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The surface modification of Ag_3PO_4 using anionic platinum complexes for enhanced visible-light photocatalytic activity

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ABSTRACT

The surface modification of Ag_3PO_4 using anionic platinum complexes was successfully prepared. The starting materials of chloroplatinic chloride hydrate, silver nitrate, and sodium dihydrogen phosphate dodecahydrate were used in the experiments. The Ag_3PO_4 (AP) and defect- Ag_3PO_4 (DAP) were firstly synthesized using the coprecipitation method. These samples were suspended in chloroplatinic chloride solution under sonication to obtain the doping of anionic platinum complexes in Ag_3PO_4 (AP/Pt) and defect- Ag_3PO_4 (DAP/Pt). Anionic platinum complexes successfully substituted the phosphate site of Ag_3PO_4 and significantly improved the photocatalytic activity.

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1. Introduction

Utilizing platinum as a dopant has been widely used to improve the catalytic activity of photocatalyst. Many types of platinum can be incorporated into photocatalyst. The most common type is the metallic Pt nanoparticles, as utilized for TiO_2 photocatalyst modifications [1,2]. Other types are platinum ion, complex-ion, and cluster ion. The Pt ions doping into the lattice of TiO_2 is supported by the similar ionic radii of Pt^{4+} and Ti^{4+} [3]. The combination of Pt^{2+} ion and metallic Pt can also be applied to enhance catalytic activity of $\alpha\text{-Fe}_2\text{O}_3$ [4]. The Pt^{2+} in $\alpha\text{-Fe}_2\text{O}_3$ increases the isolation efficiency of the photo-induced carriers that improve the lifespan of hole carriers, whereas the metallic Pt in $\alpha\text{-Fe}_2\text{O}_3$ brought to the generation of Schottky barriers. TiO_2 surface modification using the clusters ion of $[\text{Pt}_3(\text{CO})_6]_6^-$ also improves the catalytic activity [5]. Platinum clusters act as charge scavenger that inhibits charge recombination and also act as a sensitizer.

Herein, the anionic platinum complexes doping in Ag_3PO_4 was successfully synthesized. Anionic platinum complexes successfully substitute the phosphate ion of Ag_3PO_4 under sonication. The substitution effectively occurs on the silver vacancy of Ag_3PO_4 . Up to now, there is no report of incorporating the Ag_3PO_4 by platinum complexes, and the result is very significant for the improvement

of Ag_3PO_4 -based photocatalyst. The rate of catalytic increased up to 5.8 times higher compared to the pure Ag_3PO_4 . The RhB can be degraded to 99.36% for only 6 min under the blue LED irradiation of 3 W.

2. Experimental

The Ag_3PO_4 and defect- Ag_3PO_4 were prepared using the co-precipitation method based on the previous results [6]. To prepare the defect- Ag_3PO_4 , the starting material of AgNO_3 (0.85 g) and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ (1.79 g) were dissolved in 200 mL of ethanol-water (50% ethanol) and 50 mL of water, respectively. The Na_2HPO_4 aqueous solution was slowly added to AgNO_3 ethanol-aqueous solution. The precipitates in this reaction were filtered and washed with distilled water and subsequently dried in an oven at 60 °C for 4 h. The Ag_3PO_4 (defect-free sample) as a control was prepared similar to the defect- Ag_3PO_4 preparation but using only 200 mL of water to dissolve the starting material of AgNO_3 , without addition of ethanol. To incorporate the anionic platinum complexes, the Ag_3PO_4 and defect- Ag_3PO_4 (0.5 g) was suspended in 10 mL of water under sonication. An amount of 11 mL of Pt solution was added to the suspension. The mixtures were sonicated for 5 min and mixed under magnetic stirrer for 30 min. The solution of chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) in water were designed at a concentration of 1.33 mg/mL. The obtained precipitates were filtered and washed with water three times and dried in an oven at

2

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60 °C for 4 h. The samples of Ag_3PO_4 , defect- Ag_3PO_4 , $\text{Ag}_3\text{PO}_4/\text{PtCl}_6^{2-}$ and defect- $\text{Ag}_3\text{PO}_4/\text{PtCl}_6^{2-}$ were named as AP, DAP, AP/Pt, and DAP/Pt, respectively.

The structure and bandgap energy were investigated using the XRD (Bruker AXS D2 PHASER) and DRS (Shimadzu, UV-2450), respectively. The binding energy and atomic composition were analyzed using XPS (Perkin Elmer PHI 5600).

To investigate the catalytic activities, 0.1 g of catalysts was contacted to RhB solution (100 mL, 10 mg/L) and equilibrated in a dark room [7]. The photocatalytic test was carried out under the visible light irradiation (Blue LED, 3 Watt). During the photocatalytic reaction, the RhB concentration was measured by the spectrophotometer (Shimadzu 1800).

3. Results and discussion

Fig. 1 shows the XRD pattern of Ag_3PO_4 (AP), defect- Ag_3PO_4 (DAP), $\text{Ag}_3\text{PO}_4/\text{PtCl}_6^{2-}$ (AP/Pt) and defect- $\text{Ag}_3\text{PO}_4/\text{PtCl}_6^{2-}$ (DAP/Pt). All of the samples exhibited a structure of body-centered-cubic (JCPDS No.06-0505) [8]. A little shift and doublet of the XRD pattern might be due to the effect of PtCl_6^{2-} incorporation.

The absorption of samples is presented in Fig. 2, and the band-gap energies were determined by the following formula (1):

$$(Ah\nu)^2 = h\nu - E_g \quad (1)$$

where A, h, ν , and E_g were absorbance, Planck constant, light frequency and bandgap energy [9]. The calculations derived from the DRS data are shown in Fig. S1 (Supplementary Material), the band-gap energy of 2.40 eV, 2.41 eV, 2.44 eV, and 2.44 eV were gained for AP, DAP, AP/Pt and DAP/Pt, respectively. The slight blue shift occurred in AP/Pt, and DAP/Pt might be caused by a chemically bonding of anionic platinum complexes on the surface of Ag_3PO_4 .

Based on XPS analysis, the spectra of Pt in AP/Pt and DAP/Pt were observed (Fig. 3). The content of 2.94% and 3.41% of Pt existed in AP/Pt and DAP/Pt, respectively. The higher content of Pt in DAP/Pt might be induced by the silver vacancy sites in DAP. The binding energies (BEs) of 73.18 eV and 75.12 eV were assigned to $\text{Pt(II)}_{4f_{7/2}}$ and $\text{Pt(IV)}_{4f_{7/2}}$ of AP/Pt, respectively whereas the BEs of 73.06 eV and 74.99 eV were assigned to $\text{Pt(II)}_{4f_{7/2}}$ and $\text{Pt(IV)}_{4f_{7/2}}$ of DAP/Pt, respectively [10]. The decreased BE of DAP/Pt might be the effect of defect changes from the silver deficiency to the phosphor deficiency. The concentration of Pt(IV) was higher than those in both AP/Pt and DAP/Pt. There was no metallic Pt state found in Ag_3PO_4 . The state of Pt(II) might be originated from the

reduction of Pt(IV) that might be reduced by an electron from the hydroxyl group [11].

The atomic ratios of Ag/P and P/O in the samples AP, DAP, AP/Pt, and DAP/Pt were calculated from the XPS data. The Ag/P atomic ratio of DAP (2.49) was lower than that of AP (2.80), implying that the DAP contained silver vacancy defect sites. After anionic platinum complexes doping, the Ag/P atomic ratio in AP/Pt was slightly increased (2.81), on the opposite, it was significantly increased in DAP/Pt (2.97). This result indicated that the elimination of phosphate ion might occur. This phenomenon was also convinced by the decrease of phosphor concentration after Pt complexes ion doping. The phosphor contents were 10.9%, 11.5%, 9.0%, and 8.1% in AP, DAP, AP/Pt, and DAP/Pt, respectively. The decreased phosphor in AP/Pt and DAP/Pt might be caused by substituting platinum complexes ion. The lowest content of phosphor in DAP/Pt implying that the silver vacancy was no longer existed in DAP and changed into a phosphor deficiency. The P/O atomic ratios of 0.26, 0.26, 0.22 and 0.20 were observed in AP, DAP, AP/Pt, and

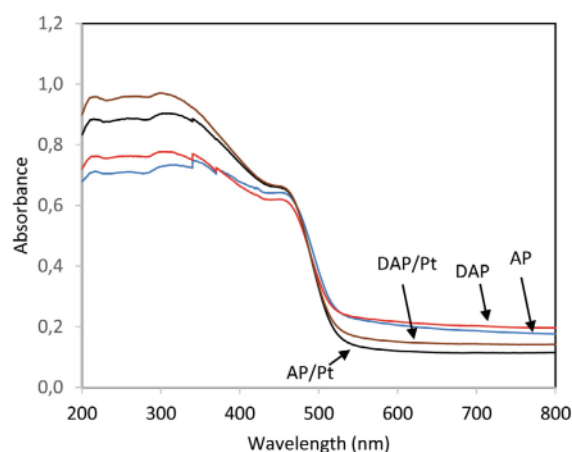


Fig. 2. The absorption of Ag_3PO_4 (AP), defect- Ag_3PO_4 (DAP), $\text{Ag}_3\text{PO}_4/\text{PtCl}_6^{2-}$ (AP/Pt), and defect- $\text{Ag}_3\text{PO}_4/\text{PtCl}_6^{2-}$ (DAP/Pt).

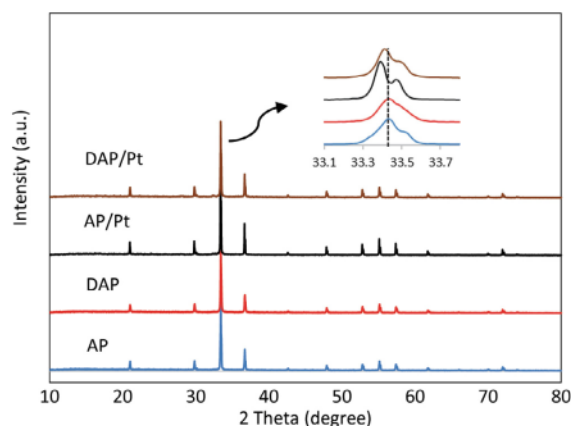


Fig. 1. The XRD pattern of Ag_3PO_4 (AP), defect- Ag_3PO_4 (DAP), $\text{Ag}_3\text{PO}_4/\text{PtCl}_6^{2-}$ (AP/Pt), and defect- $\text{Ag}_3\text{PO}_4/\text{PtCl}_6^{2-}$ (DAP/Pt).

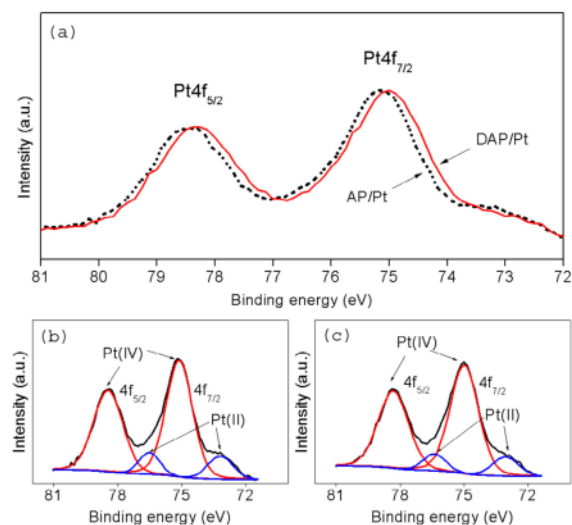


Fig. 3. The XPS profile of Pt4f in AP/Pt and DAP/Pt (a) and the deconvolution of AP/Pt (b) and DAP/Pt (c).

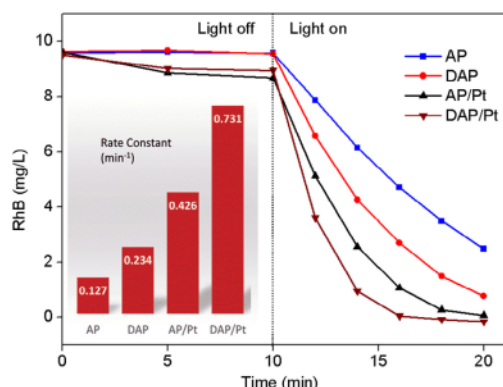


Fig. 4. Photocatalytic activity of Ag_3PO_4 (AP), defect- Ag_3PO_4 (DAP), $\text{Ag}_3\text{PO}_4/\text{PtCl}_6^{2-}$ (AP/Pt), and defect- $\text{Ag}_3\text{PO}_4/\text{PtCl}_6^{2-}$ (DAP/Pt).

DAP/Pt, respectively. The lowest P/O atomic ratio of DAP/Pt proved phosphor deficiency.

Fig. 4 shows the photocatalytic activity under blue light irradiation. The percentage of RhB removal efficiency (η in %) was calculated by the following equation (2).

$$\eta = \left(\frac{C_0 - C}{C_0} \times 100 \right) \% \quad (2)$$

where C_0 and C are the concentration at the starting time and after some time t of photocatalytic reaction, respectively [12]. The degradation percentage of 50.80%, 71.93%, 88.77%, and 99.38% has been achieved after 6 min irradiation for the samples of AP, DAP, AP/Pt, and DAP/Pt, respectively. The rates of photocatalytic reaction were also calculated using the pseudo-first-order kinetic [12], the results showed the rate constant of 0.127 min^{-1} , 0.234 min^{-1} , 0.426 min^{-1} , and 0.731 min^{-1} for AP, DAP, AP/Pt, and DAP/Pt, respectively. The sample of DAP/Pt possessed the highest catalytic activity. The catalytic rate enhanced significantly up to 5.8 times higher compared to the pure Ag_3PO_4 , and RhB completely degraded after 6 min. This result was even higher compared to other works utilized the CNT to modify Ag_3PO_4 , in which RhB dye was degraded after 12 min [9].

The silver vacancy in DAP had a significant effect on photocatalytic activity. It could trap the photogenerated electron-hole and prolongs the lifespan of photoexcited electron-hole pairs. The samples of AP and DAP treated under PtCl_6^{2-} solution resulted in AP/Pt and DAP/Pt samples, respectively. These samples exhibited higher catalytic activity with DAP/Pt showed the highest activity compared to AP and DAP, suggesting that the silver vacancy may enhance the incorporation of Pt complexes and changed it into a phosphor deficient.

The Pt complexes could be the main factor in the improvement of catalytic activity by capturing the photogenerated electron and inhibiting the electron-hole recombination. The enhanced activity

was due to efficient electron transfer between the Ag_3PO_4 conduction band and the chemically bonding of Pt(IV) species, which brought to efficient charge separation, similar to that of PtCl_4 -modified TiO_2 [13].

4. Conclusion

Anionic platinum complexes successfully substitute the phosphate ion of Ag_3PO_4 . The anionic platinum complexes incorporation in Ag_3PO_4 significantly improved the catalytic activity of Ag_3PO_4 . The excellent photocatalytic activity was ascribed to efficient electron transfer between the Ag_3PO_4 conduction band and the chemically bonding of platinum complexes brought to efficient charge separation.

6 Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matlet.2019.126848>.

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