Hydrothermal Synthesis of Copper Hydroxyposphate Hierarchical Superstructures and Its Photocatalysis Activity in UV Light

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Abstract—Copper hydroxyposphate (Cu2(OH)PO4) with uniform 3D flower-shaped microsphere hierarchical superstructure was successfully synthesized through a template-free hydrothermal route with ammonia as alkali and complexing agent. This approach provides a facile strategy to synthesize copper hydroxyposphate crystals with unique morphologies and complex architectures. Several characterization tools including X-ray powder diffraction (XRD), UV–Vis diffuse reflectance spectra (UV–Vis DRS), scanning electron microscope (SEM), and FT-IR were employed to study the phase structures, optical properties, morphologies and characteristic functional groups of the resulting hierarchical superstructures. We further demonstrated the useful photocatalytic activity of Cu2(OH)PO4 in the degradation of methylene blue (MB) dye under UV light irradiation. From the analysis of potentials of Cu2(OH)PO4, it’s theoretically deduced that the photocatalytic degradation of MB could be attributed to the •OH and hole rather than •O2− radicals.

Keywords- copper hydroxyposphate; hierarchical superstructures; hydrothermal Synthesis; photocatalysis; mechanisms.

I. INTRODUCTION

Over the past several years, since the shape and texture of materials have strong effect on their characteristic properties, shape and morphology controlled synthesis has attracted considerable attention[1-8]. Nanostructured materials with complex architectures may provide higher specific surface areas, which will improve their catalytic properties and selectivity. As an important member of copper phosphate, copper hydroxyposphate (Cu2(OH)PO4) is a rare secondary copper mineral that is noted for its deep green color and it has an orthorhombic crystal structure and consists of a PO4 tetrahedron, a Cu(1)O6 octahedron, a Cu(2)O5 trigonal bipyramid, and an OH group between the two Cu species, in which oxygen atoms are shared with each other. Copper hydroxyposphate has been widely investigated due to its novel catalytic effect on oxidation of aromatics by H2O2, and epoxidation of styrene by H2O2 or molecular oxygen[8,10]. However, until now there were few reports on the fabrication with novel complex architectures and the photocatalysis property of Cu2(OH)PO4 under UV light irradiation. Herein, we report a simple hydrothermal route to synthesize copper phosphate complex architectures via a template-free method and investigated its photocatalytic property.

II. EXPERIMENTAL

A. Preparation of Catalyst

All the reagents used in the experiments were analytical grade and used without further purification. Copper hydroxyposphate crystals was obtained by Cu(CH3COO)2 (hereafter abbreviated as CuAc2) solution and (NH4)2HPO4 solution by hydrothermal synthesis method. Synthetic copper hydroxyposphate crystals were prepared by a mixture of Cu/P ratio of 3:2 under vigorous stirring at room temperature for 10 min. Prior to the reaction, the pH of solution mixture was adjusted to different values by NH4OH or CH3COOH and sonicated in an ultrasonic water bath for 10 min. The bluish slurry mixture was then transferred into a teflonlined stainless-steel autoclave, which was filled with deionized water up to 80% of its capacity. The autoclave was heated to various temperatures and maintained at this temperature for 4 hours, and then naturally cooled down to room temperature. The deep green crystals were collected and washed several times with distilled water and absolute ethanol to remove the impurities. The final products were dried at 50 °C (for more than 5 h) for further characterization.

B. Characterization of Catalyst

The crystal structure of catalyst powder was measured by powder X-ray diffraction (XRD) on a Rigaku D/max ΠΠB diffract meter with Cu-Kα radiation at a scanning speed of 5°/min ranging from 10 to 70°. The scanning electron microscope (SEM) characterizations were performed on a Zeiss ΣΙGMA field emission scanning electron microscope. The UV-Vis absorption spectra were measured on TU-1901 UV-Vis spectrophotometer.
UV-Vis diffuse reflectance spectra (DRS) of the samples were also recorded on the above UV-Vis spectrophotometer with an integrating sphere attachment for their reflectance in the range of 200-800 nm, and BaSO4 is the reflectance standard. The FT-IR spectrum of catalyst was recorded on Tensor 27 IR spectrophotometer (Germany Bruker Co., Ltd.).

C. Evaluation of photocatalytic activity

The photocatalytic activity of Cu2(OH)PO4 was evaluated by degradation of methylene blue (MB) under UV light irradiation in a photoreaction apparatus using a 150 W Hg lamp as the light source. An amount of 25.00 mg of photocatalyst was suspended in a 50 mL aqueous solution of 1.8×10-5 mol/L MB. Prior to illumination, the suspension was magnetically stirred in the dark for 30 min to ensure the establishment of an adsorption-desorption equilibrium between the photocatalyst and MB. During irradiation, 5 mL of analytical suspension was collected at given time intervals and centrifuged to remove the suspended photocatalyst powders. Then, the UV-Vis adsorption spectrum of the centrifugated solution was recorded using a UV-Vis spectrophotometer. The concentration of MB was measured at its maximum characteristic absorption at a wavelength of 664 nm with deionized water as a reference sample. In order to investigate the effects of relevant reactive species, a quantity of different appropriate species quenchers were introduced into the photocatalytic degradation process of MB in a manner similar to the photodegradation experiment (the light source was a 250 W Hg lamp). The dosages of these species quenchers were 0.050 mol/L, which were enough to investigate the change of photocatalytic degradation rate.

III. RESULTS AND DISCUSSION

A. The Influence of Reaction Parameters on The Photocatalysis

We investigated different reaction parameters including pH value and reaction temperature. XRD analysis was carried out to investigate the phase structures of the catalysts. Fig.1 shows the XRD patterns of the as-prepared Cu2(OH)PO4 at different reaction parameters.

It shows that pH value affect the crystalline phases extraordinarily and the as-prepared samples prepared under pH=3 or 5 were well crystallized and all the diffraction peaks can well be indexed to the orthorhombic Cu2(OH)PO4 (JCPDS File No. 36-0404). In addition, the diffraction peaks of the samples at different temperature (pH=3) were sharp and intense, indicating their highly crystalline nature. And no other diffraction peaks of impurity are observed, indicating the phase pure nature of the final product.

B. Photocatalytic properties

Evaluation of the photocatalytic activities of as-prepared samples were carried out via the degradation of MB under UV light irradiation. Fig.2(a,c) show the time profiles of MB photodegradation as a function of time in the presence of the as-prepared Cu2(OH)PO4 under different reaction conditions.

Prior to illumination, an adsorption-desorption equilibrium between the photocatalyst and MB was established in dark for 30 min. According to the Langmuir-Hinshelwood (L-H) kinetics model, the photocatalytic degradation process of RhB follows the apparent pseudo-first-order model given by eq. (1).

\[
\ln \frac{C_0}{C} = k_{app} t
\]  

(1)

Where \( C_0 \) and \( C \) are the concentrations of RhB at initial time and time \( t \), respectively, and \( k_{app} \) is the apparent pseudo-first-order rate constant (min⁻¹). The \( k_{app} \) values of Cu2(OH)PO4 at different reaction parameters were shown in Fig.2(b,d).
Figure 2. Photocatalytic degradation rate curves (a,c) and $k_{app}$ values (b,d) of Cu$_2$(OH)PO$_4$ prepared at different pH value and reaction temperature respectively.

It is observed that with increasing the pH values, the adsorption ability increase accordingly. But the sample prepared at pH=3 exhibited high photocatalytic activity than the other conditions. Therefore, the adsorption ability is only a factor to accelerate the photocatalysis. Then the pH was fixed at 3 and the temperature was adjusted from 100°C to 220°C. With increasing temperature, the photocatalytic activity decreased gradually and then enhanced a little at 220°C. Therefore, the Cu$_2$(OH)PO$_4$ synthesis condition was fixed at pH=3 and 100°C.

C. SEM Analysis

The morphology and structure of the as-prepared sample at optimized condition was examined by SEM, as shown in Fig. 3. The image displays that the product was uniform and with diameter of 1-2 μm or so. The Cu$_2$(OH)PO$_4$ exhibits an hierarchical 3D flower-shaped microsphere superstructure that comprises numerous microplatelets.

D. FT-IR Analysis

Fig.4 shows the FT-IR spectrum of the sample prepared at the optimized conditions. The infrared spectrum shows typical adsorption bands at 3454 cm$^{-1}$, 1630 cm$^{-1}$, 1063 cm$^{-1}$, 947 cm$^{-1}$, 810 cm$^{-1}$, 633 cm$^{-1}$, 549 cm$^{-1}$, and 445 cm$^{-1}$, respectively[11]. The bands at 3454 cm$^{-1}$ and 1630 cm$^{-1}$ correspond to the stretching and bending modes of the hydroxyls of Cu$_2$(OH)PO$_4$ and adsorbed water[12-13]. The adsorptions at 1063, 947, and 810 cm$^{-1}$ can be ascribed to symmetric stretching vibrations of PO$_4$$^{3-}$[14-15]. The bands at 633, 603 and 549 cm$^{-1}$ are assigned to vibrations of Cu-O bond[16]. The bands at 445 cm$^{-1}$ is assigned to symmetric vibrations of PO$_4$$^{3-}$[17]. The FT-IR result also confirms the formation of pure copper hydroxyphosphate.

E. UV-Vis DRS Analysis

Fig. 5a displays the corresponding UV–Vis diffuse reflectance spectrum (DRS) of the as-prepared product. The product exhibited strong absorption in the UV light region and weak absorption near the Infrared region. The absorption edge of Cu$_2$(OH)PO$_4$ was located at about 384 nm. For a crystalline semiconductor, the optical absorption near the band edge follows the formula[18-19]:

$$a h v = A (h v - E_g)^n$$

where $a$, $h v$, $E_g$, and $A$ are absorption coefficient, light frequency, band gap energy, and a constant, respectively. Among them, $n$ is determined by the type of optical
transition of a semiconductor ($n = 1$ for direct transition and $n = 4$ for indirect transition). Therefore, the $E_g$ of different as-prepared sample can be calculated from a plot of $(ahv)^{1/2}$ versus $(hν)$ because the $n$ values of Cu2(OH)PO4 is 4, as shown in Fig.5b. The $E_g$ estimated from the intercept of the tangents to the plots were 3.04 eV for Cu2(OH)PO4.

As well, the valence band (VB) edge position and the conduction band (CB) edge position of Cu2(OH)PO4 was also estimated by the following empirical formulas [20],

\[ E_{VB} = X - E^0 + 0.5E_g \]
\[ E_{CB} = E_{VB} - E_g \]

where $E_{VB}$ is the valence band (VB) potential, $E_{CB}$ is the conduction band (CB) potential, $X$ is the electronegativity of the semiconductor (which is the geometric mean of the electronegativity of the constituent atoms), $E^0$ is the energy of free electrons on the hydrogen scale (~4.5 eV), $E_g$ is the band gap energy of the semiconductor. Herein, the $E_{VB}$ and $E_{CB}$ of Cu2(OH)PO4 was calculated to be 3.49 and 0.45 eV respectively.

**F. Possible Photocatalytic Mechanism**

In the photocatalytic oxidation process of dye, a series of photo-induced reactive species, including $h^+$, $•OH$ or $O_2^•$, will directly take part in this process after the electron-hole pairs are produced by irradiation of photocatalyst[11-22]. To evaluate the roles of these reactive species, different scavengers were applied as probes for MB degradation. In this study, benzoquinone (BQ)[23], isopropyl alcohol (IPA), Methanol (MeOH) and AgNO3 were adopted as the traps for $O_2^•$, $•OH$, $h^+$ and $e^−$ respectively. The final concentrations of BQ, IPA, MeOH and AgNO3 in the reaction system were 0.050 mol/L. Fig. 6 shows the variation of MB degradation with different quenchers.

After addition of IPA, the photodegradation of MB was inhibited significantly, which implies that $•OH$ radicals played major role in Cu2(OH)PO4 system under UV light irradiation. In addition, the MeOH can inhibited the photodegradation also, which means photogenerated $h^+$ played comparatively minor role for MB degradation. Differently, the addition of BQ or AgNO3 showed an enhanced effect in the photodegradation of MB. The pathway for the photocatalytic mechanism of Cu2(OH)PO4 under UV light irradiation was proposed as shown in Fig. 7.

**IV. Conclusion**

In summary, the photocatalyst Cu2(OH)PO4 with uniform 3D flower-shaped microsphere hierarchical superstructure was successfully synthesized through a template-free hydrothermal method. The optimized synthesis conditions were investigated and which are fixed at pH=3 and reaction temperature is 100°C. The photocatalytic activity of Cu2(OH)PO4 for the degradation of MB at UV light has been observed. On the basis of calculated energy band positions and the effects of scavengers experimental results, the possible mechanism of photocatalytic activities for Cu2(OH)PO4 is attributed to the $•OH$ radical and photogenerated hole.
REFERENCES


