

# Synthesis and photocatalytic performance of $\text{Ag}_3\text{PO}_4/\text{AgCl}$ hybrids\*

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$\text{Ag}_3\text{PO}_4/\text{AgCl}$  hybrids have been synthesized via a facile ion-exchange method. The hybrids exhibit an enhanced photocatalytic activity for degradation of rhodamine B (RhB) than the single  $\text{Ag}_3\text{PO}_4$  or  $\text{AgCl}$  under a visible light irradiation. Such a behavior might be attributed to the increased number of high active sites and suitable energy band structure. The possible mechanism is also discussed.

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Recently, the photocatalysts have attracted much attention because they provide a low-cost, high-efficiency and environment friendly utilization<sup>[1-3]</sup>. However, there is a fatal weakness affecting their industrial application, namely, a wide band gap of 3.2 eV. Thus, much attention has been paid to the narrow-band-gap semiconductors, such as  $\text{Ag}_3\text{PO}_4$ ,  $\text{Cu}_2\text{O}$ ,  $\text{BiOBr}$  and so forth<sup>[4-7]</sup>.

$\text{Ag}_3\text{PO}_4$ , with a band gap of 2.45 eV, is considered as a potential sun-assisted photocatalyst<sup>[8-10]</sup>. However,  $\text{Ag}_3\text{PO}_4$  encounters a poor stability due to a slight solubility in aqueous solution<sup>[11,12]</sup>. So a few attempts have been tried, for instance, the deposition of a stable and insoluble thin layer ( $\text{SnO}_2$ ,  $\text{AgBr}$  or  $\text{AgI}$ ) on the surface of  $\text{Ag}_3\text{PO}_4$ <sup>[13-15]</sup>. By forming a core-shell structure, both the stability and catalytic activity can be improved obviously. Nevertheless, up to now, there are still very limited reports on the synthesis of  $\text{Ag}_3\text{PO}_4/\text{AgCl}$  hybrids. One important reason might be due to the wide band gap of  $\text{AgCl}$  (about 3.2 eV). In this work, we prepared  $\text{Ag}_3\text{PO}_4/\text{AgCl}$  complex photocatalysts by the facile ion-exchange technology. It is clearly found that the hybrid microstructures show the enhanced performance than the single  $\text{Ag}_3\text{PO}_4$  or  $\text{AgCl}$  catalysts.

$\text{Ag}_3\text{PO}_4$  microcrystals were synthesized using a facile ion exchange route<sup>[9]</sup>. In a typical process, 0.003 mol of  $\text{AgNO}_3$  was dissolved in 20 mL of  $\text{H}_2\text{O}$ , and then 30 mL of  $\text{Na}_2\text{HPO}_4$  (0.001 mol) aqueous solution was added by drops into the above solution under vigorous stirring. After stirring for another 30 min, the yellow precipitate from the reaction was collected by filtration, washed with distilled water and absolute ethanol for several times, and then dried at room temperature in the air for further use.  $\text{Ag}_3\text{PO}_4/\text{AgCl}$  hybrids were synthesized via a similar process. Briefly, 1.0 g of  $\text{Ag}_3\text{PO}_4$  was dispersed in 50 mL of de-ionized water and then the suspension was sonicated

for 30 min in dark. Subsequently, different amounts of  $\text{KCl}$  aqueous solution (0.02 mol/L) were added drop by drop into the above suspension solution with vigorous stirring. The resulting mixture was subjected to constant stirring at room temperature for 3 h in the dark. The obtained samples for morphology and structure analysis were washed with deionized water and dried in a vacuum oven at 50 °C for 12 h.

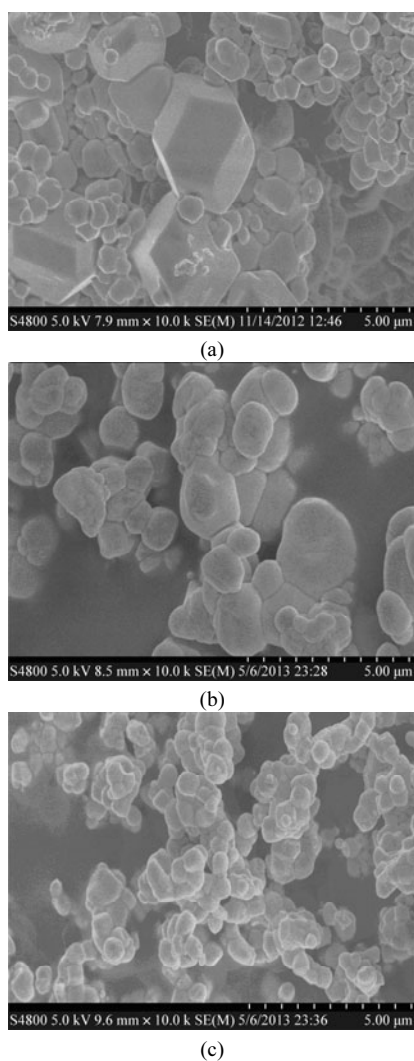
Scanning electron microscopy (SEM) images are obtained using a JEOL 2010 H microscope operating at 200 kV. All the samples for the analysis are solid after drying. X-ray diffraction (XRD) patterns are taken on a D8 Advance Bruker diffractometer using  $\text{Cu K}\alpha$  irradiation. The UV-Vis absorption spectra are obtained by a UV-Vis spectrophotometer (Varian Cary 300). Typically, the samples (0.1 g) were dispersed into a solution of RhB (100 mL, 10 mg/L) under the visible light illumination provided by a 150 W tungsten-halogen lamp (Beijing Institute of Optoelectronic Technology). The distance between the lamp and the solution was 20 cm. The suspension was firstly stirred for 30 min in dark to exclude the adsorption-desorption effect. The degradation of RhB solution was monitored by UV-Vis spectroscopy (UV-2500PC, Shimadzu). The suspensions containing the sample powders and dyes were monitored every few minutes. Prior to the spectroscopy measurement, those photocatalysts were removed from the photocatalytic reaction systems by centrifugation.

Figs.1 and 2 show the SEM images and XRD patterns of pure  $\text{Ag}_3\text{PO}_4$ ,  $\text{AgCl}$  and  $\text{Ag}_3\text{PO}_4/\text{AgCl}$  hybrids. It is clearly seen that the single-crystalline  $\text{Ag}_3\text{PO}_4$  sub-micropolyhedrons with sharp corners, edges and smooth surface have been prepared in large quantities. Besides, the  $\text{AgCl}$  particles exhibit a nearly spheric structure with average size of 3  $\mu\text{m}$ . By constructing a heterogeneous

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structure, the average diameters are reduced a lot due to the interaction between two species. As a result, the specific surface area is increased, which might be a key reason for the enhanced photocatalytic activity that would be discussed latter. Moreover, the XRD patterns clearly show that all the diffraction peaks of the obtained AgCl and Ag<sub>3</sub>PO<sub>4</sub> could be indexed to the standard XRD data (JCPDS No. 06-0505). The hybrids contain all the peaks from AgCl and Ag<sub>3</sub>PO<sub>4</sub>.



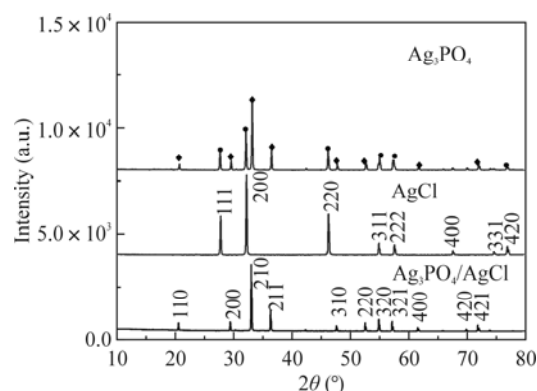
**Fig.1 SEM images of (a) pure Ag<sub>3</sub>PO<sub>4</sub>, (b) AgCl and (c) Ag<sub>3</sub>PO<sub>4</sub>/AgCl hybrids prepared by a facile solution route**

Fig.3 shows the UV-Vis absorption spectra of all the samples. It could be clearly seen that Ag<sub>3</sub>PO<sub>4</sub> and AgCl have the absorption band edges around 525 nm and 390 nm, corresponding to the band gap energy of 2.33 eV and 2.15 eV, respectively. By the way, the band gap of a semiconductor is deduced by the following equation<sup>[16]</sup>:

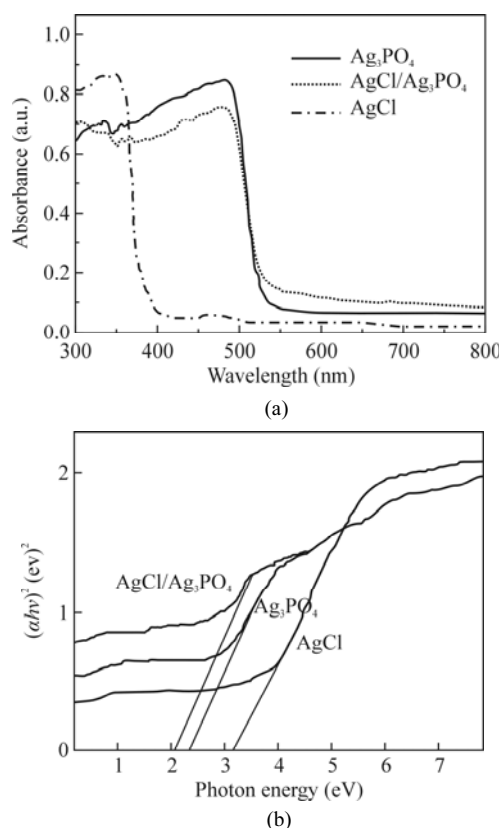
$$\alpha h\nu = C(h\nu - E_g)^{n/2} \quad (1)$$

It is clearly observed that the formation of the hybrids expands the absorption range of visible light, leading to a

more efficient absorbance of visible light. That might be a key reason for the enhanced catalytic performance.



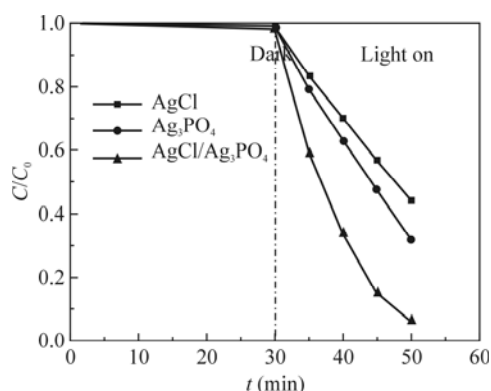
**Fig.2 XRD patterns of pure Ag<sub>3</sub>PO<sub>4</sub>, AgCl and Ag<sub>3</sub>PO<sub>4</sub>/AgCl hybrids**



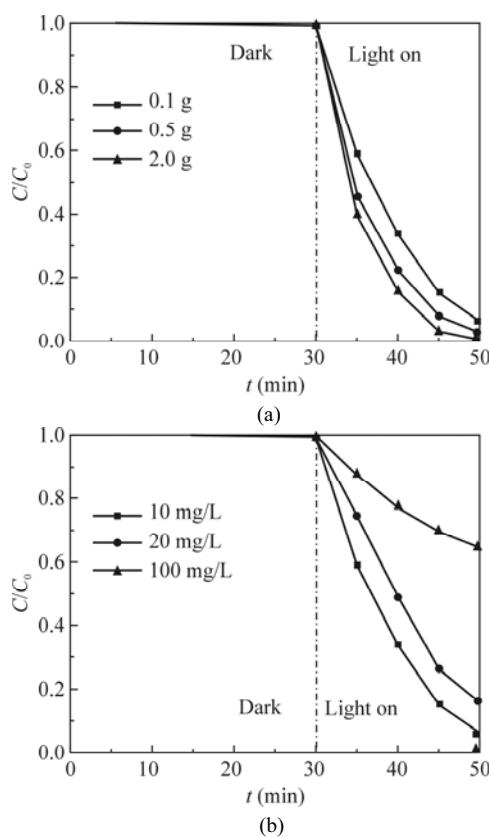
**Fig.3 (a) UV-Vis absorption spectra and (b) band gaps of pure Ag<sub>3</sub>PO<sub>4</sub>, AgCl and Ag<sub>3</sub>PO<sub>4</sub>/AgCl hybrids**

Furthermore, the photocatalytic activities of all the samples are explored for the RhB degradation under visible light irradiation at room temperature, as indicated in Figs.4 and 5. It could be clearly observed that the hybrids exhibit a higher photocatalytic activity than other single catalysts, which could completely degrade RhB dye in 50 min under visible irradiation. Two possible mechanisms are revealed from the enhanced activities of the Ag<sub>3</sub>PO<sub>4</sub>/AgCl hybrids. First, the number of the active centers is increased with a close contact between two semiconductor particles, which is indicated by a decrease

of the crystalline sizes in Fig.1(c). Second, the suitable energy band structure of the hybrids might facilitate the separation of the electron-hole pairs. Namely, the photo-excited electrons in an AgCl particle quickly transfer an Ag<sub>3</sub>PO<sub>4</sub> particle, while the holes migrate in an opposite direction. That would suppress the charge recombination and promote the carrier separation. Based on the above analysis, it could be concluded that both the abundant active sites and appropriate energy band structure contribute to the enhanced photocatalytic activity of AgCl/Ag<sub>3</sub>PO<sub>4</sub> hybrids.



**Fig.4** Degradation rate as a function of reaction time for pure Ag<sub>3</sub>PO<sub>4</sub>, AgCl and Ag<sub>3</sub>PO<sub>4</sub>/AgCl hybrids under visible light irradiation



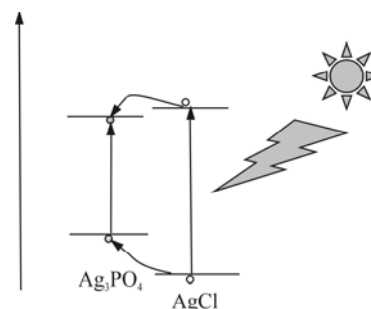
**Fig.5** Photocatalytic activities of three samples for RhB degradation under visible light irradiation with different (a) catalyst quantities and (b) solution concentrations

Fig.6 shows the schematic band structure of Ag<sub>3</sub>PO<sub>4</sub>/AgCl hybrids, where the conduction band (CB) and valence band (VB) potentials of the hybrids are deduced according to the empirical equation as follows<sup>[17]</sup>:

$$E_{VB} = \chi - E_c + 0.5E_g \quad (2)$$

$$E_{CB} = E_{VB} - E_g \quad (3)$$

where  $E_{CB}$  and  $E_{VB}$  represent the CB and VB edge potentials, respectively,  $\chi$  is the electro-negativity of a semiconductor, which is the geometric mean of the electro-negativities of the constituent atoms,  $E_c$  is the free electron energy on the hydrogen scale (about 4.5 eV), and  $E_g$  is the band gap energy of a semiconductor. By calculation, the detailed parameters of Ag<sub>3</sub>PO<sub>4</sub> and AgCl are listed in Tab.1. As could be seen, the VB potential of AgCl is more positive than that of Ag<sub>3</sub>PO<sub>4</sub>, facilitating the hole migrating from AgCl to Ag<sub>3</sub>PO<sub>4</sub>. As a result, the increased number of the holes on Ag<sub>3</sub>PO<sub>4</sub> surfaces could significantly accelerate the photo-oxidation reactions for degrading RhB.



**Fig.6** Schematic model of the energy band structure of Ag<sub>3</sub>PO<sub>4</sub>/AgCl hybrids

**Tab.1** CB and VB potentials of Ag<sub>3</sub>PO<sub>4</sub> and Co<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> by Eqs.(2) and (3)

Material	$\chi$	$E_g$ (eV)	$E_{CB}$ (eV)	$E_{VB}$ (eV)
Ag <sub>3</sub> PO <sub>4</sub>	5.96	2.33	0.29	2.62
AgCl	6.07	3.20	-0.03	3.17

In summary, we demonstrate a facile and efficient process for synthesizing Ag<sub>3</sub>PO<sub>4</sub>/AgCl hybrids at room temperature. Moreover, it indicates that the hybrids exhibit much higher catalytic activities than the single catalysts, which is attributed to the synthetic effect from the increased active sites as well as the enhanced electron-hole separation under visible light irradiation.

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