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Invited paper

The influence of MCM-41 mesoporous shell in photocatalytic activity of magnetic core-shell

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ABSTRACT

A novel Fe₃O₄@MCM-41/CuO core-shell photocatalyst was successfully fabricated by hydrothermal and precipitation methods over Fe₃O₄ core, followed by light reduction. The obtained nanocomposites were characterized by various measurements and the photocatalytic performances of the as-prepared core-shell were assessed by the degradation of methylene blue (MB) under visible-light illumination. The photocatalyst exhibits higher and wider absorption in the visible region than the pure Fe₃O₄ and it displays superior performance in the degradation of MB. The highest efficiency of Fe₃O₄@MCM-41/CuO photocatalyst to degrade MB in presence and absence of H₂O₂ was 75 and 70% at 60 min, respectively. On the basis of the obtained experimental results, the probable photocatalytic mechanism of the enhanced activity is discussed. The degradation of MB is not only influenced by active groups, but also the interaction of MCM-41 and Fe₃O₄ decreased the recombination of electron-hole pairs in CuO semiconductor due to transferring electron from mesoporous cavity of MCM-41 to iron ions in Fe₃O₄ core.

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1. Introduction

Semiconductor nanomaterials have been widely used as photocatalysts for environmental problems [1]. Among them, TiO₂ has been most extensively investigated for its nontoxicity, chemical stability, water insolubility and favorable photocatalytic properties [2]. Nonetheless, the band gap of titanium dioxide is too large to be excited by visible light, which means only 4% of the solar energy in UV light can be applied. In the other hand, it cannot be rejected that the semiconductors with small band gap exhibit high recombination rate of photogenerated electrons and holes; as a result, the efficiency of photocatalytic conversion has been greatly decreased [3]. So, it is important to find appropriate procedures to dominate these problems. Plentifully available in the earth crust, copper oxide (CuO) with a small band gap around 1.70 eV can greatly absorb visible light compared to TiO₂ [4]. In order to decrease the recombination rate of photogenerated electron-hole pairs, noble metals such as Au, Pt and Ag, have been loaded onto the surface of the catalysts or CuO is bonded with other materials such as ZnO or TiO₂ or adding H₂O₂ in reaction media [5]. Another problem in the industrial applications of CuO nanoparticles (NPs) lies in the re-collection of NPs from treated water. Using magnetic

photocatalysts is the best solution to overcome to this problem [6,7]. In our previous work [8], Fe₃O₄@MOR@CuO core-shell with two shells (mordenite zeolite and CuO), as a visible light photocatalyst, were synthesized. In order to reduce the recombination rate of photogenerated electron-hole pairs, mordenite zeolite was used instead of noble metal, bonding with other materials or adding H₂O₂. Mordenite zeolite is a microporous material with Al atoms in framework structure. These cases of mordenite structure plays an important role in reducing the recombination of electrons-holes and preparation of active species for degradation of dye. In this study, a hybrid of a magnetic Fe₃O₄ cores along with MCM-41 shell and CuO NPs were constructed. MCM-41 was used instead of mordenite zeolite. Pure siliceous MCM-41 material possesses many unique properties such as high surface area, high pore volume, as well as parallel and ideally shaped pore structures without the complications of a network [9,10]. The aim of this work was the investigation of the effect of pore size in transfer rate of electrons from conduction band of semiconductor to magnetic core. The reports indicated the preparation of magnetite core with a mesoporous shell [11,12], as well as the deposition of CuO NPs on the surface of the MCM-41 powder [13]. There is no report on the controlled synthesis of Fe₃O₄@MCM-41/CuO core-shell as a photocatalyst and study of the influence of pore size in photocatalytic mechanism.

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2. Experimental

2.1. Materials

Tetraethylorthosilicate (TEOS, 98%), ammonia (25 wt.%), the surfactant cetyltrimethylammonium bromide (CTABr), Cu (NO₃)₂·3H₂O, NaOH, NaF, Ferric trichloride hexahydrate, ethylene glycol (EG), ammonium acetate, and ethanol were purchased from Fluka and Merck (Darmstadt, Germany).

2.2. Synthesis of magnetic Fe₃O₄, Fe₃O₄@CuO, MCM-41/CuO and CuO nanoparticles

The synthesis of Fe₃O₄@CuO core-shell, Fe₃O₄ core, MCM-41/CuO nanocomposite and CuO NPs was the same as according to the previous literatures [14,15].

2.3. Synthesis of Fe₃O₄@MCM-41 core-shell

The synthesis of Fe₃O₄@MCM-41 was the same as according to the literature [16] with some modifications. See Electronic Supplementary information (ESI) for more details.

2.4. Synthesis of magnetic Fe₃O₄@MCM-41/CuO core-shell

Magnetic Fe₃O₄@MCM-41/CuO core-shell was prepared via mixing of 60 mL of Cu (NO₃)₂ solutions (0.02 M) with 1.0 g Fe₃O₄@MCM-41. The mixture was then continuously stirred for 24 h at room temperature. The solid product was washed repeatedly with distilled water and finally dried at 50 °C in a vacuum oven. The Fe₃O₄@MCM-41/Cu²⁺ was calcined in a muffle furnace at 550 °C for 6 h in air. The calcined samples are abbreviated as Fe₃O₄@MCM-41@CuO.

2.5. Evaluation of photocatalytic activity

Photodegradation experiments were performed with a photocatalytic reactor system. This bench-scale system consisted of cylindrical Pyrex-glass cell with 250 mL capacity, 10 cm inside diameter and 15 cm height. See Electronic Supplementary information (ESI) for more details.

2.6. Characterizations

The constructed properties of the MCM-41 materials were characterized using a variety of techniques. See Electronic Supplementary information (ESI) for more details.

3. Results and discussion

3.1. Characterization of Fe₃O₄@MCM-41/CuO core-shell

The crystalline structure of the Fe₃O₄@MCM-41/CuO core-shell was investigated by XRD, and the corresponding patterns were illustrated in Fig. 1. The XRD patterns of pure Fe₃O₄ pure CuO NPs, and MCM-41 were also presented as controls. The diffraction peaks for CuO and Fe₃O₄ can be indexed (Fig. 1a,b) to a CuO monoclinic phase, matching well with JCPDS 05-0661 [17] and cubic phase of Fe₃O₄ (with standard diffraction card JCPDS 19-0629) [18]. The XRD pattern of synthesized Fe₃O₄@MCM-41 core-shell indicated (Fig. 1c) different peaks at (2θ) = 30.23° (220), 35.73° (311), 43.31° (400), 57.21° (411) and 62.47° (440) corresponds to different planes of cubic phase of Fe₃O₄ and one strong diffraction at (2θ) = 2.75° (100) that corresponds to a hexagonal structure from MCM-41 [19].

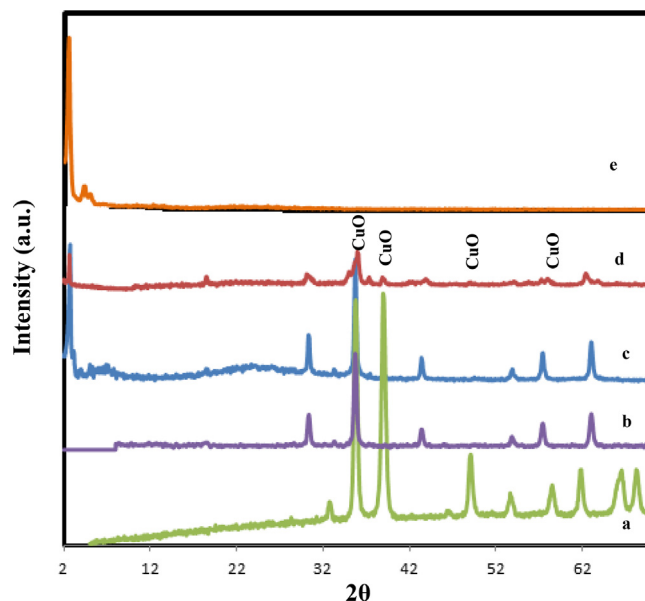


Fig. 1. XRD patterns of (a) CuO, (b) Fe₃O₄, (c) Fe₃O₄@MCM-41, (d) Fe₃O₄@MCM-41/CuO and (e) MCM-41.

The XRD pattern of Fe₃O₄@MCM-41/CuO core-shell (Fig. 1d) showed peaks that could be indexed to mesoporous structure (Fig. 1e), CuO NPs and Fe₃O₄ core. There was broadening of core-shell peaks in comparison with MCM-41, Fe₃O₄ and CuO alone, and this can be related to the quantum size effect of core-shell. Scherrer's formula [14] was used for calculating crystal size of core and shells. The average crystal size of Fe₃O₄ core, MCM-41 shell and CuO NPs were 12.00, 27.72 and 12.00 nm, respectively. Meanwhile, no obvious diffraction peaks attributed to Cu, and Cu₂O NPs were observed.

The structure of magnetic Fe₃O₄@MCM-41/CuO core-shell could also be confirmed by FTIR as shown in Fig. 2. The FT-IR spectrum of Fe₃O₄ cores showed the strong peak at 579 cm⁻¹ that in both samples (Fe₃O₄@MCM41 and Fe₃O₄@MCM-41/CuO core-shell) that observed at about 585 cm⁻¹. This peak can relate to the characteristic absorption band of Fe-O bond in Fe₃O₄ cores [20]. The FT-IR spectrum of MCM-41 matrix shows (Fig. 2 insert) bands at 1085.35, 804.26 and 462.33 cm⁻¹ which can be attributed to Si-O-Si bending and stretching vibrations. The spectrum of OH-groups in the parent MCM-41 shows bands at 3446.56 and 1641.31 cm⁻¹ which belong to acidic bridged hydroxyls [21]. The FT-IR spectrum of Fe₃O₄@MCM-41 core-shell demonstrated peaks at 1072.33, 800.76 and 450.95 cm⁻¹ which can be attributed to Si-O-Si bending and stretching vibrations. The spectrum of OH-groups in the Fe₃O₄@MCM-41 core-shell showed, band at 3430.12 cm⁻¹ belong to acidic bridged hydroxyls. The three weak peaks at around 2338.92 cm⁻¹, 2854.46 cm⁻¹, and 2925.63 cm⁻¹ were assigned to the vibrations of atmospheric CO₂ and the symmetry and asymmetry stretching vibrations of -CH₂-, respectively [21]. Usually, CuO nanostructures indicate three peaks in the range of 400–700 cm⁻¹ [22]. The FT-IR spectrum of synthesized magnetic Fe₃O₄@MCM-41/CuO core-shell indicated peaks at 469.04 and 586.47 cm⁻¹ that can be related to the Fe-O and Cu-O stretching vibration of Fe₃O₄ and CuO, respectively. All bands in Fe₃O₄@MCM-41/CuO sample, except peak at 3328.55 cm⁻¹, showed a shift to higher wave numbers and increased intensity with respect to core-shell. This confirmed the presence of CuO in Fe₃O₄@MCM-41 core-shell.

The morphological characteristics of Fe₃O₄@MCM-41 and Fe₃O₄@MCM-41/CuO core-shells can be explained by SEM images,

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