Synthesis of Cubic-relievo Ag₃PO₄ with High Visible-light Photocatalytic Activity

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Abstract: High visible-light photocatalytic activity silver phosphate (Ag₃PO₄) was successfully prepared via a facile water bath method. Scanning electron microscopy (SEM) images show that the products undergo three morphological changes during the reaction process, and the final product has uniform cubic-relievo morphology with an average particle size of about 1.6 μm. X-ray diffraction (XRD) patterns indicate that the samples are body-center cubic structure. In addition, the high resolution transmission electron microscopy (HRTEM) images show that several crystal facets are located in the surfaces of cubic-relievo Ag₃PO₄. UV-Vis absorption and photoluminescence (PL) spectra demonstrate that the products possess high visible-light responsive performance and weak PL emission intensity. The cubic-relievo Ag₃PO₄ exhibits significantly higher catalytic performance when applied on the photo-degradation of methyl orange (MO) under visible-light irradiation in comparison to the cubic Ag₃PO₄, intermediate products or commercial nitrided TiO₂ photocatalyst. This work indicates that the photocatalytic performance of the catalyst can be effectively improved by changing its surface structure.

Key words: Ag₃PO₄; cubic-relievo; crystal faces; visible-light photocatalysis

Photocatalysis is an efficient technology for the degradation of organic contaminants[11]. In the past few decades, the search for photocatalysts is prevalent. To date, many wide band gap semiconductors, such as TiO₂, have been demonstrated to be excellent photocatalysts in the fields of photodegradation[2-3]. However, for those semiconductors with high band gap energy, only ultraviolet (UV) light (λ<400 nm), which is less than 4% of the solar spectrum can be effectively used in the process of photocatalytic reactions. Accordingly, the development of visible-light responsive photocatalysts is becoming increasingly important. Forming semiconductor heterojunction is an effective way to enhance the visible-light absorption[5]. Besides, exploring new type visible-light responsive photocatalysts has aroused growing research interest recently. Since 2010, Ag₃PO₄ with a band gap of 2.36 eV, as an emerging family of promising photocatalysts, has attracted much more attention[5-7]. To date, Ag₃PO₄ was confirmed as an excellent visible-light driven photocatalyst for water splitting and degradation of organic contaminants[6-11]. For instance, Ye’s group[12] first demonstrated that Ag₃PO₄ had high visible-driven (λ>420 nm) water photooxidation, which could achieve a quantum efficiency as high as 90%. Yang, et al.[13] reported that Ag₃PO₄ exhibited high photocatalytic activity for rhodamine B (RhB) degradation. Furthermore, in order to improve and optimize their photoelectric and photocatalytic properties, many methods have been developed. Among these methods, the morphology control has been considered to be one of the most promising avenues[14-15]. The morphology of materials is related to the exposed facets of the crystals, which directly affect the properties of the catalysts[16]. Therefore, adjusting the surface structures is a promising way to improve the photocatalytic activity of Ag₃PO₄.

In this work, a novel cubic-relievo shape Ag₃PO₄ with rugged surfaces was synthesized by a facile water bath method. The as-prepared final products showed high photocatalytic activity for the degradation of methyl orange (MO) under visible light irradiation.

1 Experimental

1.1 Reagent

Silver nitrate (AgNO₃, 99.9%), ammonium hydroxide (NH₃·H₂O, 25%-28%), disodium hydrogen phosphate (Na₂HPO₄, 99%), alcohol (99.7%). All reagents were purchased from Sinopharm Chemical Reagent Co., Ltd,
and were used without further experimental purification.

1.2 Synthesis of Ag₃PO₄

The typical procedure includes three steps: (1) preparation of Tollens' reagents; (2) addition of Na₂HPO₄ solution; (3) reaction in water bath. Detailledly, 100 mg AgNO₃ was dissolved in 10 mL distilled water. Fresh Tollens' reagents was obtained when 30 mL, 0.1 mol/L ammonia solution was dropwise added to above AgNO₃ solution. Then, 20 mL, 0.15 mol/L Na₂HPO₄ aqueous solution was dropped into the above solution. Subsequently, the mixture was placed in a water bath at 30 ℃ for 24 h under magnetic stirring. It is noteworthy that Tollens' reagents and the reaction mixture should put into brown beaker flask in case photocorrosion occurs. Samples were extracted at schedule time (4, 12 and 24 h), corresponding to the initial, intermediate and final products, respectively. The obtained samples were washed with water and alcohol several times and dried in vacuum. The synthesis process and morphology evolution of samples are shown in Scheme 1.

1.3 Characterization

The structure of the samples were characterized by XRD (Rigaku D/Max-2400) using Cu-Kα radiation (40 kV, 60 mA, λ=0.1546 nm). The morphologies of the as-prepared Ag₃PO₄ were examined by field emission SEM, (TESCAN, MIRA3) and TEM (JEOL, JEM-2100F). UV-Visible absorption spectroscopy (ABs) was carried out by using a Shimadzu UV-3600 spectrophotometer. Photoluminescence (PL) spectrum was carried out on OmniPL-LF325 spectrofluorometer with 500 nm laser radiation source.

1.4 Photoreactivity measurements

In all of the photocatalytic activity experiments, the samples (10 mg) were made into an 100 mL aqueous MO solution to insure the equilibrium of the MO adsorption on the Ag₃PO₄. Then the solution was irradiated with a solution (5 mg/L) and stirred in the dark for 30 min to 500 W Xenon lamp with an ultraviolet cut-off filter (λ> 420 nm). During the irradiation, at given time intervals (10 min), 4 mL solution was sampled and centrifuged (10000 r/min) to remove the catalyst. The concentration of MB was calculated by measuring the absorbance of supernatants with a UV-3600 (Shimadzu) spectrophotometer.

2 Results and discussion

As shown in Fig. 1(a)-(b), SEM images reveal that the initial products consist of uniform cubic microcrystals with average size of 1.6 μm. Figure 1(c) indicates that the average size of final products is still 1.6 μm, and the enlarged SEM image (Fig. 1(d)) reveals that the as-prepared final products are cubic-relievo shape with rugged surfaces. Based on these results, we propose that the cubic-relievo samples are generated from the cubic products through corrosion process. Furthermore, the morphology of intermediate products (Scheme 1) can also support this viewpoint. The cubic products were obtained within 4 h reaction. With the extension of reaction time, increasing amount of free NH₃·H₂O was released to the system (as reaction below).

$$\text{HPO}_4^{2-} \rightarrow \text{PO}_4^{3-} + \text{H}^+ \quad (1)$$

$$2\left[\text{Ag(NH}_3\text{)}_2\right]^+ + \text{PO}_4^{3-} + 6\text{H}_2\text{O} \rightarrow \text{Ag}_3\text{PO}_4 + 6\text{NH}_3 \cdot \text{H}_2\text{O} \quad (2)$$

When the NH₃·H₂O concentration was high enough, the edges and the surfaces of the as-formed cubic products would be corroded by the free NH₃·H₂O. As the corrosion process continues, the Ag₃PO₄ cubes would be corroded to form the final cubic-relievo shape with rugged surfaces. To the best of our knowledge, the cubic Ag₃PO₄ has been reported, yet this kind of novel morphology has been barely reported previously.
In order to investigate the structure of the as-obtained samples, the typical powder X-ray diffraction (XRD) was performed and the XRD patterns were shown in Fig. 2. The results indicate that the XRD patterns of both cubic and cubic-relievo samples can be well indexed to the body-centered cubic structure of Ag₃PO₄ (JCPDS 06-0505)\(^{[17]}\). The structure did not change with the different morphologies. The strong and sharp peaks suggest the highly crystalline nature of Ag₃PO₄ microcrystals. Figure 3 shows the high-resolution TEM (HRTEM) images of Ag₃PO₄ samples. As shown in Fig. 3(a), the lattice fringes of cubic-relievo Ag₃PO₄ have spacing of 0.30, 0.27, 0.24 and 0.19 nm, which is in agreement with the spacing of the (200), (210), (211) and (310) planes, respectively. It’s worth noting that the (200), (211) and (310) planes locate in surfaces of cubic-relievo, and the Fig. 3(a) shows HRTEM images of (210) planes locating in the interior of the cubic-relievo Ag₃PO₄ crystal. For cubic Ag₃PO₄, by contrast, the lattice fringe spacing is 0.27 nm corresponding to (210) plane, which located in either surface or interior of the particles. The Fast Fourier Transform (FFT) patterns of HRTEM images are shown in the insets of Fig. 3(a)-(b). Two apparent rings (inset of Fig. 3(a)) indicate that several kinds of crystal facets exist in the surface of cubic-relievo Ag₃PO₄, and the distinct electron diffraction spots (inset of Fig. 3(b)) show mono-crystalline nature of the cubic Ag₃PO₄ crystals. The FFT results are well corresponding to HRTEM images. However, the XRD pattern does not reveal any information about these crystal facets with different indexes, because these facets just exist in the subgrains below 2–5 nm surface (see the dashed circle in Fig. 3(a)) and account for tiny percentage of the Ag₃PO₄ particle. From this results, it can be inferred that corrosive effect of ammonia makes different crystal facets exposed to air.

The ultraviolet-visible diffuse reflectance spectra of cubic-relievo and cubic Ag₃PO₄ are shown in Fig. 4(a). The light absorption edges of the samples were achieved by extrapolating the steep slopes in the spectra. The cubic-relievo and cubic Ag₃PO₄ exhibits absorbance peak edges around 505 and 514 nm, respectively. Furthermore, for cubic-relievo Ag₃PO₄, the absorption intensity in the wavelength range from 380 nm to 500 nm is higher than that of cubic Ag₃PO₄. In our opinion, this enhancement is attributed to several crystal faces in the surfaces of cubic-relievo Ag₃PO₄. It’s revealed that surface morphology is an important factor affecting diffuse reflectance spectra of the samples. The relationship between the coefficient and band gap energy can be described by the equation: $(\alpha h \nu)^2 = A(h \nu - E_g)$, in which $\alpha$, $\nu$, $A$, and $E_g$ are absorption coefficient, light frequency, proportionality constant and band gap, respectively$^{[18]}$. The plots of light energy $(\alpha h \nu)^2$ versus photon energy ($h \nu$) for the as-prepared samples are shown in Fig. 4(b), the band gap of cubic Ag₃PO₄ (2.47 eV) and cubic-relievo Ag₃PO₄ (2.45 eV) are evaluated by

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{XRD patterns of cubic and cubic-relievo products}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{HRTEM images of (a) cubic-relievo Ag₃PO₄ and (b) cubic Ag₃PO₄ with insets showing the corresponding FFT patterns of HRTEM images}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{(a) Ultraviolet-visible diffuse reflectance spectra, and (b) plots of light energy $(\alpha h \nu)^2$ vs. photon energy ($h \nu$) for the determination of the direct optical band gap of cubic-relievo Ag₃PO₄ and cubic Ag₃PO₄}
\end{figure}
extrapolating the straight line to the $h\nu$ axis intercept. This slightly broadening of band gap is believed to have little effect on the photocatalytic activity.

The PL spectra of the as-prepared samples are performed to characterize the separation efficiency of the photo-generated electrons and holes. As shown in Fig. 5, the cubic Ag$_3$PO$_4$ possess strong emission intensity in the range between 510–600 nm. Accordingly, this PL emission peaks usually generated from the recombination of electron and holes. However, the emission intensity of cubic-relievo Ag$_3$PO$_4$ is weaker than that of the cubic Ag$_3$PO$_4$. As it is well known, weaker PL intensity indicating higher separation efficiency, and which would lead to a higher photocatalytic activity. It means that cubic-relievo Ag$_3$PO$_4$ should have higher efficiency for separating the photogenerated electron-holes.

As known to all, photocatalytic activity of materials depends not only on the crystal structure, but also on the surface structure. Compared with cubic Ag$_3$PO$_4$, the novel cubic-relievo Ag$_3$PO$_4$ would present more crystal faces. In order to investigate the surface effects on the photocatalytic activity, the photocatalytic performance of cubic and cubic-relievo Ag$_3$PO$_4$ was evaluated by determining the degradation of MO under visible-light irradiation ($\lambda$$>$420 nm). For comparison, the performance of commercial nitrided TiO$_2$ and the intermediate product was also investigated, and the degradation efficiency is presented in Fig. 6(a). The adsorption abilities of the catalysts to MO are almost negligible in dark. Therefore, the photocatalytic activities are attributed to the degradation ability of the catalysts under visible-light irradiation.

It is obvious that the cubic-relievo Ag$_3$PO$_4$ photocatalysts exhibited best photocatalytic activities for the MO degradation, and nearly 100% of MO was degraded after about 20 min irradiation under visible light irradiation. This results indicate that the photocatalytic activity of Ag$_3$PO$_4$ was significantly improved after the etching process with the extension of time. The cubic-relievo Ag$_3$PO$_4$ degraded 98% of MO and showed a photodegraded rate constant of 0.194 min$^{-1}$, representing a high photocatalytic activity (as shown in Fig. 6(b)).

It is known that the photodegradation of organic pollutants is a surface oxidation process, which is driven by photogenerated electron-hole pairs correlated with the surface structure. For the photocatalytic behavior of Ag$_3$PO$_4$, the most crucial factor is the chemical adsorption and reaction of target molecules occurring on the surfaces of Ag$_3$PO$_4$. Therefore, The high photocatalytic activity of cubic-relievo Ag$_3$PO$_4$ can be attributed to the active sites exposed on the rugged surfaces. The schematic illustration of the catalytic mechanism is shown in Fig. 7. Several crystal facets exist in the rugged surfaces of cubic-relievo Ag$_3$PO$_4$, as we know, the photogenerated electrons on different crystal facets possess different energy and activity. Moreover, the synergy between different crystal facets can enhance photocatalytic performance.
3 Conclusion

In conclusion, a novel cubic-relievo Ag₃PO₄ photocatalyst with rugged surfaces was prepared via a corrosion method. The evolution of the morphology form cubic to cubic-relievo shape has been investigated with the reaction time extending. The as-prepared cubic-relievo Ag₃PO₄ exhibited outstanding photocatalytic activity under visible-light irradiation. It is found that the different crystal facets exist on the surfaces of cubic-relievo Ag₃PO₄ which can effectively enhance the photocatalytic performance. This research proposed a new design and synthetic method to improve the performance by changing the surfaces of the materials.

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