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Novel magnetic Fe_3O_4/ZnO/$NiWO_4$ nanocomposites: Enhanced visible-light photocatalytic performance through p-n heterojunctions

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ABSTRACT

Fe_3O_4/ZnO/$NiWO_4$ nanocomposites with p-n heterojunctions were synthesized through a facile refluxing method at 96 °C. The as-prepared samples were characterized using XRD, EDX, SEM, TEM, UV–vis DRS, FT-IR, PL, and VSM instruments. It was found that in the nanocomposites, Fe_3O_4, ZnO, and $NiWO_4$ components were uniformly combined to each other. Photocatalytic activity of the nanocomposites was evaluated by degradation of rhodamine B under visible-light irradiation, revealing that the nanocomposites exhibit enhanced photocatalytic activity compared to the Fe_3O_4/ZnO and Fe_3O_4/$NiWO_4$ samples. Photocatalytic activity of the Fe_3O_4/ZnO/$NiWO_4$ (40%) nanocomposite was enhanced 36 and 6.3-times relative to the Fe_3O_4/ZnO and Fe_3O_4/$NiWO_4$ samples, respectively. This enhancement was explained by the efficient separation of the photogenerated electron–hole pairs due to formation of p-n heterojunctions between $NiWO_4$ and ZnO semiconductors. Additionally, it was found that h^+ and $\cdot O_2^-$ species generated in the photocatalytic process played a key role in the degradation reaction. More importantly, the nanocomposite can be separated from the reaction media by applying an external magnetic field and it can be reused for five cycles without significant changes in the degradation efficiency.

1. Introduction

With the population growth and industrial development in the past decades, the environment has seriously deteriorated [1]. It is well known that water pollution considerably influences on our living standards. According to World Health Organization, about 780 million people have no access to affordable drinking water [2]. On the other hand, sources of fresh water is strongly limited. Hence, purification of wastewaters from industrial, agricultural, and pharmaceutical sources has attracted much attention from the research communities. For this purpose, different strategies such as physical, chemical, and biological methods have been used for decades [3,4]. Heterogeneous photocatalytic processes, as one of the most effective and green methods of advanced oxidation processes, are promising procedures to manipulate different environmental concerns [5]. In photocatalytic processes using semiconductors, one can ideally degrade wide variety of organic pollutants to non-hazardous components. Among various photocatalysts, ZnO has extensively employed, owing to its attractive properties such as nontoxicity, low price, and high stability [6]. Unfortunately, this wide band gap semiconductor mainly absorbs UV fraction of the solar irradiation with nearly 4% of its total energy, restricting its industrial application [7]. Hence, a large number of attempts have been paid to achieve higher visible-light absorption capacity of ZnO through doping different elements and combining narrow band gap semiconductors [8–19]. In addition, recombination of the photogenerated electron-hole pairs decreases efficiency of the photocatalytic processes. To overcome this problem, an appropriate combination of semiconductors are generally applied [20–25].

Metal tungstate semiconductors with formula of MWO_4 (M is cation of transition metals such as Fe, Co, Ni, and Cu with +2 charge) have a wide range of applications including gas sensors, optical fibers, humidity sensors, pigments, and catalysts [26–32]. Nickel tungstate is an intrinsic p-type semiconductor with a narrow band gap of 2.20 eV [27,28]. Very recently this semiconductor was prepared and applied as catalyst, heterogeneous photocatalyst for degradation of pollutants, antimicrobial material, and generation of hydrogen through water splitting [33–35]. As a p-type semiconductor, $NiWO_4$ has a potential to form p-n heterojunction with ZnO. Hence, it seems that by formation of p-n heterojunction between $NiWO_4$ (as a narrow band gap semiconductor) and ZnO (as a wide band gap semiconductor), not only significant numbers of electron-hole pairs could be produced under visible-light irradiation, but also the photogenerated charge carriers could be

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efficiently separated, resulting in highly enhanced photocatalytic performance [36–39]. On the other hand, the separation and recycling of the applied catalysts are still a serious problem for the heterogeneous photocatalytic processes. Fabrication of magnetically separable photocatalysts are convenient strategy to overcome this problem using an external magnetic field [40].

In this paper, novel magnetic Fe_3O_4/ZnO/$NiWO_4$ nanocomposites with highly enhanced photocatalytic activity are reported. The as-prepared samples were characterized for the structural, morphological, optical, and magnetic properties using X-ray diffraction (XRD), energy dispersive analysis of X-rays (EDX), scanning electron microscopy (SEM), transmission electron microscopy (TEM), UV–vis diffuse reflectance spectroscopy (DRS), Fourier transform-infrared spectroscopy (FT-IR), photoluminescence spectroscopy (PL), and vibrating sample magnetometer (VSM). For evaluation photocatalytic activity of the prepared nanocomposites under visible-light irradiation, three dye pollutants of rhodamine B (RhB), methylene blue (MB) and methyl orange (MO) were applied. The matching of energy-band structures between ZnO and $NiWO_4$ semiconductors through p-n heterojunctions induced an efficient way for transfer of the photogenerated charge carriers, resulting in the subsequent promotion of photocatalytic activity. Meanwhile, through combining of Fe_3O_4 nanoparticle with ZnO and $NiWO_4$ semiconductors, the novel ternary photocatalyst showed magnetically separability. In addition, the prepared nanocomposites showed considerably activity in degradation of different dye pollutants under visible-light irradiation. Finally, a plausible mechanism for the enhanced activity was proposed for the ternary nanocomposites.

2. Experimental

2.1. Materials

All reagents were at least of analytical grade and used without further purification. Some chemicals, such as zinc nitrate ($Zn(NO_3)_2{\cdot}4H_2O$), ferric chloride ($FeCl_3{\cdot}6H_2O$), ferrous chloride ($FeCl_2{\cdot}4H_2O$), sodium hydroxide, and nickel nitrate ($Ni(NO_3)_2{\cdot}6H_2O$) were purchased from Loba Chemie Company. Other chemicals such as hydrochloride acid, RhB, MO, and MB, sodium tungstate ($Na_2WO_4{\cdot}H_2O$), 2-propanol, ammonium oxalate, benzoquinone, and absolute ethanol were supplied by Merck Company. All experiments were carried out in deionized water.

2.2. Instruments

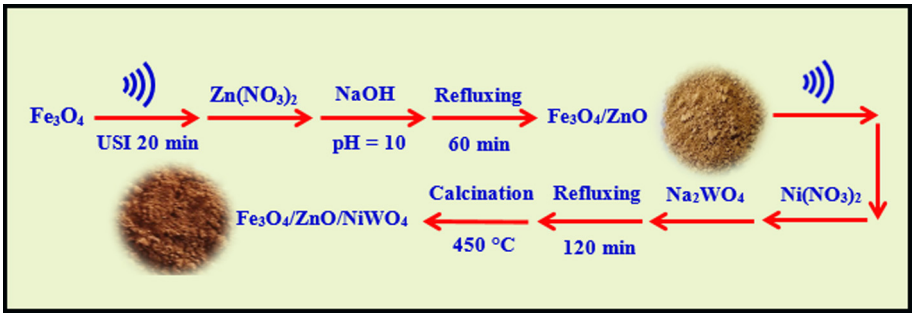
The XRD patterns were recorded by a Philips Xpert X-ray diffractometer with Cu Ka radiation ($\lambda = 0.15406$ nm), employing scanning rate of 0.04°/s. Surface morphology and distribution of particles were studied by LEO 1430VP SEM, using an accelerating voltage of 15 kV. The purity and elemental analysis of the products were obtained by EDX on the same SEM instrument. The TEM investigations were performed by a Philips CM30 instrument with an acceleration voltage of 150 kV. The DRS spectra were recorded by a Scinco 4100 apparatus. The FT-IR spectra were obtained by a Perkin Elmer Spectrum RX I apparatus. The PL spectra of the samples were studied using a Perkin Elmer (LS 55) fluorescence spectrophotometer with an excitation wavelength of 300 nm. UV–vis spectra for the degradation reaction were studied using a Cecile 9000 spectrophotometer. Magnetic properties of the samples were obtained using a VSM instrument (Meghnatis Kavir Kashan Co., Iran). The ultrasound radiation was performed using a Bandelin ultrasound processor HD 3100 (12 mm diameter Ti horn, 75 W, 20 kHz). The pH of solutions was measured using a Metrohm digital pH meter of model 744.

2.3. Preparation of the samples

Nanoparticles of Fe_3O_4 were prepared using a chemical co-precipitation process described elsewhere [41]. The Fe_3O_4/ZnO (1:4) nanocomposite was prepared using the method reported by our research group [42]. For combining $NiWO_4$ to Fe_3O_4/ZnO nanocomposite, 0.3 g of the Fe_3O_4/ZnO nanocomposite was dispersed in 150 mL of water under ultrasonic irradiation for 5 min. Then, 0.189 g of nickel nitrate was added and the suspension was mechanically stirred 30 min. Afterwards, 0.214 g of sodium tungstate was separately dissolved in water. Then, the solution was added dropwise into the Fe_3O_4/ZnO suspension under constant stirring for 30 min. Thereafter, the suspension was refluxed at 96 °C for 2 h. The formed Fe_3O_4/ZnO/$NiWO_4$ nanocomposite was washed with water and ethanol for several times and recovered by magnetic separation. Finally, the dried particles were calcined at 450 °C for 3 h in air atmosphere (Scheme 1).

2.4. Photocatalysis experiments

Photocatalysis experiments were performed under a LED lamp of 50 W, as visible-light source. Experiments were carried out in a glass reactor with a circulating water system to maintain the temperature at 25 °C. In each test, 0.1 g of the photocatalyst was added into 250 mL of the solution containing RhB, MB, or MO with concentration of 1×10^{-5} M. Then, the suspension was stirred in the dark for 60 min to achieve the adsorption–desorption equilibrium prior to visible-light irradiation. During the light irradiation, about 2 mL of the suspension was taken out and the photocatalyst removed before measurement concentration of the dyes at 553, 664, and 477 nm corresponding to the maximum absorption wavelengths of RhB, MB, and MO, respectively.



Scheme 1. Schematic illustration for the preparation of Fe_3O_4/ZnO/$NiWO_4$ nanocomposites.