Preparation and Photocatalytic Activity of $\text{Cu}_2\text{O}/\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ Microtubules†

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Combining the dip-calcination method, nickel-zinc ferrite ($\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$) microtubules were prepared using absorbent cotton as template. The $\text{Cu}_2\text{O}/\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ microtubules were prepared by low-temperature liquid phase method in ethanol/polyethylene glycol/ H_2O system of three-phase solution, which is using copper acetate and modified $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ microtubules as the raw materials and glucose as a reducing agent. The as-prepared samples were characterized by X-ray diffraction and scanning electron microscopy. The photocatalytic activity of the $\text{Cu}_2\text{O}/\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ composite microtubules was evaluated by degradation of methyl orange under ultraviolet lamp. The results show that the microtubule external diameter is between 6 and 8 μm , the wall thickness is between 0.5 and 2 μm . The $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ microtubules are composed of numerous spherical $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanocrystals with the nearly uniform size about 125 nm. The results also show that $\text{Cu}_2\text{O}/\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ microtubules have photocatalytic activity under the ultraviolet lamp and can be separated from the system by applying magnetic field.

Key Words: Nickel-zinc ferrite, Photocatalysis, Cu_2O , Microtubule, Absorbent cotton.

INTRODUCTION

In recent years, biomorphic mineralization has been noteworthy as a new nanofabrication technique for functional materials, which is a technique that produces materials with morphologies and structures resembling those of nature living things, through employing bio-structures as templates for mineralization¹. Recently, porous hierarchical architectures of semiconducting metal oxide are extensively fabricated by using cotton as template²⁻⁴. In this study, a simple biomorphic synthesis technique was applied to prepare magnetic Ni-Zn ferrite microtubules by using absorbent cotton as the template and $\text{Cu}_2\text{O}/\text{nickel-zinc ferrite}$ were prepared by coating Cu_2O on it. The photocatalytic activity was examined.

EXPERIMENTAL

Preparation of nickel-zinc ferrite microtubules: All chemicals used were of analytical grade. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 20.20 g, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 3.2856 g, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ 3.7186 g were solubled in 50 mL deionized water. It was placed in 80 °C constant temperature water-bath pot to form gel after the water evaporated. The short and loose cotton fibers were immersed into the solution under the right conditions. After stirring for 24 h, the cotton fibers were taken out, dried at 80 °C for 12 h and calcined in air at 900 °C, for 3 h. Finally, the nickel-zinc ferrite microtubules formed.

Preparation of $\text{Cu}_2\text{O}/\text{nickel-zinc ferrite}$ microtubules:

The nickel-zinc ferrite microtubules were modified using EDTA⁵ and the $\text{Cu}_2\text{O}/\text{nickel-zinc ferrite}$ microtubules were prepared by Low-temperature liquid phase method in ethanol/polyethylene glycol/ H_2O system of three-phase solution, which is using copper acetate and modified nickel-zinc ferrite microtubules as the raw materials and glucose as a reducing agent⁶.

The crystalline phase of the as-prepared samples was performed by means of X-ray diffraction (XRD, Model Y2000). Their morphology was observed by scanning electron microscope (SEM, Model Sirion 200).

Photocatalytic experiment: 200 mg $\text{Cu}_2\text{O}/\text{nickel-zinc ferrite}$ microtubules 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 enough time to allow the system to reach adsorption equilibrium. The methyl orange solution was taken 5 mL away every 30 min to test the transmittance of methyl orange ($\lambda = 460 \text{ nm}$) during the reaction procedure using 721 spectrophotometer.

RESULTS AND DISCUSSION

Characterization of nickel-zinc ferrite microtubules:

Fig. 1 shows the XRD pattern of sample $\text{Zn}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$

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microtubules. We can see 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 match well with those of JCPDS card No.52-0278.

Fig. 1. XRD pattern of $\text{Zn}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$ microtubules

The SEM photographs of the nickel-zinc ferrite microtubules are displayed in Fig. 2. It showed that the nickel-zinc ferrite microtubule's outlook basically retains the cotton fiber biological morphology (A, B and C). Its external diameter is between 6 and 8 μm , the wall thickness is between 0.5 and 2 μm . Besides, as we see in D, the Ni-Zn ferrite microtubules are composed of numerous spherical Ni-Zn ferrite nanocrystals with the nearly uniform size about 125 nm and there are many pores on the surface of microtubules.

Fig. 2. SEM images of the $\text{Zn}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$ microtubules

Characterization of $\text{Cu}_2\text{O}/\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ microtubules:

Fig. 3 shows an X-ray powder diffraction pattern of $\text{Cu}_2\text{O}/\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ microtubules. 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 crystalline phase of Cu_2O is cubic structure, the diffraction patterns and relative intensities of all diffraction peaks match well with those of JCPDS card No.05-0667. It also reveals that no impurity phases (Cu and CuO) were detected.

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

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

$$D \% = (A_0 - A_t) / A_0 \times 100 \% \quad (2)$$

Fig. 3. XRD pattern of $\text{Cu}_2\text{O}/\text{nickel-zinc ferrite}$ composite microtubules

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.

Table-1 shows the photocatalytic efficiencies of the $\text{Cu}_2\text{O}/\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ microtubules catalyst. It is clear that 89.1 % methyl orange can be degraded using $\text{Cu}_2\text{O}/\text{nickel-zinc ferrite}$ microtubules photocatalyst after 3 h irradiation treatment. Using magnetic property of $\text{Cu}_2\text{O}/\text{nickel-zinc ferrite}$ microtubules, the $\text{Cu}_2\text{O}/\text{nickel-zinc ferrite}$ can be separated from the solution after the degradation treatment using magnetic iron.

TABLE-1
RESULTS OF THE $\text{Cu}_2\text{O}/\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ MICROTUBULES
CATALYTIC EXPERIMENT

Time (h)	0.25	0.25	1.0	1.5	2.0	2.5	3.0
D (%)	34.8	56.8	70.9	78.9	83.9	87.0	89.1

Conclusion

(1) Nickel-zinc ferrite microtubules were prepared using absorbent cotton as template. The microtubule external diameter is between 6 and 8 μm , the wall thickness is between 0.5 and 2 μm . The Ni-Zn ferrite microtubules are composed of numerous spherical Ni-Zn ferrite nanocrystals with the nearly uniform size about 125 nm. (2) The $\text{Cu}_2\text{O}/\text{nickel-zinc ferrite}$ microtubules were prepared by low-temperature liquid phase method in ethanol/polyethylene glycol/ H_2O system of three-phase solution, which is using copper acetate and modified nickel-zinc ferrite microtubules as the raw materials and glucose as a reducing agent. Cu_2O coating the nickel-zinc ferrite microtubules is cubic structure. (3) The $\text{Cu}_2\text{O}/\text{nickel-zinc ferrite}$ composite microtubules have photocatalytic activity and can be separated from the system by applying magnetic field.

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