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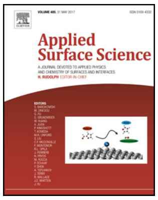

Full Length Article

Enhanced photocatalytic performance and degradation pathway of Rhodamine B over hierarchical double-shelled zinc nickel oxide hollow sphere heterojunction

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ABSTRACT

In this study, hierarchical double-shelled NiO/ZnO hollow spheres heterojunction were prepared by calcination of the metallic organic frameworks (MOFs) as a sacrificial template in air via a one-step solvothermal method. Additionally, the photocatalytic activity of the as-prepared samples for the degradation of Rhodamine B (RhB) under UV–vis light irradiation were also investigated. NiO/ZnO microsphere comprised a core and a shell with unique hierarchically porous structure. The photocatalytic results showed that NiO/ZnO hollow spheres exhibited excellent catalytic activity for RhB degradation, causing complete decomposition of RhB (200 mL of 10 g/L) under UV–vis light irradiation within 3 h. Furthermore, the degradation pathway was proposed on the basis of the intermediates during the photodegradation process using liquid chromatography analysis coupled with mass spectroscopy (LC–MS). The improvement in photocatalytic performance could be attributed to the *p-n* heterojunction in the NiO/ZnO hollow spheres with hierarchically porous structure and the strong double-shell binding interaction, which enhances adsorption of the dye molecules on the catalyst surface and facilitates the electron/hole transfer within the framework. The degradation mechanism of pollutant is ascribed to the hydroxyl radicals ($^{\bullet}$OH), which is the main oxidative species for the photocatalytic degradation of RhB. This work provides a facile and effective approach for the fabrication of porous metal oxides heterojunction with high photocatalytic activity and thus can be potentially used in the environmental purification.

1. Introduction

Photocatalytic technology, an advanced oxidation process, has shown a great potential being cost effective, environment friendly for air purification and wastewater treatment using solar energy and complete degradation of organic pollutants [1–4]. However, the limits of semiconductor photocatalysts are that most of the catalysts have a large band gap and recombination of the photogenerated electrons and holes [5]. In recent years, considerable effort has been made on the design and preparation of heterostructure to improve the photocatalytic activity [6]. The composite heterojunction has been recognized as an effective method to improve photocatalytic efficiencies by enhancing the utilization of sunlight or improving the separation/transportation of the electron-hole pairs [7–9] (e.g. NiO/hematite [10], ZnO/TiO$_2$ [11], Cu$_2$O/ZnO [12], BiPO$_4$/BiOBr [13]). Recent research found that ZnO-based heterojunctions [14], such as CdS, BiOI, NiO, TiO$_2$, SnO$_2$, CdSe, and SnS$_2$ could significantly promote the transfer of electrons and inhibit the recombination of electrons-holes by heterojunctions. Among these composites, nickel oxide (NiO) is an ideal p-type semiconductor [15]. When NiO and ZnO fabricate a heterojunction, the transfer of photogenerated electron-holes can be enhanced and recombination can be reduced, thereby improving the photocatalytic efficiency [16].

Hollow micro-/nano structures are a class of special micro-/nano materials being named on the basis of their morphologies [17,18]. They show their advantages on promising photocatalysts in several aspects, such as better charge separation [19]. Many methods have been developed to fabricate this type of micro/nano materials including Kirkendall effect [20], Ostwald ripening [21] and template-directed synthesis [22,23]. Among these methods,

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template-directed synthesis, with either hard or soft templates, is one of the most effective methods to fabricate hollow structures.

Metal-organic frameworks (MOFs) are crystalline coordination polymers that form multiple dimensional structures and can be constructed by using a wide range of metal ions and organic ligands. Compared with common inorganic material such as zeolite, MOFs have higher pore volume, specific pore structural, high surface area and structural diversity; therefore have been widely used in various fields. Owing to their permanent porosity, tunable porosity and diversity in metal ions and organic ligands of MOFs makes them feasible as templates for preparation of desired products with unique structures [24,25].

In this study, a novel facile approach was adopted to fabricate hierarchical double-shelled NiO/ZnO hollow spheres heterojunction derived from zinc nickel bimetal-organic frameworks microspheres. The composites showed significant enhanced photocatalytic activity in RhB and p-nitrophenol degradation, moreover the mechanism of RhB was also investigated systematically.

2. Materials and methods

2.1. Materials

Nickel nitrate hexahydrate, terephthalic acid (H_2BDC), nickel nitrate hexahydrate, N, N-dimethylformamide (DMF), ethylene glycol, ethanol, methanol, isopropanol, rhodamine B, p-nitrophenol, sodium hydroxide and sodium sulfate were all obtained from Sinopharm Co. Ltd. (China) and used without any further purification.

2.2. Sample preparation

2.2.1. Synthesis of Ni/Zn MOF microspheres

Ni/Zn MOF spheres were fabricated by a solvothermal method. The preparation processes were as followed: 0.2 g Ni $(NO_3)_2{\cdot}6H_2O$, 0.2 g Zn $(NO_3)_2{\cdot}6H_2O$ and 0.12 g terephthalic acid (H_2BDC) were dissolved in a mixture of 20 mL ethylene glycol and 32 mL N, N-dimethylformamide (DMF) with a ultrasonication lasting 30 min followed by a continuous stirring for 1 h which was then transferred to a Teflon-lined stainless steel reactor and heated at 150 °C for 6 h. After that the colloids were centrifuged and further washed with DMF and alcohol. Thus, different weight ratios of Ni/Zn were prepared. The Ni/Zn MOF with original $Ni(NO_3)_2{\cdot}6H_2O/Zn(NO_3)_2{\cdot}6H_2O$ weight ratios of 1:3, 2:2 and 3:1 were denoted as Ni/Zn MOF-1, Ni/Zn MOF-2, Ni/Zn MOF-3 respectively. In order to study the photocatalytic activity of *p-n* heterojunction and unique hollow structure, pure NiO, pure ZnO and NiO/ZnO without MOF precursors were prepared using the same experimental conditions, but different reactants. They were named Ni MOF, Zn MOF and Ni/Zn-n without Zn $(NO_3)_2{\cdot}6H_2O$, Ni $(NO_3)_2{\cdot}6H_2O$ and H_2BDC, respectively.

2.2.2. Synthesis of NiO/ZnO hollow spheres heterojunction

The prepared Ni/Zn-MOF spheres were calcined in a muffle furnace for 1.5 h from room temperature to 400 °C in air. According to the annealed time, the samples were named as NiO/ZnO–1 h, NiO/ZnO-2 and NiO/ZnO–2 h. The different annealed temperatures were also investigated (400 °C, 500 °C and 600 °C) and the composites were named as NiO/ZnO-2, NiO/ZnO-500 and NiO/ZnO-600. Moreover, aforementioned Ni/Zn MOF-1, Ni/Zn MOF-2, Ni/Zn MOF-3, Ni MOF, Zn MOF and Ni/Zn-n (without MOF precursor) were also annealed at 400 °C in air for 1.5 h and were named as NiO/ZnO-1, NiO/ZnO-2, NiO/ZnO-3, NiO, ZnO and NiO/ZnO-n. The names of all samples are shown in Table S2.

2.3. Characterization

X-ray diffraction patterns (XRD) of the composites were characterized by HZG41B-PC (Japan) and Cu-Kα irradiation was used. X-ray photoelectron spectroscopy (XPS) measurement was recorded by VG ESCALAB 210 electron spectrometer (UK). X-ray fluorescence (XRF) was performed by PANalytical Epsilon3-XL (Netherlands). Field emission scanning electron microscopy was observed by Hitachi S-4800 (Japan) and scanning electron microscopy was performed by JSM-IT 300 (Japan). Transmission electron microscopy (TEM) was conducted by JEOL JEM-2100F (Japan). The Brunauer-Emmett-Teller (BET) surface area was determined by Micromeritics ASAP 2020 nitrogen adsorption apparatus (USA). The pore-size distribution was calculated using the Barret-Joyner-Halender (BJH) method. The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were determined by SDT Q600 V5.0 Build 63 (USA). The UV–vis absorbance and diffuse-reflectance spectra were performed at room temperature between 200 and 800 nm by PerkinElmer Lambda 750 S (USA) with an integrating sphere diffuse reflectance attachment using $BaSO_4$ as reference. The photoluminescence (PL) was performed by Renishaw inVia Reflex laser Raman spectrometer (UK) using 325 nm He-Cd light source.

2.4. Photoelectrochemical measurements

The electrochemical impedance spectroscopy (EIS) was determined by Princeton Applied Research VersaSTAT 4 (USA) and 1 M Na_2SO_4 solution was used as the supporting electrolyte.

The Mott-Schottky plots (MS) were carried out using a standard three-electrode cell, a platinum wire as counter electrode and Ag/AgCl as the reference electrode, 100 mL of Na_2SO_4 solution (1 M) was used as the electrolyte by an electrochemical workstation (CHI 660E, Shanghai Chenhua, China).

Hall Effect measurement was performed by Swin HALL 8800 (Taiwan).

2.5. Photocatalytic activity tests

The photocatalytic performance of pure NiO, pure ZnO and different NiO/ZnO composites were estimated by photodegradation of RhB and p-nitrophenol with a concentration of 10 mg/L. For reaction, 100 mg of photocatalysts were added into 200 mL of solution in a quartz beaker. The mixture was first kept in the dark condition for 0.5 h under magnetic stirring. The initial pH of RhB and p-nitrophenol of the solution were 4.76 and 5.78 respectively, without adjustment during the photocatalysis process. Afterwards, a 350 W Xenon lamp equipped was used as a UV–vis light source (320 nm–800 nm). At every interval time, the UV–vis spectra of RhB solution and p-nitrophenol solution were measured, and the absorbance at 553 nm and 318 were used to estimate the RhB and p-nitrophenol concentration. Agilent 1260 High Performance Liquid Chromatography (HPLC, USA) and Agilent 6410 Liquid Chromatography Mass Spectrometer (LC–MS, USA) were also used to identify the degradation intermediates of RhB.

3. Results and discussion

3.1. Structure characterization

3.1.1. XRD patterns analysis

Fig. 1 shows the XRD patterns results of the pure NiO, pure ZnO, and NiO/ZnO composites with different ratios of Ni/Zn and NiO/ZnO without MOFs structure. For pure NiO the same diffraction peaks of NiO have been evidently detected, in which the peaks at 37.2°, 43.3°, 62.9° and 75.4° are corresponding to the diffraction peaks of

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