Synthesis of novel coral-like Ag$_3$PO$_4$ microspheres under the aid of trisodium citrate and acetic acid

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Based on a sonochemical route, the effect of trisodium citrate and acetic acid, which served as the structure-directing agents, on the synthesis of Ag$_3$PO$_4$ nano/microstructures was investigated. It is found that the sample prepared at $n$(AgNO$_3$) = 3 mmol, $n$(KH$_2$PO$_4$) = 2 mmol, $n$(Na$_3$Cit) = 1 mmol and $n$(CH$_3$COOH) = 3 mL is composed of coral-like microspheres. When varying the contents of reagents to other levels or in the absence of acetic acid, it brings about the formation of mesoporous microspheres or polyhedrons. The photocatalytic activity of the as-prepared Ag$_3$PO$_4$ samples was evaluated by the degradation of rhodamine B (RhB) under simulated-sunlight irradiation. Compared to the mesoporous microspheres or polyhedrons, the coral-like microspheres exhibit a superior photocatalytic activity, and the degradation percentage of RhB after photocatalysis reaction for 60 min reaches 96.8%.

Key-words: Coral-like Ag$_3$PO$_4$ microspheres, Structure-directing agents, Trisodium citrate, Acetic acid, Photocatalytic performance

1. Introduction

During recent years silver orthophosphate (Ag$_3$PO$_4$) with a bandgap energy of $\sim$2.4 eV has been extensively studied as a promising visible-light-driven photocatalyst$^{1,2}$ This semiconductor possesses a highly dispersive band structure of the conduction-band minimum resulting from Ag-s-Ag s hybridization without localized d states,$^{21}$ and furthermore, it has a high separation of photoexcited electrons and holes and a high quantum efficiency up to 90% at wavelengths larger than 420 nm.$^{1,2}$ These make Ag$_3$PO$_4$ an excellent photocatalytic activity for the decomposition of organic compounds as well as O$_2$ evolution from water splitting under visible light irradiation. One disadvantage of this photocatalyst is that it has an inferior cycling stability because the lattice Ag$^+$ in Ag$_3$PO$_4$ is readily reduced into metallic Ag by the photoexcited electrons during the photocatalytic process. It is also well established that the morphology of Ag$_3$PO$_4$ has an important effect on its photocatalytic activity. For example, compared to Ag$_3$PO$_4$ cubes bounded entirely by {100} facets, rhombic dodecahedrons of Ag$_3$PO$_4$ with only {110} facets exposed were shown to exhibit much higher photocatalytic performances.$^{2}$ This is primarily due to the fact that {110} facets have the higher surface energy than {100} facets. The strong dependence of morphology on the photocatalytic activity has stimulated a great deal of work on the synthesis of Ag$_3$PO$_4$ nano/microstructures of various morphologies, such as dodecahedrons,$^{2,4}$ tetrahedrons,$^{2,4,5}$ tetrapods,$^{2,4,5,6}$ concaves,$^{7,8}$ dendrites,$^{9,10}$ porous microcrystals,$^{11}$ flower-like microspheres,$^{12}$ nanorods$^{13}$ and spherical nanoparticles.$^{14,15}$ In most of the synthesis routes, structure-directing agents or surfactants (e.g., urea, oleic acid, trisodium citrate, polyethylene glycol, ammonia, triethanolamine, ethylenediamine, hexamethylenetramine and glacial acetic acid) were used to tailor the morphology of Ag$_3$PO$_4$ nano/microstructures. In this work, we synthesized for the first time coral-like Ag$_3$PO$_4$ microspheres by a sonochemical method under assistance of trisodium citrate (Na$_3$Cit) and acetic acid (CH$_3$COOH). The photocatalytic activity of the as-prepared samples was evaluated by degrading rhodamine B (RhB) under simulated-sunlight irradiation.

2. Experimental

Stoichiometric amounts of AgNO$_3$, KH$_2$PO$_4$, Na$_3$Cit and CH$_3$COOH were dissolved in 20, 10, 10 and 10 mL of distilled water. Then to the AgNO$_3$ solution were added in turn the Na$_3$Cit, NaH$_2$PO$_4$ and CH$_3$COOH solutions slowly drop by drop. Every step mentioned above was accompanied by a constant magnetic stirring. The resultant mixed solution was placed in an ultrasonic bath and ultrasonically irradiated at a frequency of 40 kHz and a temperature of 50°C. After reaction for 1 h, the formed precipitate was collected and washed with distilled water and absolute ethanol for 5 times, and then submitted to drying on an electrothermostat constant-temperature dry box at 60°C for 12 h. The effect of the content of reagents on the synthesis of Ag$_3$PO$_4$ samples was investigated. The fabrication parameters and corresponding samples are listed in Table 1.

The phase purity of the as-prepared Ag$_3$PO$_4$ samples was examined by powder X-ray diffraction (XRD) with Cu-Kα radiation. The morphology of the samples was investigated by a field-emission scanning electron microscope (SEM). The UV–visible diffuse reflectance spectrum (DRS) was measured on a UV–visible spectrophotometer with an integrating sphere attachment.

The photocatalytic activity of the samples was evaluated by degrading RhB in aqueous solution under simulated-sunlight irradiation from a 200 W xenon lamp. The initial concentration of RhB was 5 mg L$^{-1}$ and the catalyst loading was 0.05 g in 100 mL of RhB solution. Prior to photocatalysis, the suspension was magnetically stirred in the dark for 30 min to establish the adsorption–desorption equilibrium of RhB on the catalyst. During the photocatalysis process, 3 mL of the suspension was pipetted out at given time intervals, and then centrifuged at

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4000 min\(^{-1}\) for 20 min to remove the catalyst. The RhB concentration was determined by measuring the absorbance of the solution at a fixed wavelength of \(\lambda = 554\) nm on a UV–visible spectrophotometer.

### 3. Results and discussion

**Figure 1** shows the XRD patterns of Ag\(_3\)PO\(_4\) samples, along with the standard XRD line pattern for Ag\(_3\)PO\(_4\) cubic structure (JCPDS No. 06-0505). It is seen that samples Y1, Y2, Y4, Y5 and Y6 crystallize in a single Ag\(_3\)PO\(_4\) cubic phase without the presence of other secondary phases. Sample Y3 contains small amount of impurities besides the major phase of Ag\(_3\)PO\(_4\) cubic structure. Samples Y7 and Y8 form mainly impurities with appearance of only a minor Ag\(_3\)PO\(_4\) cubic phase. The XRD results reveal that when introducing Na\(_3\)Cit into the precursor solution, phase-pure Ag\(_3\)PO\(_4\) cannot be formed in a stoichiometric ratio of 3:1 between AgNO\(_3\) and KH\(_2\)PO\(_4\), but an excess of KH\(_2\)PO\(_4\) is required for the synthesis of phase-pure samples. Moreover, the addition of Na\(_3\)Cit in excess also cannot result in the formation of single Ag\(_3\)PO\(_4\) phase.

**Figure 2** shows the SEM images of the phase-pure Ag\(_3\)PO\(_4\) samples as prepared. The morphologies and sizes of the samples are summarized in Table 1. It is particularly interesting that the sample (Y1) prepared at \(n(\text{AgNO}_3) = 3\) mmol, \(n(\text{KH}_2\text{PO}_4) = \cdots\)

| Samples | AgNO\(_3\) (mmol) | KH\(_2\)PO\(_4\) (mmol) | Na\(_3\)Cit (mmol) | CH\(_3\)COOH (mL) | Morphology | Size (\(\mu\)m) | Bandgap energy (eV) | Degradation percentage (%) |
|---------|------------------|------------------------|------------------|-----------------|------------|----------------|-----------------|-----------------------------|
| Y1      | 3                | 2                      | 1                | 3               | coral-like microspheres | 3–4   | 2.54 | 96.8            |
| Y2      | 3                | 2                      | 1                | 0               | mesoporous microspheres | 4–5   | 2.53 | 29.9            |
| Y3      | 3                | 1                      | 1                | 3               | impurity               |       |       |                |
| Y4      | 3                | 3                      | 1                | 3               | mesoporous microspheres | 5–7   | 2.53 | 38.3            |
| Y5      | 3                | 2                      | 0.1              | 3               | microspheres/polyhedrons | 2–4   | 2.51 | 76.3            |
| Y6      | 3                | 2                      | 0.5              | 3               | microspheres/polyhedrons | 2–4   | 2.51 | 79.9            |
| Y7      | 3                | 2                      | 2                | 3               | impurity               |       |       |                |
| Y8      | 3                | 2                      | 3                | 3               | impurity               |       |       |                |

Fig. 1. XRD patterns of Ag\(_3\)PO\(_4\) samples prepared at various experimental parameters.

Fig. 2. SEM images of the phase-pure Ag\(_3\)PO\(_4\) samples as prepared.
2 mmol, $n(\text{Na}_3\text{Cit}) = 1$ mmol and $n(\text{CH}_3\text{COOH}) = 3$ mL is composed of coral-like microspheres. As far as we know, such Ag$_3$PO$_4$ morphology has not been reported before. However, when varying the contents of reagents to other levels (Y4, Y5 and Y6) or in the absence of acetic acid (Y2), it cannot bring about the formation of coral-like microspheres but rather mesoporous microspheres or polyhedrons. The formation mechanism of coral-like microspheres can be simply described as follows. At the initial stage of the reaction, Ag$_3$Cit precursor is formed, which serves as the reactant source as well as the morphology modifier. Orthophosphate anions ($\text{PO}_4^{3-}$) are slowly released from the potassium dihydrogen phosphate and react with Ag$_3$Cit to form Ag$_3$PO$_4$ nuclei. The nuclei gradually grow into nanocrystals with simultaneous consumption of Ag$_3$Cit precursor. To reduce the overall surface energy, the nanocrystals tend to aggregate together to form larger microparticles. These freshly-formed Ag$_3$PO$_4$ microparticles could simultaneously undergo a localized Ostwald ripening process (i.e., dissolution-crystallization process) since they are in a thermodynamic non-equilibrium state. As a result, the aggregates are further etched to form mesoporous structures. Thus under the assistance of trisodium citrate, mesoporous microspheres are expected to be prepared, which is similar to previous reported results. On the other hand, when an amount of acetic acid is added into the reaction system, the number of Ag$_3$PO$_4$ nuclei could be decreased in the initial reaction stage and they tend to grow into dendritic nanocrystals. The freshly-produced dendritic nanocrystals self-assemble into superstructured microspheres, which will further evolve into coral-like microspheres by a localized Ostwald ripening process. Therefore, under the simultaneous assistance of trisodium citrate and acetic acid, which are in an appropriate stoichiometric proportion ($n(\text{Na}_3\text{Cit}) = 1$ mmol, $n(\text{CH}_3\text{COOH}) = 3$ mL), coral-like microspheres are expected to be prepared.

Figure 3(a) shows the UV–visible diffuse reflectance spectra of Ag$_3$PO$_4$ samples and Fig. 3(b) shows the corresponding first derivative spectra. The peak at around 490 nm is attributed to the absorption peak, from which the bandgap energy $E_g$ of the samples can be obtained. The obtained result is given in Table 1. It is seen that the samples have a very similar bandgap energy of 2.51–2.54 eV.

Figure 4 shows the photocatalytic degradation of RhB over Ag$_3$PO$_4$ samples under simulated-sunlight irradiation as a function of irradiation time $t$. The degradation percentage of RhB after 60 min of photocatalysis reaction is given in Table 1, where the degradation efficiency is defined as $(C_0 - C_t)/C_0 \times 100\%$ ($C_0$ represents the initial RhB concentration and $C_t$ represents the remaining RhB concentration after photocatalysis for time $t$). It is seen that sample Y1 exhibits a much higher photocatalytic activity than the other samples, and the degradation percentage of RhB after reaction for 60 min reaches 96.8%. This can be attributed to the fact that the coral-like structures have a large exposed surface area and can provide more surface active sites for the photocatalytic reaction. In addition, due to the coral-like structures sample Y1 exhibits a relatively higher adsorption toward RhB compared to the other samples (about 9% for sample Y1, while about 4–7% for samples Y2, Y4, Y5 and Y6).

4. Conclusions

We systematically investigated the effect of the structure-directing agents—trisodium citrate and acetic acid on the synthesis of Ag$_3$PO$_4$ nano/micro structures based on a sonochemical route. When trisodium citrate and acetic acid are in an appropriate stoichiometric proportion, i.e., $n(\text{Na}_3\text{Cit}) = 1$ mmol and $n(\text{CH}_3\text{COOH}) = 3$ mL, coral-like microspheres are prepared. However, when trisodium citrate and acetic acid deviate from this stoichiometric proportion, it cannot bring about the synthesis of coral-like microspheres but rather mesoporous microspheres or polyhedrons. The photocatalytic experiments reveal that the coral-like microspheres exhibits a superior photocatalytic activity toward the degradation of RhB under simulated-sunlight irradiation compared to the other samples, where 96.8% of the dye is observed to be degraded after 60 min of the photocatalysis reaction.

**Fig. 3.** (a) UV–visible diffuse reflectance spectra of Ag$_3$PO$_4$ samples and (b) the corresponding first derivative spectra.

**Fig. 4.** Photocatalytic degradation of RhB over Ag$_3$PO$_4$ samples under simulated-sunlight irradiation as a function of irradiation time $t$. 

$n(\text{Na}_3\text{Cit}) = 1$ mmol and $n(\text{CH}_3\text{COOH}) = 3$ mL, coral-like microspheres are prepared. However, when trisodium citrate and acetic acid deviate from this stoichiometric proportion, it cannot bring about the synthesis of coral-like microspheres but rather mesoporous microspheres or polyhedrons. The photocatalytic experiments reveal that the coral-like microspheres exhibits a superior photocatalytic activity toward the degradation of RhB under simulated-sunlight irradiation compared to the other samples, where 96.8% of the dye is observed to be degraded after 60 min of the photocatalysis reaction.
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