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Photocatalytic and antibacterial properties of copper hydroxyphosphate with hierarchical superstructures synthesized by a hydrothermal method

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HIGHLIGHTS

- Hierarchical Cu2PO4OH was synthesized in a simple hydrothermal route.
- Hierarchical Cu2PO4OH exhibit excellent photo-catalytic performance.
- Hierarchical Cu2PO4OH showed apparent antibacterial properties.
- Cu2PO4OH obtained under pH 5 and 7 show the better performance.

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ABSTRACT

Copper hydroxyphosphate, Cu_2PO_4OH, with various architectures was synthesized by adjusting pH values in a simple hydrothermal route. The photocatalytic activity of the Cu_2PO_4OH hierarchical superstructures was strongly related to their micro-morphology, as demonstrated by the degradation of eosin Y dye with a solar simulator. Excellent photocatalytic performance was achieved by Cu_2PO_4OH obtained under the pH values of 7 and 5. The antibacterial properties of the Cu_2PO_4OH complex superstructures were also explored by Escherichia coli (ATCC 8739) culturing. Cu_2PO_4OH showed apparent antibacterial properties but the samples obtained under the pH values of 5 and 7 exhibited better antibacterial properties than those of the Cu_2PO_4OH under the pH value of 2.5. Thus, Cu_2PO_4OH can be a promising photocatalyst with excellent antibacterial properties achieved by simply controlling its hierarchical superstructures by adjusting the pH values during feasible synthesis.

1. Introduction

Synthetic complex organic dyes are widely used in textile industries, causing increasingly severe water pollution. Thus, removal of the dyes from wastewater is environmentally important. Various physical, chemical, and biological methods have been utilized to resolve this problem [1–3]. Although some conventional physical and chemical techniques can efficiently remove dyes from wastewater, these methods have limitations such as expensive raw materials and equipment, secondary pollution, and large quantities of sludge. Degradation of dye molecules by microorganisms in the environment can be very slow. Eosin Y, a biological stain, has attracted much interest because of its wide usage as the dye in dye-sensitized solar cells, printing, leather, and fluorescent pigment. It is of synthetic origin and toxic in nature, with suspected carcinogenic and genotoxic effects. Thus, directly releasing eosin Y into water can create a serious environmental problem because of its high toxicity. However, traditional methods of dealing with eosin Y pollution have notable limitations. Sorbents such as chitosan [4,5] or activated carbon [6,7] have been used to separate eosin Y from water, and membrane separation technology can also perform similar work. These methods are based only on phase transformation, and are ineffective for the decolorization of eosin Y

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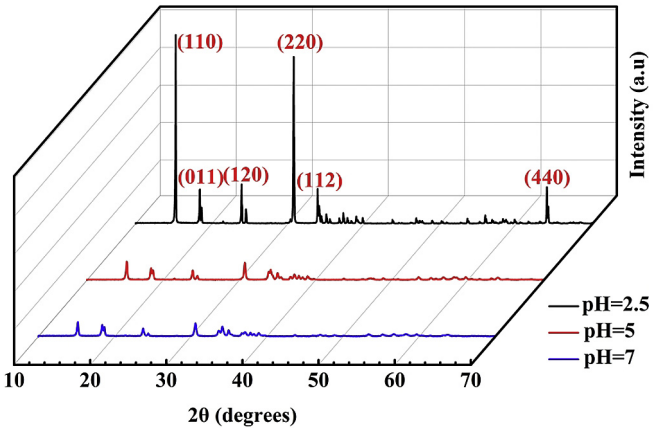

Fig. 1. XRD patterns of Cu_2PO_4OH fabricated under different pH values.

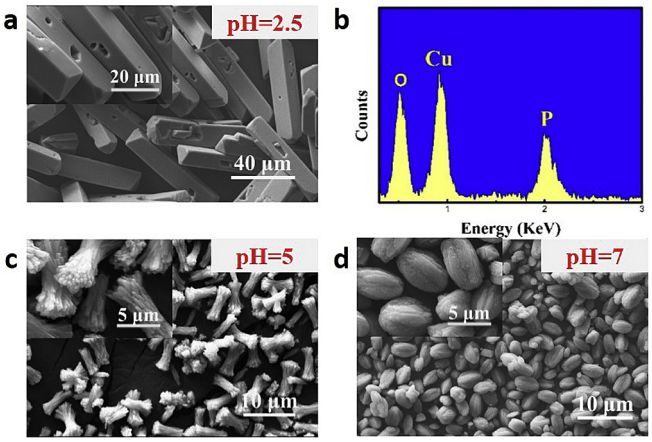

Fig. 2. SEM images of Cu_2PO_4OH prepared at different pH values (a) pH = 2.5, (b) EDX spectrum of Cu_2PO_4OH prepared at pH = 2.5, (c) pH = 5, and (d) pH = 7.

because of its stability and complex chemical structure. Photocatalytic degradation has been regarded as a more effective method for solving the eosin Y pollution problem. Shao et al. used Si/Pd nanostructure as the photocatalyst of eosin Y, demonstrating high catalytic activity of the Si/Pd nanostructure, with the performance of Si/Pd being superior to that of polymer supported Pd [8]. Ahmaruzzaman et al. used SnO_2 quantum dots as a photocatalyst in the degradation of eosin Y by solar irradiation [9]. Suganthi et al. utilized TiO_2 nanoparticles to degrade eosin Y [10]. However, these nanostructured photocatalysts require use of a noble or rare metal, inevitably increasing costs. Furthermore, a postprocessing treatment for the nanoparticles would be needed to minimize adverse impacts of the nanomaterials.

Copper hydroxyphosphate (Cu_2PO_4OH), also known as libethenite, has been found to possess catalytic, magnetic, and optical properties by virtue of its special crystal structure [11,12]. Hong et al. demonstrated that Cu_2PO_4OH possessed good photocatalytic degradability for methylene blue [13]. Thus, libethenite might be a potential photocatalyst for eosin Y. The relationship between the microstructures and photocatalytic degradability has seldom been studied. In this study, therefore, we report the simple preparation of various 3D hierarchical superstructures of Cu_2PO_4OH by adjusting the pH values via a hydrothermal route. The photocatalytic activity of synthesized Cu_2PO_4OH in the degradation of eosin Y dye under visible light irradiation was explored.

It has also been found that microbes existed extensively in organic wastewater. The use of several inorganic antimicrobial agents, such ZnO, TiO_2, and SnO_2 [14–18], has been reported for the control of microbes. In this study, the antibacterial properties of Cu_2PO_4OH samples were also investigated to demonstrate their multifunctionality.

2. Experimental section

Cu_2PO_4OH was synthesized by a hydrothermal method. First, 0.25 mL $Cu(NO_3)_2$ $3H_2O$ solution was added into 0.5 ML $Na_2HPO_4 \cdot 12H_2O$ solution (1:1, v/v). After 30 min stirring, NH_3 H_2O was added to adjust the pH value. Solutions of the mixture with different pH values (2.5, 5, and 7, respectively) were transferred individually to a Teflon-lined stainless-steel autoclave. The autoclave was maintained at 180 °C for 2 h. Then, the samples were collected by centrifugation at 5000 rpm for 15 min Cu_2PO_4OH powders were collected after washing by DI water and drying. The phase and crystallographic structure of the samples were determined by a powder X-ray diffractometer (PANalytical X'Pert PRO) equipped with a copper anode (Cu Kα radiation, λ = 1.54187 Å). The X-ray source was operated at 40 kV and 40 mA. The measurements were performed using a θ-2θ scan. Microphotographs of samples were obtained by a field-emission scanning electron microscope (SEM, Carl Zeiss Ultra 55). Microcrystalline structures of the Cu_2PO_4OH powders were studied by high-resolution transmission electron microscopy (HR-TEM) and selected area electron diffraction with TEM (JEOL, JEM-2100F). The thermal stability of the Cu_2PO_4OH powders fabricated under different pH values was studied using a thermogravimetric analyzer (Q500 TGA). The sample weight was about 5 mg. All the samples were heated from 40 °C to 800 °C at a heating rate of 10 °C/min.

Table 1
Cell parameters of the samples with different pH values.

pH	a (Å)	b (Å)	c (Å)	Volume (Å^3)
2.5	8.059 ± 0.004	8.403 ± 0.004	5.896 ± 0.005	399
5	8.073 ± 0.008	8.415 ± 0.010	5.905 ± 0.005	401.
7	8.082 ± 0.003	8.465 ± 0.004	5.886 ± 0.002	403

The photocatalytic activities of the Cu_2PO_4OH samples fabricated with different pH values were evaluated via the degradation of eosin Y dye in an aqueous solution under visible light irradiation. The eosin Y dye solution was carefully prepared and well preserved during all the degradation process. For each pH value, 0.15 g of Cu_2PO_4OH powder was added into a 100 mL eosin Y solution. The time and the initial concentrations of the eosin Y were explored. The light source was a 450 W xenon lamp (Oriel) equipped with an AM 1.5G filter (Lot-Oriel), and the intensity was calibrated to 100 mW cm^{-2} by a standard Si reference diode equipped with an infrared cutoff filter (KG-3, Schott). The distance between the lamp and the liquid level of the eosin Y solution was maintained at about 15 cm. Before the irradiation process, the eosin Y solution was stirred in the dark for 20 min to ensure adsorption/desorption equilibrium. The eosin Y solution was kept in a 250-mL beaker with stirring during the entire irradiation process. Samples were taken from the eosin Y solutions at given time intervals and the products were centrifuged. The filtrate was then analyzed using a UV–Vis spectrophotometer (Model 3900, Hitachi).

Escherichia coli (ATCC 8739) was used to evaluate the antibacterial activity of the Cu_2PO_4OH samples. All bacteria were cultured in Luria-Bertani (LB) broth. During antibacterial testing, Cu_2PO_4OH samples with pH values of 2.5, 5, and 7 before and after high-temperature sintering were selected as the experimental groups,