



Preparation and Photocatalytic Activity of Cu₂O/Nickel-Zinc Ferrite Magnetic Photocatalyst†

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Nickel-zinc ferrite powders were prepared by EDTA-complexing method, Cu₂O/nickel-zinc ferrite magnetically separable photocatalyst was prepared by the hydrazine hydrate reduction method. The as-prepared sample was characterized by X-ray diffraction, high resolution transmission electron microscopy, Fourier transform infrared spectroscopy, the photocatalytic activity of the sample was evaluated by degradation of methyl orange under the UV illumination. The results show that the Cu₂O coating nickel-zinc ferrite is cubic structure. Cu₂O/nickel-zinc ferrite powders have photocatalytic activity under the irradiation of ultraviolet light, the Cu₂O/nickel-zinc ferrite powders still have magnetic property and can be separated from the system by applying magnetic field.

Key Words: Nickel-Zinc Ferrite, Load, Cu₂O, Magnetic photocatalyst.

INTRODUCTION

In recent years, the semiconductor photocatalysis technique has attracted significant attention as a way to solve the problems of environmental pollution^{1,2}. Cu₂O is a *p*-type semiconductor with a direct band gap of 2.0 eV and has important application in hydrogen production, superconductors, solar cells and negative electrode materials for lithium ion batteries, *etc.*³. It also has a potential application in degradation of organic pollution⁴. In addition, because the Cu₂O photocatalytic reaction is generally carried out in a suspension of Cu₂O particles, an additional separation step is required to remove the catalyst from the treated solution. To simplify the catalyst recovery step, an immobilization process has been used, in which Cu₂O is coated on recoverable substrates. In this paper, we prepared Cu₂O/nickel-zinc ferrite magnetically separable photocatalysts using the hydrazine hydrate reduction method. Based on its properties of high photocatalytic activity and easy separation and recovery, the photocatalyst will have a promising application.

EXPERIMENTAL

Preparation of nickel-zinc ferrite powders: Spinel Zn_{0.5}Ni_{0.5}Fe₂O₄ powders were prepared by the EDTA-complexing method. An appropriate amount of ethylene diamine tetraacetic acid (EDTA) was dissolved in NH₄OH and formed a transparent solution, into which a stoichiometric amount of

ethylene glycol (EG), Ni(NO₃)₂·6H₂O, Zn(NO₃)₂·6H₂O and Fe(NO₃)₃·9H₂O were added with vigorous stirring, the molar ratios of Ni²⁺:Zn²⁺:Fe³⁺:EDTA:EG are 0.5:0.5:2:3:12. Subsequently the solution was consecutively stirred at about 80 °C for 3 h, the volume of the solution decreased and the viscosity increased continuously until a dark-brown viscous gel formed, without any visible formation of precipitation or turbidity. The gel was further dried and charred at 140 °C for 2-4 h to yield a solid precursor. Finally the precursor was calcined at 900 °C for 3 h in air to obtain spinel crystalline powders.

Preparation of Cu₂O/nickel-zinc ferrite powders: 1 g nickel-zinc ferrite and 50 mL 0.1 mol/L CuSO₄·5H₂O solution were added into a beaker, continuously magnetic stirring for 0.5 h and still-setting for 24 h. Subsequently 10 mL of 1 mol/L NaOH was added quickly into the solution. After stirring and ageing 10 min, 10 mL of 0.3 mol/L hydrazine hydrate solution was added dropwise into the mixed solution under stirring. The products were filtered, rinsed with deionized water and then dried in vacuum at 60 °C to obtain the Cu₂O/nickel-zinc ferrite magnetic photocatalyst.

Photocatalytic experiment: 50 mg Cu₂O/nickel-zinc ferrite powders were added into 50 mL 20 mg/L methyl orange solution with strong stirring to form a mixture. The ultraviolet irradiation source was a 30 W ultraviolet lamp. Before the irradiation, the solution was stirred for 15 min to allow the system to reach adsorption equilibrium. The methyl orange solution was taken 5 mL away every 0.5 h to test the transmit-

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tance of methyl orange ($\lambda = 460$ nm) during the reaction procedure using 721 spectrophotometer. The photocatalyst was separated from the solution using magnetic force and then rinsed with distilled water for future use.

Absorbency and degradation rate were calculated by using the following formula:

$$A = -\log T \quad (1)$$

$$D (\%) = \frac{(A_0 - A_t)}{A_0} \times 100 \quad (2)$$

where T is transmittance, A is absorbency, A_0 is absorbency of undegraded methyl orange solution, A_t is absorbency of degraded methyl orange solution after the corresponding time, D % is degradation rate of methyl orange solution after the corresponding time.

Analytical methods: Structural characterization of the as-prepared samples was performed by means of X-ray diffraction (XRD, Model Y2000) with $\text{CuK}\alpha$ radiation. Their morphology was observed by a high resolution transmission electron microscopy (HRTEM, JEM-2010). Fourier transform infrared spectrometer (FT-IR, WQF-300) was used for monitoring the structure changes of the product from 4000-400 cm^{-1} . The result of photocatalytic degradation of methyl orange were evaluated by spectrophotometer (721).

RESULTS AND DISCUSSION

Characterization of nickel-zinc ferrite: Fig. 1 shows the XRD pattern of sample $\text{Zn}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$ obtained from calcining precursor at 900 °C for 3 h. It is observed that all the diffraction peaks can be indexed to the spinel phase structural $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$. The diffraction patterns and relative intensities of all diffraction peaks matches well with those of JCPDS card No. 52-0278. It also reveals that the sample is pure spinel $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$, no impurity phases are detected.

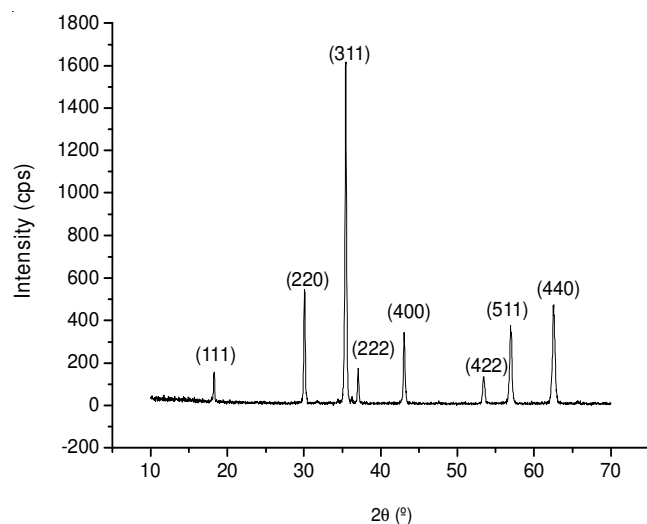


Fig. 1. XRD pattern of $\text{Zn}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$ obtained from calcining precursor

Fig. 2 shows the FT-IR spectrum for the $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ powders. It is observed that the sample exhibits one absorption peak in 600-500 cm^{-1} region. The absorption peak is attributed to the characteristic stretching vibration on the tetrahedral

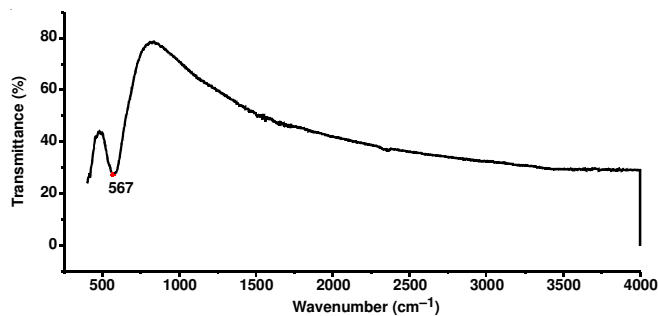


Fig. 2. FT-IR spectrum of $\text{Zn}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$ powders

position of Fe-O bond⁵. This is a reliable indication of the formation of the spinel structure. Moreover, no other absorption peak can be observed for the sample in Fig. 2, suggesting that the organic matters have been completely decomposed and a single metal oxide is formed in the product. It is also confirmed from the XRD results.

Characterization of Cu_2O /nickel-zinc ferrite: Fig. 3 shows an X-ray powder diffraction pattern of Cu_2O /nickel-zinc ferrite powders. All diffraction peaks correspond to the spinel phase $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ and Cu_2O . Fig. 3 also shows that the main crystalline phase of Cu_2O is cubic structure, there are three peaks with 2θ values of 36.6, 42.4 and 61.5°, corresponding to (111), (200) and (220) crystal planes of pure Cu_2O , respectively, which are in good agreement with the literature (JCPDF card No. 05-0667). It also reveals that no impurity phases (Cu and CuO) were detected.

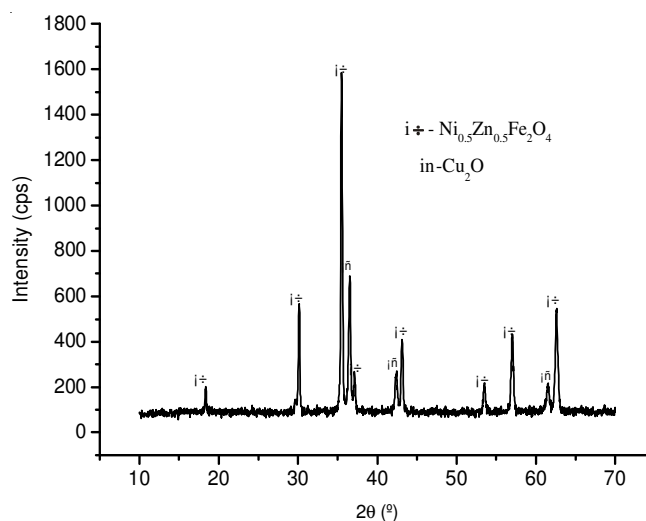


Fig. 3. XRD pattern of Cu_2O /nickel-zinc ferrite powders

The high resolution transmission electron microscopic (HRTEM) photograph of the Cu_2O /nickel-zinc ferrite powders is displayed in Fig. 4, which shows that the shape of Cu_2O particles is irregular and looks as spherical. The particles have a core/shell geometry, in which the magnetic nickel-zinc ferrite core is predominantly in the center of the composite material. Because $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ is magnetic materials, electronic absorption capacity is far greater than that of the Cu_2O , so $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ at the nuclear part is dark, while the shell layer of Cu_2O is light⁶.

Photocatalytic activity: Fig. 5 shows the photocatalytic efficiencies of the recovered Cu_2O /nickel-zinc ferrite catalysts.

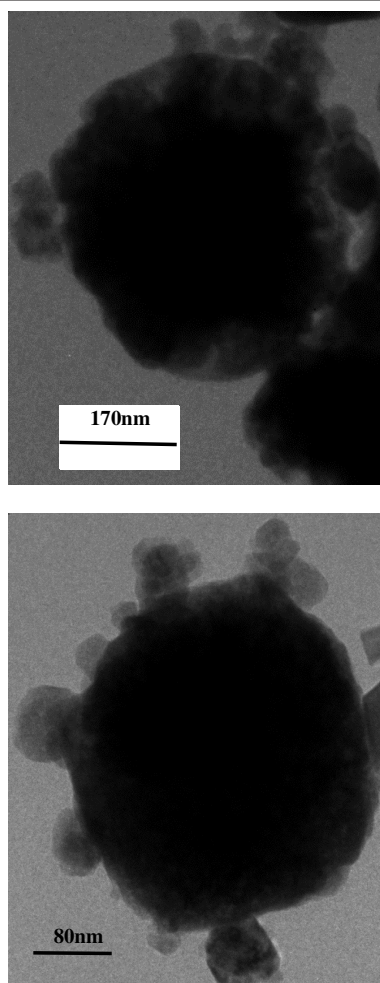


Fig. 4. HRTEM photographs of Cu₂O/nickel-zinc ferrite powders

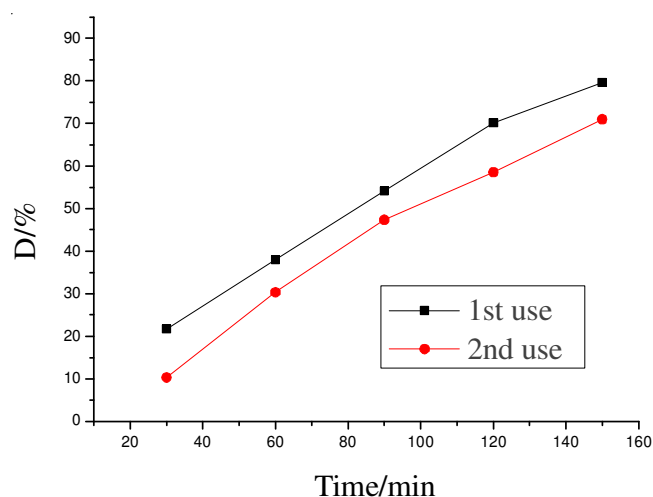


Fig. 5. Results of the reuse of Cu₂O/nickel-zinc ferrite

It is clear that over 79 % methyl orange can be degraded using Cu₂O/nickel-zinc ferrite photocatalyst after 150 min irradiation treatment. Using magnetic property of Cu₂O/nickel-zinc ferrite (Fig. 6), the Cu₂O/nickel-zinc ferrite can be separated from

the solution after the degradation treatment using magnetic iron and its photocatalytic efficiency could be kept over 70 % for the next experiment with fresh aqueous solution of methyl orange. It can be seen the Cu₂O/nickel-zinc ferrite sample keeps good photocatalytic activity after being separated by magnetic force and reused several times.



Fig. 6. Photo of magnetic property of Cu₂O/ferrite in the degradation methyl orange nickel-zinc ferrite

Conclusion

The conclusions from this study are: (1) The nickel-zinc ferrite powders were prepared by EDTA-complexing method. (2) The Cu₂O/nickel-zinc ferrite magnetically separable photocatalyst was prepared by the hydrazine hydrate reduction method, Cu₂O coating the magnetic cores is cubic structure. (3) The Cu₂O/nickel-zinc ferrite powders have photocatalytic activity and can be separated from the system by applying magnetic field and reused, suggesting it's one of promising candidates for photocatalytic treatment of wastewater.

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