ZnCo₂O₄ 纳米粒子的可见光催化性能

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摘要: 研究了共沉淀分解法制备的 ZnCo₂O₄ 纳米粒子的光学和可见光催化性能, 并对其晶体结构和微观结构用 X 射线衍射、热重/差热分析、透射电镜和高分辨透射电镜等手段进行了表征. 结果表明, 制备的纳米粒子为纯相的 ZnCo₂O₄, 平均粒径约为 10–20 nm. 紫外-可见吸收光谱估计出 ZnCo₂O₄ 纳米粒子的能带隙为 3.39 和 2.09 eV. 可见光($\lambda > 420$ nm)照射下, 纳米粒子表现出降解亚甲基蓝溶液的光催化活性. ZnCo₂O₄ 纳米粒子的光催化活性可以归结为紫外和可见光下纳米粒子吸收光子(能量大于能带隙)的能力, 以及它们的纳米尺寸. 基于实验结果, 本文提出了 ZnCo₂O₄ 可能的能带结构.

关键词: 光催化; 纳米结构; 尖晶石氧化物; 能带结构; ZnCo₂O₄
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Visible Light Induced Photocatalytic Activity of ZnCo₂O₄ Nanoparticles

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Abstract: ZnCo₂O₄ nanoparticles were synthesized by a co-precipitation decomposition method and their optical and photocatalytic properties were investigated. Their crystal structure and microstructures were characterized using X-ray diffraction (XRD), thermogravimetry (TG)/differential scanning calorimetry (DSC), transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM). The ZnCo₂O₄ nanocrystallites obtained were single-phase with an average size of 10–20 nm. The optical bandgap energies of the nanoparticles were estimated to be 3.39 and 2.09 eV from the UV-Vis absorption spectrum. The ZnCo₂O₄ nanoparticles exhibited high photocatalytic activity for the degradation of methylene blue dye solution under visible light irradiation ($\lambda > 420$ nm). The photocatalytic activity of the ZnCo₂O₄ nanoparticles is attributed to their ability to absorb bandgap photons under UV and visible light as well as their nanoscale particle size. Based on these experimental results, a possible band structure of ZnCo₂O₄ is proposed.

Key Words: Photocatalysis; Nanostructure; Spinel oxide; Band structure; ZnCo₂O₄

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1 Introduction

ZnCo_2O_4 belongs to a group of spinel oxides with catalytic activities.^{1–3} It was found to be an active electrocatalyst for O_2 evolution reaction⁴ and offered high catalytic activity for the oxidation of $\text{CO}+\text{H}_2$ mixtures.⁵ Recently, it was revealed to be an attractive anode material for the lithium ion batteries.^{6,7} ZnCo_2O_4 is generally regarded to adopt a spinel structure in which Zn^{2+} occupies the tetrahedral sites and Co^{3+} resides in the octahedral sites. In its structure, the solid state redox couple $\text{Co}^{3+}/\text{Co}^{2+}$ is present,^{1,2,4} which provides a notable catalytic activity.

The visible light responsive photocatalyst appears to be the ideal photocatalyst because visible light accounts for 43% of solar energy. However, there have been only a few studies of visible light responsive photocatalyst. TiO_2 -based photocatalysts, such as reduced TiO_x ($\text{TiO}_{2-x}\text{N}_x$) and Au-TiO_2 photocatalyst,^{8–10} have been used in the degradation of methylene blue (MB), a model dye contaminant which evaluates the activity of a photocatalyst^{8,11,12} under visible light; however, the efficiency of TiO_2 -based photocatalysts is limited by the light absorption characteristics of TiO_2 .^{8,9}

Recently, the spinel oxide semiconductors, such as NiCo_2O_4 ^{1,2} and MIn_2O_4 ($\text{M}=\text{Ca}, \text{Sr}, \text{Ba}$),^{3,13} were developed for MB degradation under visible light. In addition, the spinel oxides, such as BaAl_2O_4 , ZnFe_2O_4 , CuMn_2O_4 , and ZnMn_2O_4 ,^{14–16} were discovered to be attractive photocatalysts for splitting water to generate hydrogen.

In previous, ZnCo_2O_4 nanomaterials have been prepared by several solution-assisted synthesis methods. ZnCo_2O_4 nanoparticles have been obtained by thermal decomposition of Zn-Co gel using oxalic acid as a chelating agent¹⁷ and by a urea combustion method⁶. The main advantages of solution-assisted synthesis are low reaction temperatures, mixing at molecular level which facilitates the formation of homogeneous polycrystalline particles, and improved catalytic properties due to high surface areas of the obtained particles.

In this study, the as-synthesized ZnCo_2O_4 nanoparticles were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), and optical UV-Vis absorption measurements. The photocatalytic degradation of MB under UV and visible light was investigated to evaluate the photocatalytic activity of ZnCo_2O_4 . To understand their photocatalytic properties, an electronic band structure of ZnCo_2O_4 was proposed. A description of the correlation between the photocatalytic activity and the electronic band structure was attempted.

2 Experimental

The ZnCo_2O_4 nanoparticles were synthesized *via* a co-precipitation decomposition method. In a typical synthesis, 1.485 g ($0.005 \text{ mol} \cdot \text{L}^{-1}$) of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (>99.9%), and 2.91 g ($0.01 \text{ mol} \cdot \text{L}^{-1}$) of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (>99.9%) were dissolved in deionized water (50 mL). The resulting solution was stirred under flowing N_2 atmosphere at room temperature for 1 h, followed

by the addition of NaOH ($2 \text{ mol} \cdot \text{L}^{-1}$, 25.0 mL, >99.9%) within 5 min. To inhibit the crystalline growth, the co-precipitates were immediately filtered and washed with deionized water and ethanol (>99.7% pure), and dried at room temperature under vacuum overnight. The co-precipitates were heated in air to a temperature T ($T=250, 300, 350, 400, 450 \text{ }^\circ\text{C}$) as follows: the co-precipitates were first heated very slowly to $250 \text{ }^\circ\text{C}$ at a rate of $25 \text{ }^\circ\text{C} \cdot \text{h}^{-1}$, then heated rapidly from $250 \text{ }^\circ\text{C}$ to temperature T at a rate of $600 \text{ }^\circ\text{C} \cdot \text{h}^{-1}$, and annealed at temperature T for 1 h to obtain the powder products.

The thermogravimetry (TG) and differential scanning calorimetry (DSC) curves of the co-precipitates were measured using a TGA2050-DSC2910 apparatus (Shimadzu, Japan). The co-precipitates were heated from room temperature to $1000 \text{ }^\circ\text{C}$ at a rate of $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ under air atmosphere at a gas flow rate of $20 \text{ mL} \cdot \text{min}^{-1}$. The crystalline structures of the precursor and the as-synthesized products were evaluated by XRD analysis using a D/max-RB X-ray diffractometer (RIGAKU, Japan) with filtered $\text{Cu K}\alpha$ radiation of wavelength 0.15418 nm . The precursor and the product were scanned from 10° to 90° , at a scanning rate of $4 (^\circ) \cdot \text{min}^{-1}$. Conventional TEM analysis and high-resolution transmission electron microscopy (HRTEM) were conducted using a JEM-TEM (JEM 2010F, JEOL, Japan). UV-visible absorption spectrum was recorded using a spectrophotometer (UNICAM, UV 500, ThermoSpectronic, UK) at room temperature. The solutions in ethanol were prepared ultrasonically for the UV-visible measurements.

The photocatalytic activities of ZnCo_2O_4 nanoparticles were measured by the degradation of MB in an aqueous solution. A 300 W Xe lamp (PLS-SXE 300UV) was used as a light source supplying the full wavelength illumination. Its emission is strongest from 300 to 700 nm ,¹⁸ covering both UV and visible light region. The Xe lamp with a filter whose cut-off wavelength is 420 nm was used as a visible light source ($\lambda > 420 \text{ nm}$). The photocatalyst (0.2 g) was suspended in a 100 mL aqueous solution of $2.5 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ MB. Before the photocatalytic experiment, the suspension was stirred in the dark for 1 h. The concentration of the MB solution was monitored by measuring the maximum absorbance of MB at 664 nm using the UV-Vis spectrum¹⁹.

3 Results and discussion

3.1 Characterization of materials

Fig.1 shows XRD patterns of the co-precipitate and calcined powder samples at different temperatures. The results show that the co-precipitate is a mixture of $\text{Zn}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$. The calcined powders exhibit diffraction peaks corresponding to a single phase cubic spinel structure for ZnCo_2O_4 . The value of the lattice parameters, ranging from 0.80874 to 0.81342 nm for the samples obtained from 250 to $450 \text{ }^\circ\text{C}$, are in good agreement with the value of 0.80946 nm given in the JCPDS 20-0781 file for ZnCo_2O_4 and no impurities are discernible.

TG and DSC curves of the co-precipitate precursor are

Fig.1 XRD patterns of the co-precipitate and calcined powder samples at different temperatures

Miller indices (*hkl*) of ZnCo_2O_4 are shown.

shown in Fig.2, and it can be seen that thermal decomposition undergoes two distinct stages. The first major stage with a mass loss of 12.76%, observed between the room temperature and 400 °C, is due to the elimination of the hydrated water from hydrate precursor. The theoretical value calculated from Eq.(1) is 13.33%. The difference between the calculated and experimentally determined value is likely due to a higher oxygen content²⁰ corresponding to $\text{ZnCo}_2\text{O}_{4+\delta}$ ($\delta=0.11$). The corresponding mass loss of 3.84% of the second stage, observed between 890 and 950 °C, is due to the decomposition of the ZnCo_2O_4 spinel structure.²⁰ This process (Eq.(2)) is represented by an endothermic peak at 923 °C in the DSC curve (Fig.2).

The microstructures of the as-synthesized ZnCo_2O_4 (calcined at 250 °C) were characterized by TEM and HRTEM. In Fig.3a, the dominant morphology is nanoparticles with a spherical shape and an average size of 10–20 nm. A typical HRTEM image of the nanoparticles is shown in Fig.3b. The two spacings (*d*) of the planes in the lattice image are 0.245 and 0.287 nm, corresponding to ZnCo_2O_4 (311) and (220) planes, respectively. This matches well with the most intense lines in the XRD pattern (Fig.1). The fast Fourier transform (FFT) of the nanoparticle is shown in Fig.3c. The HRTEM observations together with its FFT show that the as-synthesized particles are spinel-structure ZnCo_2O_4 .

Fig.2 TG/DSC curves of the co-precipitate precursor

Fig.3 TEM and HRTEM photographs of ZnCo_2O_4 calcined at 250 °C

(a) low-magnification TEM image; (b) HRTEM lattice image, the lattice spacing of 0.245 nm corresponds to the (311) lattice planes, and the lattice spacing of 0.287 nm corresponds to the (220) lattice planes; (c) corresponding FFT image

ture ZnCo_2O_4 .

3.2 Photophysical and photocatalytic properties

The darkish ZnCo_2O_4 nanoparticles display good absorbance of light between 200 and 600 nm, as shown in Fig.4a. The absorption bandgap energy, E_g , can be determined by the following equation:^{2,21,22}

$$(ah\nu)^n = K(h\nu - E_g) \quad (3)$$

Fig.4 (a) UV-Vis absorption spectrum for the ZnCo_2O_4 nanoparticles; (b) $(ah\nu)^2-h\nu$ curve for the ZnCo_2O_4 nanoparticles indicating that the two direct bandgap energies are 3.39 and 2.09 eV

where $h\nu$ is the photo energy, α is the absorption coefficient, K is a constant relative to the material, and n is either 2 for a direct transition or 1/2 for an indirect transition. The $(\alpha h\nu)^2-h\nu$ curve for the ZnCo_2O_4 nanoparticles is shown in Fig.4b. The bandgap energies of the ZnCo_2O_4 nanoparticles are calculated to be 3.39 and 2.09 eV, by the extrapolation of Eq.(3). No linear relation was found for $n=1/2$, suggesting that the ZnCo_2O_4 nanoparticles are semiconduct with direct transitions at these energies.

The photocatalytic activity of ZnCo_2O_4 nanoparticles was evaluated by measuring the degradation of MB aqueous solution (Fig.5). The concentration of MB solution with ZnCo_2O_4 photocatalyst keeps nearly constant in the absence of light, indicating that no chemical reactions occur inside the system without light irradiation. When the filter (whose cut-off wavelength is 420 nm) was used, the MB degradation was caused by only visible light (Fig.5). When the filter was not used, the MB degradation was caused by both UV and visible light. By subtracting the MB degradation by visible light from this curve, the MB degradation by UV light can be estimated. As shown in Fig.5, ZnCo_2O_4 nanoparticles show higher photocatalytic activity in the visible light region than in the UV light region.

3.3 Discussion of band structure

It is generally accepted that in the spinel structure of ZnCo_2O_4 , the divalent cations (Zn^{2+}) occupy the tetrahedral sites, whereas the trivalent cations (Co^{3+}) reside in the octahedral sites.^{14,23} The general description of the electron configuration in this structure²³ is tetrahedral high spin Zn^{2+} ($e_g^4 t_{2g}^6$) with octahedral low spin Co^{3+} (t_{2g}^6). The band structure of ZnCo_2O_4 is generally defined by taking O 2p orbital as the valence band and Co 3d orbital as the conduction band.^{2,14,23} Since the high level Co 3d- e_g orbital is not filled, the excitation of electrons from the partially filled Co 3d- t_{2g} orbital to the empty Co 3d- e_g orbital is possible. The internal electron transitions in partially filled Co 3d orbitals may make a significant contribution to the band structure of ZnCo_2O_4 , as in the case of Ni-doped InTaO_4 ,²⁴ NiCo_2O_4 ,² and BaCr_2O_4 .¹⁴

Taking into account the band gap energies calculated from

Fig.5 Photocatalytic MB degradation under dark, visible light ($\lambda > 420$ nm), UV+visible light, and UV light (estimated) at room temperature over the ZnCo_2O_4 nanoparticles

Fig.6 Schematic illustration of the electronic band structure of ZnCo_2O_4

different photoexcitations of electrons: (1) from O 2p to Co 3d- e_g , (2) from O 2p to Co 3d- t_{2g} and (3) from Co 3d- t_{2g} to Co 3d- e_g , they are induced by the irradiation of UV and visible lights accordingly.

the UV-Vis absorption spectrum, a simplified electronic band structure of ZnCo_2O_4 is proposed and schematically illustrated in Fig.6. However, the absolute values of O 2p, Co 3d- e_g , and Co 3d- t_{2g} energy levels could not be resolved from this study. It can be assumed that three kinds of photoexcitation of electrons can take place with respect to the energy of incident photons: (1) from O 2p to Co 3d- e_g ; (2) from O 2p to Co 3d- t_{2g} ; and (3) from Co 3d- t_{2g} to Co 3d- e_g . The photoexcitations (1) and (2) correspond to two direct energy bandgaps of ZnCo_2O_4 , respectively, which are 3.39 and 2.09 eV. The photoexcitation (3) is also possible, which may play an important role in the photoexcitation and photocatalytic activity.^{2,14,24}

The photocatalysis of an oxide semiconductor involves the absorption of bandgap photons, the separation of electron-hole pairs, and the redox reaction on the surface of catalyst. The excitation of an electron from the valence band to the conduction band is initiated by the absorption of a photon with energy equal to or greater than the bandgap energy of the semiconductor. Under UV light irradiation, for ZnCo_2O_4 , an electron generated by a photon with the energy higher than 3.39 eV ($\lambda < 366$ nm, according to the equation: $\lambda = 1240/E_g$ (where λ in nm, E_g in eV)), can be directly excited from the O 2p valence band to the Co 3d- e_g conduction band. Under visible light irradiation, an electron generated by a photon with the energy higher than 2.09 eV ($366 \text{ nm} < \lambda < 593 \text{ nm}$), can be directly excited from the O 2p valence band to the Co 3d- t_{2g} conduction band. In addition an electron can be firstly excited from the O 2p valence band to the Co 3d- t_{2g} conduction band, and then transferred from the Co 3d- t_{2g} conduction band to the Co 3d- e_g conduction band. Eventually, the photogenerated electrons and holes are thought to participate in the complex redox reaction on the surface of catalyst, leading to the degradation of MB.^{8,11,12}

For ZnCo_2O_4 photocatalyst, the high UV-visible light absorption is effective in generating charge carriers (e^-/h^+). In addition, ZnCo_2O_4 nanoparticles exhibit a nanoparticle size (10–20 nm). For nanoparticles, the diffusion length of electrons and holes (e^-/h^+) from the bulk to the surface is short, which helps accelerate

the migration rate of e^-/h^+ to the surface of the nanoparticle to participate in the reaction process.^{25,26} Therefore, the MB degradation efficiency of the ZnCo₂O₄ nanoparticles is attributed to their ability to absorb bandgap photons under UV and visible light as well as their nanoparticle size.

4 Conclusions

ZnCo₂O₄ nanoparticles synthesized by a co-precipitation decomposition method were characterized and their photocatalytic properties were investigated. The ZnCo₂O₄ nanocrystallines obtained were single-phase with an average size of 10–20 nm. From the UV-Vis absorption spectra, the optical bandgap energies of the nanoparticles were estimated to be 3.39 and 2.09 eV. The ZnCo₂O₄ nanoparticles exhibited high photocatalytic activity for the degradation of MB solution under visible light irradiation (>420 nm). The photocatalytic activity of the ZnCo₂O₄ nanoparticles is attributed to their ability to absorb bandgap photons under UV and visible light as well as their nanoparticle size. On the basis of these experimental results, a possible band structure was suggested, where the valence band of the photocatalyst was the O 2p level and conduction bands were composed of the Co 3d- e_g and Co 3d- t_{2g} levels, respectively.

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