Facile Synthesis of In$_2$S$_3$ Modified Ag$_3$PO$_4$ Nanocomposites with Improved Photoelectrochemical Properties and Stabilities

Yi-Kai Zeng$^1$, Shenyu Bo$^3$, Jun-hui Wang$^1$, Bin Cui$^1$, Hao Gu$^1$, Lei Zhu$^{1,2*}$ and Won-Chun Oh$^{2*}$

$^1$Key Laboratory for Advanced Technology in Environmental Protection of Jiangsu Province, Yancheng Institute of Technology, Yancheng, 224051, PR. China
$^2$Department of Advanced Materials Science & Engineering, Hanseo University, Seosan 31962, Republic of Korea
$^3$Suzhou Taicang Ecological Environment Bureau, Taicang City, Suzhou, 215400, PR. China

(Received September 23, 2020 : Revised October 13, 2020 : Accepted October 14, 2020)

Abstract In this work, Ag$_3$PO$_4$/In$_2$S$_3$ nanocomposites with low loading of In$_2$S$_3$ (5-15 wt %) are fabricated by two step chemical precipitation approach. The microstructure, composition and improved photoelectrochemical properties of the as-prepared composites are studied by X-ray diffraction pattern (XRD), field emission scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), photocurrent density, EIS and amperometric i-t curve analysis. It is found that most of In$_2$S$_3$ nanoparticles are deposited on the surfaces of Ag$_3$PO$_4$. The as-prepared Ag$_3$PO$_4$/In$_2$S$_3$ composite (10 wt %) is selected and investigated by SEM and TEM, which exhibits special morphology consisting of larger size substrate (Ag$_3$PO$_4$), particles and some nanosheets (In$_2$S$_3$). The introduction of In$_2$S$_3$ is effective at improving the charge separation and transfer efficiency of Ag$_3$PO$_4$/In$_2$S$_3$, resulting in an enhancement of photoelectric behavior. The origin of the enhanced photoelectrochemical activity of the In$_2$S$_3$-modified Ag$_3$PO$_4$ may be due to the improved charge separation, photocurrent stability and oriented electrons transport pathways in environment and energy applications.

Key words Ag$_3$PO$_4$, In$_2$S$_3$, photocurrent, charge separation, photoelectrochemical property.

1. Introduction

Solar energy represents one of the most abundant renewable natural energy but still least harvest resource.$^{1,2}$ Recently, photoelectrochemical water splitting by semiconductor photocatalysts has been considered as an effective route to convert solar energy directly into hydrogen for future renewable energy applications.$^{3,4}$ The water splitting process involves two half-cell reactions, the hydrogen evolution reaction (HER) on photocathodes and the oxygen evolution reaction (OER) on photoanodes. The latter is usually more complex and sluggish because it requires the removal of four electrons and two protons from two H$_2$O molecules, which is twice that required for HER. Silver phosphate (Ag$_3$PO$_4$), naturally crystallizing in a P43n body-centered cubic structure, is a n-type semiconductor with a direct bandgap of 2.43 eV and an indirect bandgap of 2.36 eV, ensuring that Ag$_3$PO$_4$ absorbs solar energy of the wavelength shorter than 530 nm.$^5$ This material has received considerable attention because of its versatile photooxidation applications such as OER catalysis and oxidation of organic pollutants,$^6$ which can be traced back to as early as 1988 when Tennakone and co-workers reported the first photocleavage of water using Ag$_3$PO$_4$.$^7$

It is well known that Ag$_3$PO$_4$ is slightly soluble in aqueous solution, which reduces its structural stability. Moreover, the conduction band potential of Ag$_3$PO$_4$ is more positive than that of the hydrogen potential.$^8$ Thus, Ag$_3$PO$_4$ absorbs a photon to generate an electron and a hole, and then the electron combines with an interstitial silver ion (Ag$^+$) to give a silver atom (Ag), which results in the photocorrosion of Ag$_3$PO$_4$ in the absence of a sacrificial reagent. The appeared black metallic Ag particles would suspend in the photocatalytic reaction systems and attach onto the surface of the Ag$_3$PO$_4$ catalyst, which would inevitably prevent the visible light absorption and

$^*$Corresponding authors
E-Mail : leizhu2016@ycit.edu.cn (L. Zhu, Yancheng Inst.Tech.)
wc_oh@hanseo.ac.kr (W.-C. Oh, Hanseo Univ.)

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decrease the photocatalytic activity.\textsuperscript{9} One of the effective ways is to build composite structures by assembling \( \text{Ag}_2\text{PO}_4 \) with other semiconductors such as \( \text{CeO}_2,\textsuperscript{10} \text{Nb}_2\text{O}_5,\textsuperscript{11} \text{GO},\textsuperscript{12} \text{In}_2\text{S}_3\textsuperscript{13} \) etc. In those systems, the composites exhibited a better photocatalytic performance compared with the pure \( \text{Ag}_2\text{PO}_4 \) and the enhanced photocatalytic activity is attributed to the synergistic effect including the matched bandgap structures, the improved visible light absorption and the enhanced separation rates of photogenerated electron-hole pairs.

Impressively, \( \text{In}_2\text{S}_3 \) is an n-type III–VI group chalcogenide semiconductor, which consists of elements with low toxicity. Moreover, \( \text{In}_2\text{S}_3 \) has been demonstrated to be a very promising optoelectronic material,\textsuperscript{14} and widely utilized in solar cell,\textsuperscript{15} photocatalysis,\textsuperscript{16} and PEC water splitting.\textsuperscript{17,18} In particular, \( \text{In}_2\text{S}_3 \) has favorable bandgap (2.0–2.3 eV), moderate charge transport characters, and relatively negative conduction band edge for photoelectrochemical hydrogen generation.\textsuperscript{19}

Herein, we demonstrate a successful and general procedure to resolve the above problems by the growth of \( \text{In}_2\text{S}_3 \) on the surfaces of \( \text{Ag}_2\text{PO}_4 \) crystals as shown in Fig. 1. The insoluble \( \text{In}_2\text{S}_3 \) could effectively protect the \( \text{Ag}_2\text{PO}_4 \) core-crystals from dissolution in aqueous solutions and enhance their stabilities during the photoelectric response process. Moreover, the experimental results confirm that these novel hetero crystals all exhibit much higher photoelectrochemical activities and stabilities than pure \( \text{Ag}_2\text{PO}_4 \) crystals.

2. Experimental Details

2.1 Materials

All of the reagents used in this experiment were analytical reagent grade and without further purification.

2.2 Sample preparation

Tetrahedral \( \text{Ag}_2\text{PO}_4 \) mesocrystals were easily prepared via the well-known silver ammonia assisted process. In a typical synthesis, \( \text{AgNO}_3 \) was added into 10 mL of deionized water to form transparent solution. Subsequently, 3 mL of ammonia water (25%) was added dropwise into the above solution under vigorous stirring for 1 h and subsequent heated at 140 °C for 0.5 h under argon gas flowing. The resulting solid product was collected by centrifugation, washed with distilled water, and dried in an oven at 60 °C. In this manner, different weight contents (5–15 wt%) of \( \text{In}_2\text{S}_3 \) in \( \text{Ag}_2\text{PO}_4/\text{In}_2\text{S}_3 \) composites were obtained, respectively. Pure \( \text{Ag}_2\text{PO}_4 \) and \( \text{In}_2\text{S}_3 \) samples were respectively prepared using the same procedures.

2.3 Characterization

The crystal structures of prepared compounds were performed by X-Ray Diffraction (XRD) with Cu Ka irradiation (XPert3, PANalytical), while the morphology and microstructure of the compounds were characterized by Scanning Electron Microscopy (SEM, Nova NanoSEM 450) and Field Emission Transmission Electron Microscopy (FE-TEM, JEM-2100F). X-ray photoelectron spectroscopy (XPS) was conducted to distinguish the chemical state (ThermoScientific, Escalab 250Xi).

2.4 Photoelectric Conversions

The photocurrent and the electrochemical impedance spectra (EIS) of the photocatalysts were obtained using an electrochemical workstation (CHI660E, China). A standard three-electrode system was performed in this photochemical study including counter electrode (Pt foil), reference electrode (saturated Ag/AgCl electrode) and working electrodes (glassy carbon electrode).\textsuperscript{21} To prepare the working electrode, 4 mg of catalysts and 30 mL of Nafion solution were dispersed in 1 mL of water-ethanol solution by sonicating for 2 h to form a homogeneous mixture. Then 5 mL of this solution was drop-cast onto a glassy carbon electrode (GCE) with a diameter of 3 mm, and was left to dry at room temperature. 0.1 mol/L sodium sulfate aqueous solution was acted as electrolyte. The simulated light source was a 500 W xenon lamp equipped with a simulated light source of the solar spectrum (AM 1.5).

![Fig. 1. Schematic of the facile fabrication process for \( \text{Ag}_2\text{PO}_4/\text{In}_2\text{S}_3 \) nanocomposite.](image)
with an AM 1.5 G filter operating at an illumination intensity of 100 mWcm⁻². According to the Nernst equation, the potential vs. reversible hydrogen electrode (RHE) could be obtained from the measured potential vs. Ag/AgCl. The EIS was implemented at 5 mV amplitude and frequency range of 1,000 kHz to 0.1 Hz.

3. Results and Discussion

3.1 Phase and morphology

Fig. 2A shows the X-ray diffraction (XRD) patterns of pure Ag₃PO₄ nanocrystals and In₂S₃. For pure Ag₃PO₄, all the diffraction peaks could be indexed to the cubic Ag₃PO₄ (JCPDS no.06-0505). Diffraction peaks of In₂S₃ correspond to tetragonal In₂S₃ (JCPDS cards no. 73-1366). No other miscellaneous peaks appear, suggesting the pure phase nature for the samples. As increasing the original In₂S₃ concentration from 5 wt% to 15 wt%, the Ag₃PO₄/In₂S₃ composites exhibits similar diffraction peaks as the pure In₂S₃ and Ag₃PO₄ as shown in Fig. 2B. Moreover, it should be noted that the diffraction peaks of Ag₃PO₄ in Ag₃PO₄/In₂S₃ composites gradually weaken when the In₂S₃ content increases, reflecting the decoration of more In₂S₃ particles onto Ag₃PO₄ surfaces which may prevent photocorrosion of pure Ag₃PO₄.

SEM was used to investigate the morphology and particle size of the as–prepared samples. As presented in Fig. 3(a,b), Ag₃PO₄ particles have an irregular spherical shape, particle size distribution is between 100 to 300 nm. It is also noticed that most Ag₃PO₄ particles have been growth larger after modification with In₂S₃ nanoparticles as shown in Fig. 3(c-h), which agreed with the XRD results. After higher temperature treatment, Ag₃PO₄ particles were growing into larger size which may provide more substrate for distribution of In₂S₃ nanoparticles. Thus more In₂S₃ nanoparticles can be easily dispersed on the surface of Ag₃PO₄. It’s worth noting that, while the content of In₂S₃ was 10 wt%, the shape of In₂S₃ comprises most small particles and some nanosheets as shown in Fig. 3(e, f). The proper morphology was one of the factors that influenced the photoelectric performance of composites under visible light irradiation. These results imply that nanosheet provides considerable effect for enhancing charge transport and visible-light absorption. However, as the content of In₂S₃ increases to 15 wt% in Fig. 3(g,h), it clear shows that more nanoparticles of In₂S₃ were aggregated together on the surface of Ag₃PO₄.

In order to ascertain the detail decoration of In₂S₃ on the surface of Ag₃PO₄, a typical Ag₃PO₄/In₂S₃ composite (10 wt%) was selected and further investigated by TEM. Fig. 4a shows that the Ag₃PO₄/In₂S₃ composite is special morphology consisting of lager size substrate (Ag₃PO₄), particles and some nanosheets (In₂S₃), in accordance with the SEM results. As shown in Fig. 4(b), it can be clearly observed that some small nanoparticles with size <25 nm of In₂S₃ are highly dispersed on the Ag₃PO₄ which size is above 200 nm. Clear observation can find that two phases of In₂S₃ and Ag₃PO₄ closely contact to form an intimate interface, which favors the charge transfer between In₂S₃ and Ag₃PO₄ and may promote the separation of photogenerated electron-hole pairs.

3.2 Chemical state

Inder to distinguish the chemical state of Ag₃PO₄/In₂S₃ (10 wt%) composite, XPS measurement was performed as shown in Fig. 5. The full XPS spectrum [Fig. 5(a)] indicates that the Ag₃PO₄/In₂S₃ composite is mainly composed of In, S, P, O and Ag elements. The XPS peak of C 1 s at 284.8 eV is assigned to residual carbon from the XPS instrument. There were two individual peaks at

![Fig. 2. XRD patterns of as-prepared samples: (A) pure Ag₃PO₄, pure In₂S₃; (B) (a) Ag₃PO₄/In₂S₃ 5 wt%, (b) Ag₃PO₄/In₂S₃ 10 wt%, (c) Ag₃PO₄/In₂S₃ 15 wt%.]
Fig. 3. FE-SEM micrographs of as-prepared samples: (a, b) pure Ag₃PO₄, (c, d) Ag₃PO₄/In₂S₃ 5 wt%, (e, f) Ag₃PO₄/In₂S₃ 10 wt%, (g, h) Ag₃PO₄/In₂S₃ 15 wt%.
374.0 and 368.0 eV in Fig. 5(b), which could be assigned to 3d\(_{3/2}\) and 3d\(_{5/2}\) of Ag\(^+\) respectively.\(^{26}\) In Fig. 5(c), the P 2p peak was at 133.0 eV, which corresponds to P\(^{5+}\) coming from Ag\(_3\)PO\(_4\).\(^{27}\) For the O 1s XPS spectra shown in Fig. 5(d), the binding energy of 530.8 eV was attributed to the O\(^{2-}\) in the Ag\(_3\)PO\(_4\), while the peak at 532 eV probably corresponded to the hydroxyl group.\(^{28}\) The two strong peaks at 445.2 and 452.7 eV can be attributed to
binding energies of In 3d$_{5/2}$ and In 3d$_{3/2}$, respectively. The peak at 161.5 eV is assigned to the binding energy of the S$_{2p}$ transition. These values agree well with the reported data for In$_2$S$_3$.\textsuperscript{20,29}

3.3 Photoelectrochemical performance

It is well known that semiconductors exhibit unique photoelectric properties owing to their intrinsic band-gap structure, which provides a simple and economical light-to-electric conversion approach for various energy-related applications. Therefore, the PEC activities of samples were investigated by transient photocurrent responses (Fig. 6) under visible light illuminations at an applied potential of -0.20 V vs Ag/AgCl in 0.1 M Na$_2$SO$_4$ aqueous

![Fig. 6. Transient photocurrent response (a-e) and Electrochemical impedance spectroscopy (f) of as-prepared samples: (a) pure Ag$_3$PO$_4$, (b) pure In$_2$S$_3$, (c) Ag$_3$PO$_4$/In$_2$S$_3$ 5 wt%, (d) Ag$_3$PO$_4$/In$_2$S$_3$ 10 wt%, (e) Ag$_3$PO$_4$/In$_2$S$_3$ 15 wt%.](image-url)
solutions. As shown in Fig. 6(a,b), the pure In$_2$S$_3$ exhibit a higher and stable photoelectric current than pure Ag$_3$PO$_4$ crystals which possess the lowest photoelectric behavior and obvious photocorrosion characteristics. In addition, the visible light response properties of the as-obtained Ag$_3$PO$_4$/In$_2$S$_3$ (5~15 wt%) composite samples were fairly improved shown in Fig. 6(c-e). Special for Ag$_3$PO$_4$/In$_2$S$_3$ (10 wt%), it exhibits higher and stable photocurrent response characteristics. To perform the transportation of photoelectron, we carried out electrochemical impedance spectroscopy as shown in Fig. 6(f). In general, the smaller slope of arc represents and Ag$_3$PO$_4$/In$_2$S$_3$ (10 wt%) composite exhibits the lowest charge-transfer resistance about 72.5 W. Therefore, the results of EIS and photocurrent response demonstrated that the introduction of In$_2$S$_3$ was effective to improve the charge separation and the transfer efficiency of Ag$_3$PO$_4$/In$_2$S$_3$, resulting in the enhancement of its photoelectric behavior.

The PEC activities of the as-prepared samples were further investigated by linear sweep voltammetry (LSV) (Fig. 7) under intermittent visible light irradiation with an illumination intensity of 100 mW cm$^{-2}$. Apparently, the photocurrents of all the hybrid electrode yield improvement compared with the corresponding pure Ag$_3$PO$_4$ in a wide potential range of 0 - 1.9 V vs. RHE under visible light irradiation. Compared with Ag$_3$PO$_4$ nanoparticles, the applied bias photon-tocurrent efficiency of Ag$_3$PO$_4$ increases efficiently, it achieves sequential improvement by introduction of co-catalyst In$_2$S$_3$. On the basis of the above results, we attribute the best PEC performance for Ag$_3$PO$_4$/In$_2$S$_3$ (10 wt%) composite mainly to better electron transport and efficient electron-hole separation. Above all, it can be clearly seen that the In$_2$S$_3$ could serve as excellent co-catalyst for Ag$_3$PO$_4$ to enhance its photoelectrochemical performance.

4. Conclusion

In summary, a series of novel Ag$_3$PO$_4$/In$_2$S$_3$ composites with different In$_2$S$_3$ content were successfully prepared. Most of In$_2$S$_3$ nanoparticles were grown on surface of Ag$_3$PO$_4$ through a modified facile solvothermal method. Ascribed to the good electrical interconnection, exposure of the high-active surface, the Ag$_3$PO$_4$/In$_2$S$_3$ can be directly used as electro and exhibit an excellent response to visible-light, which realized two orders of magnitudes enhancement in PEC activity than pure Ag$_3$PO$_4$. In addition, In$_2$S$_3$ (10 wt%) modified Ag$_3$PO$_4$ composite exhibits a much higher photocurrent density and stable PEC properties may attribute to its special morphology of In$_2$S$_3$ which exhibits mixture of nanoparticle and nanosheet.

Acknowledgements

This research was supported by the National Natural Science Foundation of China (11604288) and the Korea Electrotechnology Research Institute (KERI) primary research program through the National Research Council of Science & Technology (NST) funded by the Ministry of Science, ICT (MSIT) (No. 20A01029).

References


Author Information
Yi-Kai Zeng
Yancheng Institute of Technolog, Student
Shenyu Bo
Suzhou Taicang Ecological Environment Burea, Assistant Engineer
Jun-hui Wang
Yancheng Institute of Technolog, Student
Bin Cui
Yancheng Institute of Technolog, Student
Hao Gu
Yancheng Institute of Technolog, Student
Lei Zhu
Yancheng Institute of Technology Assistant Professor
Won-Chun Oh
Hanseo University Professor