



Bimetal-organic frameworks derived carbon doped ZnO/Co₃O₄ heterojunction as visible-light stabilized photocatalysts

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ABSTRACT

The construction of transition-metal oxygen heterojunction photocatalysts has been paid close attention for application of versatile functionalities. Many methods have been developed and applied to improve photocatalytic performance, such as doping and morphology control. In this study, carbon (C)-doped binary oxide heteronanostructures with hollow dodecahedra morphology are fabricated by means of topotactic transformation of metal-organic frameworks. The converted hollow C doping ZnO/Co₃O₄ nanocomposite with large specific area has advantage in charge transfer and charge-separation efficiency, and then is evaluated by degrading methylene blue (MB) under visible light irradiation ($\lambda > 400$ nm). The experiment demonstrates the optimal catalytic performance is about 8.4-fold k values of pure ZnO. Importantly, the in-situ synthesized composites show noteworthy stability and recyclability, even after five runs. A possible photocatalytic mechanism also is mentioned, the results illustrate that synergistic effect of coupled semiconductor system with C doping dramatically suppresses the recombination of photogenerated electron-hole pairs, and the hydroxyl radicals (\cdot OH) and holes play a critical role. This work exhibits an effective method for the design of other nonmetal doping sound heterojunctions with well-controlled morphology that significantly enhance photocatalytic behavior.

1. Introduction

Solar energy is the most abundant and available clean energy source today [1–3]. In this manner, it is essential to utilize solar energy for green environmental pollution management [4–6]. Inspiration by the pioneering work of Fujishima and Honda in 1972, semiconductor-based photocatalysts and photocatalytic processes have attracted much attention recently [7]. Compared with TiO₂ investigated mostly, Co₃O₄ is an intriguing semiconductor revealing excellent optical, electronic, and other physical and chemical property [8–11]. Besides, the narrow band gap of Co₃O₄ could reduce the excitation energy of electron-hole pairs separating, while the high electron mobility of Co₃O₄ is benefit for photocatalytic activity improvement [12]. Unfortunately, it is generally accepted that the fast recombination of photogenerated electron-hole pairs is still a significant challenge.

It is well established that the heterojunction is an ideal solution for efficacious electron collection and separation of semiconductor [13]. For the principle, the p-type and n-type semiconductor could create an interface, the formed p-n heterojunction with a space-charge region at the interfaces demonstrates an electronic field caused by the migration

of electrons and holes, which emerges an outstanding ability to separate the electron-hole pairs [14–18]. Numerous efforts for blending with other compounds such as Bi₂O₃, Bi₂WO₆, g-C₃N₄, etc. have been gotten to optimize Co₃O₄-based photocatalysis property [19–22]. However, the incongruous position of energy band and low efficiency remain an enormous challenge. It's worth noting that the n-type ZnO is attractive and utilized in catalytic field and energy storage, and the appropriate band gap would regulate the recombination of photogenerated electron-hole pairs after compositing with Co₃O₄. Nonetheless, there have been a number of high profile cases compromising to indicate that the normal synthetic methods of metal oxides invariably generate a low specific area [24], limited exposure of active sites by the poor surface area would restrict the catalytic efficiency [25]. Furthermore, the direct ZnO/Co₃O₄ heterojunction without the linkage is unbeneficial for the rapid charge transfer via the boundary. Hence, it's urgent to take measures to further advance photocatalytic performance.

Recent developments of metal organic frameworks (MOFs) have attracted much attention because of its abundant porous and large specific area, which make it have potential utilization in energy storages, light harvesting, catalysis and drug delivery [26–28].

Abbreviations: MOFs, metal-organic frameworks; ZnCo12, ZnO/Co₃O₄ 1:2; ZnCo11, ZnO/Co₃O₄ 1:1; ZnCo21, ZnO/Co₃O₄ 2:1; MB, methylene blue

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Moreover, the carbon doping metal oxides ramifications derived from MOFs also continue to be a great capacity. In addition to this, the morphology of ramifications could be tailored and epitaxial prepared by the unique structure of MOF precursors, which provides a fresh route for nonmetal doping of metal oxides synthesis [29–31].

In this study, we design and synthesize hollow C doping ZnO/Co₃O₄ (ZnO/Co₃O₄/C) dodecahedron heterojunctions with MOF precursors. Although the ZnO/Co₃O₄ hybrid composites were mentioned in previous reports, to the best of our knowledge, the hollow ternary compound involved amorphous carbon is generated firstly with MOFs precursor as photocatalysts. Importantly, the as-obtained sample simultaneously possesses initial MOF morphology (porous structure with connected nanoparticles) along with abundant C doping, which promote the charge transfer and separation [32]. Therefore, the sufficient physical integration of nanoparticle and C doping is a promising approach to obtain superior performance photocatalysts. To sum up, The as-prepared ZnO/Co₃O₄/C composites reveal several extensional advantages: 1) large specific area of MOF based materials is benefit for exposure of active sites; 2) C doping can serve as a potentially vital pathway to increase the charge mobility of photocatalysts most efficiently; 3) the in situ synthesized composite could furnish more inter-operable interface than ex situ process; 4) the composite was prepared with a simple method, which avoids the complex dislodge template process of hollow structure; 5) the hollow structures further magnify the contact of catalyst and dye. Moreover, The ZnO/Co₃O₄/C composite displays an enhancement of inherent absorbance than the pure ZnO for visible light.

2. Materials and methods

2.1. Preparation of MOFs

In a typical synthesis process, 2.97 g Zn(NO₃)₂·6H₂O (10 mmol) and 1.45 g Co(NO₃)₂·6H₂O (5 mmol) were dissolved in 150 mL methyl alcohol and stirred for 30 min to form a solution A. 4.97 g 2-methylimidazole was added into 50 mL methyl alcohol to form a clear solution B. Then solution B was poured into solution A slowly with continuous stirring for 15 min. The resulted solution was aged for 24 h at room temperature. And the MOF after centrifugation was dried at 60 °C for 12 h. The different MOFs were prepared with different molar ratios of Zn(NO₃)₂·6H₂O and Co(NO₃)₂·6H₂O.

2.2. Preparation of metallic oxide

The ZnO/Co₃O₄/C was synthesized by one-step calcination process. The as-prepared MOFs were transferred into a crucible and heated to 400 °C for 100 min. The ZnO/C and Co₃O₄/C were obtained with different MOF precursors.

2.3. Characterization

The crystalline phase and phase composition analysis of all the prepared samples were carried out by the X-ray diffractometer (XRD) using Cu Kα (λ = 1.5406 Å) radiation source. The morphologies of all the samples were performed by Transmission electron microscopy (TEM) on a JEOL JEM-2100 at the acceleration voltage of 200 kV and Scanning electron microscopy (SEM), moreover, High resolution transmission electron microscopy (HRTEM) and elemental mapping were also used to characterize the samples. The surface chemistries of the as-prepared samples were measured by X-ray photoelectron spectroscopy (XPS) in ESCALAB250Xi system with Mg Kα X-ray sources. The C1s peak at 284.6 eV was utilized to calibrate the whole of XPS spectra. The specific surface area was detected by BET N₂ adsorption-desorption isotherms. UV–vis absorption spectra were acquired with the use of a UV-2550, Shimadzu, Japan spectrophotometer. The photoluminescence (PL) spectra analyses were conducted with Horiba

Jobin Yvon iHR320 imaging spectrometer.

2.4. Catalytic activity measurements

The activities of the catalysts were evaluated in a 200 mL reaction vessel containing MB as a model organic contaminant with the initial concentration of 10 mg/L⁻¹. A 300 W Xe lamp provided a visible light source with a 400 nm cutoff filter at 15 cm distance. The process temperature was maintained via using circulation condensed water. In each typical experiment, 100 mL of MB aqueous solution containing 50 mg of catalytic amount was first kept in the dark under magnetical stirring for 1.5 h to establish the adsorption-desorption equilibrium. Then, at each 20 min interval of irradiation time, 3–5 mL of suspensions was taken and centrifuged (13,000 rpm, 1 min). Soon afterwards, the liquid supernatants was collected to monitor the change process of MB concentration by using the UV–vis spectrophotometer at 664 nm [31].

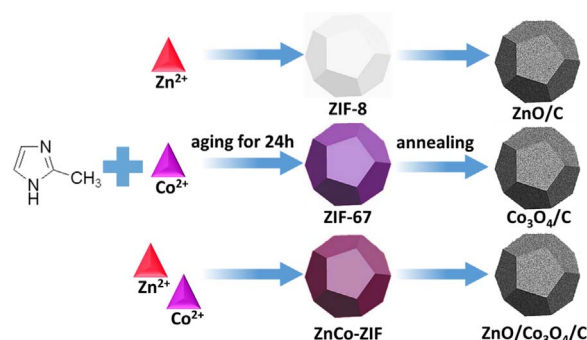
3. Results and discussion

3.1. Characterization of the as-prepared samples

The typical synthesis process of the materials was exhibited in Scheme 1. The MOFs were prepared by dropping 2-methylimidazole into metallic solution and aged for 24 h, and the metallic oxides were synthesized with one-step carbonization process of the obtained MOFs. The molar ratio of ZnO to Co₃O₄ in the preparation of different heterojunctions was approximately 1:2 for ZnCo12, 1:1 for ZnCo11, and 2:1 for ZnCo21. And the bare ZnO/C and Co₃O₄/C were also prepared with singular metallic solution as contrast.

The understanding of crystal phases for ZnO/Co₃O₄/C composites supported by the XRD analysis was revealed in Fig. 1a. The three samples showed the existing of both crystal ZnO (JCPDS No. 76-0704) and Co₃O₄ (JCPDS No. 74-2120), which meant that the crystalline had no change by adjusting the metal ratios. However, the peak intensity of each oxide in the three samples was completely different. The peaks of ZnO turned weakness with the increment of Co₃O₄, this phenomenon indicated the oxides had the same crystal state but different concentration in different composites. Thermogravimetric analysis (TG) was carried out for the sake of clearness the process of synthesizing ZnCo12 by MOFs precursor (Fig. 1b). First weight loss before 200 °C corresponded to the removal of water molecules, and pyrolysis occurred at 310 °C, that generated carbon and metal oxide, and then quality rapidly reduced at 520 °C due to the oxidation of carbon in the material. Until 600 °C, weightlessness was to stop and the carbon in the material remove. Experiment showed that ZnO, Co₃O₄ and carbon species existed at the same time with calcination temperature of 400 °C.

The morphologies of the samples were characterized by SEM and TEM images. As revealed in Fig. 2a, the MOFs had a normative regular dodecahedron structure with a diameter of approximately 400 nm, while after calcination, the samples of oxide turned into a sunken hollow dodecahedron structure. For the ZnO/Co₃O₄/C composites



Scheme 1. Synthesis scheme of ZnO/C, Co₃O₄/C and ZnO/Co₃O₄/C.

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