structures [23–28]. This not only increases the specific surface area of the material, the charge transportation and separation, but also increases the photocatalytic and photoelectrochemical properties, resulting from the electron distribution on the surface of the novel structure.

Another way to improve the photocatalytic activity is the formation of semiconductor-semiconductor p-n heterojunctions. Over the past decades formation of p-n heterojunctions has been attempted: NiO/ZnO [29], ZnO/Co_3O_4 [30], CoO–TiO_2 [31], NiO/TiO_2 [26], and Co_3O_4/TiO_2 [32]. It was found that the p-n junctions formed in combination with both p-type and n-type semiconductors can effectively reduce the recombination rate of the photogenerated electro/hole pairs, which subsequently enhances the photocatalytic activity [26,29–32]. Among these p-n heterojunctions, Co_3O_4/ZnO is of great interest; ZnO is an n-type semiconductor (wide and direct band gap (3.37 eV) and large exciton binding energy (60 meV)). It is versatile, economical, stable, abundant, nontoxic, environmentally friendly, and has been regarded as one of the most ideal photocatalyst for environment applications [11,29,33–36]. Co_3O_4 is an excellent antiferromagnetic p-type semiconductor (direct optical band gaps 1.48 and 2.19 eV) and was used pure [37] or combined with other semiconductors for photocatalytic degradation of contaminants in water [15,38–40]. The combination of p-type Co_3O_4 and n-type ZnO leads to the build-up of an inner electric field at the p-n junction interface that can be advantageous for photocatalytic applications [41]. However, their Photocatalytic properties heavily depend on the synthesis methods utilized [30]. Co_3O_4/ZnO heterojunctions for photocatalytic application have been prepared via different synthesis routes; high energy milling [30], thermal decomposition [28], hydrothermal method [15], and electrospinning process [39]. However, to the best of our knowledge, to date, the fabrication strategy to form Co_3O_4/ZnO p-n heterostructure via a solid state reaction and its photocatalytic performance has not been explored yet.

In this paper, a facile solid-state reaction route was used for the preparation of the Co_3O_4/ZnO p-n heterostructure without any surfactant or template at room temperature for the mass-productive synthesis of Co_3O_4/ZnO photocatalysts.

2. Experimental

2.1. Fabrication process

Almost all reagents were of analytical grade and used without further purification. Zinc acetate dehydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$, $Zn(AC)_2{\cdot}2H_2O$), cobalt acetate tetrahydrate ($Co(CH_3COO)_2{\cdot}4H_2O$, $Co(AC)_2{\cdot}4H_2O$), sodium hydroxide (NaOH), absolute alcohol (CH_3-CH_2OH), Rhodamine B (RhB) are all purchased from Sinopharm Chemical Reagent Co, Ltd. Deionized water was used in all experiments. Co_3O_4 nanoparticles was synthesized via a simple precipitation route, basically 0.5 g of $Co(AC)_2{\cdot}4H_2O$ was dissolved in 25 ml of ethanol and stirred for 15 min, meanwhile, 0.32 g of NaOH was dissolved in ethanol under gentle stirring. Then the two solutions were mixed whereupon the precursor for Co_3O_4 nanoparticles began to grow. The precipitate was centrifuged; washed with distilled water and ethanol in turn, and dried at 80 °C for 12 h. Finally, Co_3O_4 nanoparticles were obtained by calcining the precipitate at 500 °C for 2 h in air. To produce Co_3O_4/ZnO nanocomposite, $Zn(AC)_2{\cdot}2H_2O$ (1.0 mmol) and different amounts of Co_3O_4 were blended together in an agate mortar and ground thoroughly for 20 min at room temperature. The precursor of Co_3O_4/$Zn(AC)_2{\cdot}2H_2O$ of molar ratios 0%, 2%, 5%, 7%, and 10% was firstly prepared, and NaOH (8 mmol) was a precipitator of $Zn(OH)_2$ to add the Co_3O_4/$Zn(AC)_2{\cdot}2H_2O$ mixture and ground for further 20 min. Then, to remove unreacted reactants and by-products, the mixture of Co_3O_4/$Zn(OH)_2$ was washed several times in turn with distilled water and absolute ethanol, followed by drying at 80 °C for 12 h. Finally, the dried powder of Co_3O_4/$Zn(OH)_2$ was annealed at 500 °C for 2 h to obtain Co_3O_4/ZnO heterostructures. We refer to these samples as S0 for pure Co_3O_4, S1, S2, S3, S4, and S5, representing the Co_3O_4/$Zn(AC)_2{\cdot}2H_2O$ molar ratios of 0%, 2%, 5%, 7%, and 10%, respectively.

2.2. Characterization and properties

The X-ray diffraction (XRD) measurements, which were used to characterize the crystalline phase, as well as the phase composition of all samples, were carried out using an X-ray diffractometer (X'pert PRO MPD, Philips, Eindhoven, The Netherlands) with Cu Kα radiation (λ = 1.5406 Å) at 40 kV, and 30 mA over the 2θ of range 15–80°. The morphology and the elemental analysis of the nanocomposites were investigated using field emission scanning electron microscopy (FE-SEM; JSM-6701F, JEOL, Tokyo, Japan) along with energy dispersive spectroscopy (EDS; Feature Max, Oxford Instruments, Abingdon, Oxford shire, UK), and high resolution transmission electron microscopy (HRTEM; Tecnai F30G2, FEI, Hillsboro, OR, USA). Surface properties of the samples were analyzed using X-ray photoelectron spectroscopy (XPS; VG ESCALA–B220i–XL, Thermo Scientific, Surrey, UK) using an Al Kα ($h\nu$ = 1486.6 eV) source at a residual gas pressure below 10^{-8} Pa. All the binding energies were referenced to the C 1s peak at 284.6 eV of the surface adventitious carbon. Their light absorption abilities were analyzed in the range of 300–800 nm by the UV–visible spectrometer (HITACHI, U-3900H, Tokyo, Japan), during which $BaSO_4$ was employed as the internal reflectance standard. The measurements of the photoluminescence (PL) spectra were performed at room temperature on an F-4600 fluorescent spectrophotometer (Hitachi Corp., Tokyo, Japan) with 325 nm pulse laser radiation (nano-LED) used as the excitation source. The specific surface area was calculated with Brunauer–Emmett–Teller (BET) method by using the nitrogen adsorption–desorption isotherms (V-Sorb2800P, Gold APP Corp., Beijing, China).

The synthesized Co_3O_4/ZnO samples were utilized for the photocatalytic degradation of Rhodamine B dye. For the photocatalytic experiments, 10 mg of the as-prepared samples were added to 30 mL of RhB suspension (5 mg/L). Initially, the solution was magnetically stirred in dark for 30 min to reach absorption–desorption equilibrium. After equilibrium, the dye solution was exposed to UV light for about 105 min. The UV light source was provided by a 500 W UV lamp with maximum wavelength emission at 365 nm. The lamp source was laid in the empty chamber of the annular quartz condensing tube with a cooling water jacket outside to immediately remove the heat released from the lamp. At given irradiation time intervals, 4 mL of the suspension were collected and centrifuged (9000 rpm, 3 min) to separate the photocatalyst particles. The RhB concentration was evaluated by UV–visible Spectrophotometer (UV-2450, Shimadzu, Kyoto, Japan) monitoring the absorption at λ = 554 nm. Blank experiment was also conducted without the catalysts when the solution containing the dissolved dye was illuminated. To determine the degradation efficiency:

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