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An urchin-like Ag₃PO₄/Pd/LaPO₄ photocatalyst with Z-scheme heterojunction for enhanced hydrogen evolution

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An urchin-like LaPO₄-based nanocomposite integrating Ag₃PO₄ and Pd has been initially synthesized via a controllable self-assembly route, with enhanced photocatalysis and ultrastable structure for the synergistic hydrogen (H₂) evolution under sunlight. Citric acid was employed as a structure-mediated agent to guide the oriented growth of LaPO₄ along [101] facet at room temperature, showing the urchin-like 3D structure. Furthermore, Pd and Ag₃PO₄ were coated in turn resulting in the Ag₃PO₄/Pd/LaPO₄ nanocomposite, in which Pd and Ag₃PO₄ could act as the functions of electron receptor and electron donor in the photocatalysis, respectively. It was discovered that the as-developed nanocomposite could present the robust photocatalysis and stable morphology after consecutive uses. Based on the band structure analysis, a Z-scheme system of Ag₃PO₄/Pd/LaPO₄ was thereby proposed for the sunlight photocatalysis, as testified by DMPO spin trapping ESR spectra. Also, the photoluminescence and electrochemical impedance of nanocomposites were conducted, indicating that the improved carriers properties should be responsible mainly for the dramatically enhanced photocatalytic activities. Moreover, the outstanding photocatalytic performances of Ag₃PO₄/Pd/LaPO₄ were demonstrated in H₂ evolution (1084.3 μmol·g⁻¹·h⁻¹) under sunlight. Importantly, such a citric acid-controlled self-assembly route may pave the way toward the fabrication of multi-component photocatalyst tailored for the wide photocatalytic applications.

1. Introduction

Up to date, semiconductor photocatalysts have been extensively fabricated for many photocatalytic applications like hydrogen generation of water splitting and removals of organic pollutants [1,2]. Moreover, in order to achieve more efficient photocatalysis performances especially under sunlight, the synthesis of various photocatalytic composites by integrating functional materials has been preferably explored in recent years [3–7]. For example, You et al. demonstrated g-C₃N₄ nanorods integrated with hollow InVO₄ nanospheres could allow for the enhanced photocatalytic degradation of methylene blue [8]. Lu and co-workers reported that Ni₃P dispersed with g-C₃N₄ could realize the highly efficient photocatalytic H₂ evolution [9]. Nevertheless, most of the current photocatalysts composed of functional elements can be trapped by some formidable disadvantages such as the complicated preparation, structural instability, and especially low synergistic photocatalysis efficiency, which may have challenged their practical applications on a large scale.

Recent years has witnessed the rapid development of metal phosphates as promising photocatalytic nanomaterials [10,11]. As a particular member of such family, LaPO₄ has attracted increasing attentions for the photocatalytic applications [12,13]. It is widely recognized that LaPO₄ can display a preeminent capacity for electron reduction due to its more negative conduction band potential, of which the photo-generated electrons with strong reduction can readily restore H₂O into H₂. Yet, some inhere defects of LaPO₄ have enormously limited its practical photocatalytic applications, such as functional singleness, low conductivity, and especially high recombination of photo-induced electron-holes leading to low photocatalysis. Hence, it is of great interest to integrate some functional elements to synergistically enhance the photocatalysis performances of the LaPO₄-based photocatalysts. Moreover, as another important member of metal phosphates, Ag₃PO₄...
has concentrated great efforts in the photocatalysis field because of its excellent quantum efficiency over visible light area [14–17]. Alternatively, Ag3PO4 has been employed as a photosensitizer or active site to be modified on other photocatalysts. For example, Liu's group found that Ag3PO4 nanoparticles in situ grown on the surface of two-dimensional MoSe2 nanoarchitectures could act as a noble metal-free cocatalyst for photocatalytic oxygen evolution under LED-light irradiation [18]. Yang et al. reported g-C3N4 nanorods integrated with Ag3PO4 using Ag and graphene as mediators showing the enhanced photocatalytic performances for water oxidation [19]. Besides, photocatalyst integrated with Ag3PO4 has been usually testified forming a Z-scheme heterojunction distinguished from the conventional heterojunction. Specifically, the reduced metallic Ag nanoparticles can play a role as the electron mediator in promoting the separation and transferring of charge carriers on Ag surfaces, resulting in the Z-scheme mechanism for improved photocatalysis [20,21].

In the present work, we seek to employ the self-assembly route to synthesize an urchin-like LaPO4 nanorods by using citric acid as the structure-mediated agent, followed by the integration of functional materials of Pd and Ag3PO4. The resulting nanocomposites could display dramatically enhanced photocatalysis for the synergistic H2 evolution, due to their improved carriers transferring and especially synergistic photocatalysis efficiency of self-assembled elements. Also, an extremely stable urchin-like structure, instead of a simple mixture, could be expected for the resulting nanocomposites, showing a preeminent specific surface area together with numerous unsaturated active sites exposed from their poignant profile. Also, photosensitive Ag3PO4 would be decomposed to produce Ag elements serving as the bridge for transferring photogenerated electrons so as to efficiently construct the Z-scheme heterojunction to endow the enhanced photocatalytic activity of Ag3PO4/Pd/LaPO4, of which the efficient photocatalysis performances were subsequently demonstrated in photocatalytic H2 evolution. The fabrication procedure and main photocatalytic mechanism of Ag3PO4/Pd/LaPO4 nanocomposite is schematically illustrated in Scheme 1. To the best of our knowledge, this is the first report on the fabrication of an urchin-like photocatalyst of LaPO4-based nanocomposite integrating functional elements of Pd and Ag3PO4 by the controllable self-assembly route, achieving the enhanced photocatalysis and ultrastable structure for synergistic H2 evolution under sunlight.

2. Experimental section

2.1. Materials and instruments

La(NO3)3·6H2O (99.0%) was purchased from Sigma-Aldrich Co. Ltd. (Shanghai, China). Pd(C2H3O2)2 (Pd ≥ 47.0%) was obtained from Dibai Biotechnology Co. Ltd. (Shanghai, China). AgNO3 (99.8%), Na3PO4·12H2O (98.0%) and C6H8O7·H2O (99.5%) were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). H3PO4 (85.0%) was bought from Kaitong Chemical Co. Ltd. (Tianjin, China). Lactic acid, ethanol, and TiO2 powders are commercially available of analytical grade and used as received. Deionized water (> 18.2 Megohm/cm), which was obtained from an ultra-pure water system (Pall, USA), was used for the preparation of all solutions. LabSolar-III AG photocatalytic on-line analysis system was bought from PerfectLight Technology Co. Ltd. (Beijing, China).

2.2. Preparation of photocatalytic materials

2.2.1. Synthesis of LaPO4

Typically, 216.5 mg of lanthanum nitrate and 50 mg of citric acid were dissolved in 50 mL deionized water. An aliquot of 30 µL of phosphoric acid was added in 5 mL water and then slowly dropped into the above mixture to be stirred for 30 min at room temperature. The resulting LaPO4 white precipitate was centrifuged and washed with water and ethanol each for several times. Finally, the obtained LaPO4 products were calcined at 200 °C for 2 h and further collected in the dryer. In addition, the preparation of Ag3PO4 was detailed in supporting information.

2.2.2. Synthesis of Pd/LaPO4

Typically, an aliquot of 150 mg of LaPO4 powder and 1.6 mg of palladium acetate were dispersed in 30 mL ethanol. The mixture was

![Scheme 1](image-url)
sonicated for 5 min, and then stirred in the dark overnight. The obtained gray product of Pd/LaPO₄ was washed with ethanol to eliminate the impurities, followed by being dried at 60 °C for 12 h.

2.2.3. Synthesis of Ag₃PO₄/Pd/LaPO₄

In a typical synthesis route, 200 mg of Pd/LaPO₄ powder was dispersed into 10 mL water, followed by adding 4.9 mg of silver nitrate. Furthermore, 3.6 mg of sodium phosphate was dissolved in 10 mL water and then added drop by drop into the above mixture to be stirred for 1 h in dark. The resultant Ag₃PO₄/Pd/LaPO₄ nanocomposites were centrifuged and washed with water and ethanol for several times, and subsequently dried at 60 °C to be further stored in the dryer.

2.3. Characterization of photocatalytic materials

The phase compositions of the prepared products were determined by X-ray diffraction (XRD, PANalytical/X’pert3). The diffraction patterns were recorded in the range of 2θ = 15°–60° using Cu Kα radiation. X-ray photoelectron spectra (XPS) were determined by a spectrometer (ESCALAB 250Xi) using Al Kα radiation. The morphological structures of the materials were examined separately by the field emission scanning electron microscopy (SEM, JEOL/JSM-6700F and Carl Zeiss AG/Sigma 500 VP) with electron energy of 5 kV and the transmission electron microscopy (TEM, JEOL/JEM-2100PLUS). The inductively coupled plasma (ICP) tests were carried out by an emission spectrometer (ICP/2060 T). The optical properties of material samples, i.e., UV–vis diffuse reflection spectra (DRS), were explored by UV-3600

![Fig. 1. (a) XRD patterns of different samples; XPS spectra of (b) La 3d, (c) Ag 3d, (d) Pd 3d, (e) P 2p, and (f) O 1s.](image-url)
spectrophotometer (Shimadzu, Japan) using BaSO₄ as reference in the range of 250–700 nm. The photoluminescence spectra of the samples were measured using the fluorescence spectrometer (Horiba/FluoroMax-4). DMPO electron spin resonance (ESR) tests were conducted by a spectrometer (JEOL/JES-FA200) to prove the existence of ·O₂⁻ and ·OH in the photocatalytic reactions. The electrochemical workstation (CHI 760D) was used to record the electrochemical impedance spectroscopy (EIS) using a platinum plate and a saturated calomel electrode as the counter electrode and reference electrode, respectively. The working electrode was made by dip-coating a sample slurry (5 mg·mL⁻¹ in ethanol) on titanium plate with the area at 1.5 × 1.0 cm, followed by air drying, and 0.10 M KCl solution was used as the electrolyte.

2.4. Photocatalytic H₂ evolution experiments

The activities of photocatalytic materials in the photocatalytic H₂ evolution reactions were investigated under simulated sunlight irradiation by using LabSolar-III AG photocatalytic on-line analysis system similar to the previous report [22]. Typically, an aliquot of 0.1 g of photocatalysts was dispersed in 45 mL of water. Further, 5 mL of lactic acid was added as the sacrificial reagent for the holes capture. The simulated sunlight source of a 300 W Xe-lamp (PerfectLight Technology Co. Ltd., PLS-SXE300) was placed 20 cm apart from the reaction solution. The temperature of reaction solution was kept at 15 ± 2 °C by cooling water. At given time intervals, H₂ concentrations so evolved were determined online using the gas chromatography (Agilent Technologies Co. Ltd., GC-7890B, MS-5A column, TCD, N₂ carrier).

![Fig. 2. (a) SEM images and (b) size distribution of Ag₃PO₄/Pd/LaPO₄ nanocomposites; (c–d) TEM images of Ag₃PO₄/Pd/LaPO₄ of different magnifications; (e) EDS element mapping of Ag₃PO₄/Pd/LaPO₄ composing of O, P, La, Ag, and Pd elements.](image-url)
3. Results and discussion

3.1. Fabrication and characterization of Ag₃PO₄/Pd/LaPO₄

The fabrication procedure of Ag₃PO₄/Pd/LaPO₄ nanocomposite is schematically illustrated in Scheme 1a. Herein, during the controlled self-assembly synthesis of urchin-like LaPO₄ photocatalyst, La³⁺ ions were coordinated with citric acid, and reunited together to form the La³⁺-citric acid complex. When H₃PO₄ was subsequently added in above system, the crystals grew along the [101] direction to develop the urchin-like structure of LaPO₄, which was subsequently stabilized by calcination. Afterwards, Pd nanoparticles (high work function) were deposited, aiming to restrain the recombination of carriers to achieve more reduction sites of photogenerated electrons of LaPO₄, and significantly strengthened the visible light absorption [23,24]. The resulting Pd/LaPO₄ was further coated with Ag₃PO₄ to yield the Ag₃PO₄/Pd/LaPO₄ nanocomposites. Thereunto, Ag₃PO₄ would be decomposed to produce Ag elements (low work function) to serve as the bridges between LaPO₄ and Ag₃PO₄ for boosting the transferring of photogenerated electrons. [25,26]. The main photocatalytic mechanism of Ag₃PO₄/Pd/LaPO₄ nanocomposite was described in Scheme 1b, which would be discussed in more detail afterwards.

The crystal structure of the prepared Ag₃PO₄/Pd/LaPO₄ photocatalyst was determined by comparing to Pd/LaPO₄ and LaPO₄ using the X-ray powder diffraction (XRD) patterns (Fig. 1a). Accordingly, the Ag₃PO₄/Pd/LaPO₄ has the diffraction peaks at 19.8°, 28.9°, 31.2°, 41.5°, and 48.0° corresponding to the (101), (200), (102), (211) and (212) facets, respectively, indexed for the crystalline phase of hexagonal LaPO₄ (JCPD standard card No.46-1439) [27]. It was a pity that no significant diffraction peaks of Ag₃PO₄ or Pd were observed for the nanocomposite, which might presumably due to that Pd and Ag₃PO₄ were highly dispersed on the surface of the LaPO₄ with relatively low contents of Pd and Ag in Ag₃PO₄/Pd/LaPO₄ were determined by ICP-AES. Moreover, the morphology features of Ag₃PO₄/Pd/LaPO₄ products were characterized separately using scanning electronic microscopy (SEM) and transmission electronic microscopy (TEM) (Fig. 2). It was found that LaPO₄ could present the urchin-like 3D structure composed of massive nanorods (Fig. S2). After the deposition of Pd and Ag₃PO₄ elements, the yielded Ag₃PO₄/Pd/LaPO₄ could evidently retain the orientation accumulation of nanorods (Fig. 2a), which could feature the high dispersity with the rod length of 190-270 nm (Fig. 2b). Importantly, the well retained urchin-like structure of Ag₃PO₄/Pd/LaPO₄ would provide a large surface area to enhance the contact of the photocatalysts with water and lactic acid afterwards, which would help to improve the photocatalytic activity in the H₂ evolution. Also, urchin-like Ag₃PO₄/Pd/LaPO₄ could be topologically composed of numerous nanorods, with the average size of about 10 nm in diameter (Fig. 2c), which could help to improve the separation of photogenerated carriers substantially. Moreover, one can note from Fig. 2d that the lattices, which were measured from the selected areas, illustrate the spacings of 0.45 nm and 0.27 nm, corresponding to the (101) lattice facets of hexagonal LaPO₄ and the (210) lattice plane of cubic Ag₃PO₄, respectively. Pd nanoparticles deposited on nanocomposites can present an average size of about 5.0 nm in diameter. Moreover, high-resolution TEM imaging was further performed for Ag₃PO₄/Pd/LaPO₄ to explore the presence of Ag₃PO₄ with the results shown in Fig. S3, showing that Ag₃PO₄ nanorods (indicated with red arrows) were coated on LaPO₄ nanorods. In addition, X-ray energy dispersive spectroscopy (EDS) element mapping was employed to probe the spatial distribution of chemical elements of Ag₃PO₄/Pd/LaPO₄ with disparate color contrasts (Fig. 2e). As expected, the elements of O, P, La, Ag, and Pd could be uniformly distributed on the surface of the nanocomposites. Besides, the contents of Pd and Ag in Ag₃PO₄/Pd/LaPO₄ were determined by ICP measurements, with the data listed in Table S1.

The optical absorption properties of the prepared photocatalysts were further explored by the diffuse reflectance spectra (DRS) (Fig. 3a). Herein, the band gaps of different photocatalyst samples; (b) plots of (ahv)¹/² versus hv of Ag₃PO₄ and LaPO₄.

where α is the optical absorption coefficient, hν represents photonic energy, A represents proportionality constant, and Eg is the band gap, respectively. One can note that the Pd element could significantly enhance the visible light absorption of Pd/LaPO₄, showing a strong harvest over the wavelength range from 520 nm to higher. Also, an increased light harvest from 420 to 480 nm wavelengths could be observed after adding Ag₃PO₄ sensitizer into the Pd/LaPO₄. More importantly, after the sunlight illumination, Ag₃PO₄ would be decomposed into Ag nanoparticles so as to give rise the surface plasma resonance of Ag in the nanocomposites, which would dramatically
enhance the absorption over the range of 360–700 nm. In addition, Fig. 3b manifests that in contrast to Ag₃PO₄ with a band gap energy of 2.29 eV, pure LaPO₄ with a band gap energy of 3.42 eV (362 nm of absorption edge) itself may not be efficiently excited by the visible light. Therefore, Pd and Ag₃PO₄ components decorated on LaPO₄ can endow the resulting nanocomposites with the enhanced photocatalytic activities, partly due to the broadened solar light harvest.

3.2. Photocatalytic hydrogen evolution and Z-scheme mechanism of Ag₃PO₄/Pd/LaPO₄

The photocatalysis performances of Ag₃PO₄/Pd/LaPO₄ nanocomposites for the photocatalytic H₂ evolution were comparably assessed, with the data shown in Fig. 4a, b. As revealed in Fig. 4a the synthesized products could have the different abilities in the photocatalytic H₂ generations. Especially, the Ag₃PO₄/Pd/LaPO₄ nanocomposites could present the better photocatalytic activity than those of other photocatalysts of TiO₂, LaPO₄, and Pd/LaPO₄. Moreover, the H₂ evolution rates for commercial TiO₂, LaPO₄, Pd/LaPO₄ and Ag₃PO₄/Pd/LaPO₄ samples were calculated to be 0.30, 2.40, 704.9, and 1084.3 μmol·g⁻¹·h⁻¹, respectively (Fig. 4b). Apparently, the H₂ evolution rate of Ag₃PO₄/Pd/LaPO₄ is over 3600 and 450 times larger than those of commercial TiO₂ and pure LaPO₄, respectively. Also, much higher H₂ yield could be obtained for the Ag₃PO₄/Pd/LaPO₄ nanocomposites for the photocatalytic H₂ evolution.
nanocomposites, which could reach 216.9 μmol in the 2 h under simulated sunlight, corresponding to 1084.3 μmol·g⁻¹·h⁻¹ on average.

The stability tests of photocatalytic hydrogen evolution were carried out by using Ag₃PO₄/Pd/LaPO₄. As seen in Fig. 4c, a gradual decrease in the rate of H₂ evolution could be observed for Ag₃PO₄/Pd/LaPO₄, which might be attributed to the behavior of photo-decomposition of Ag₃PO₄ materials, slightly challenging the photocatalytic stability of composites. Yet, the favorable photocatalytic stability of nanocomposites could be verified for consecutive uses of five runs. One can note that an increased H₂ evolution rate of Ag₃PO₄/Pd/LaPO₄ could be observed at 8 h. Such as phenomenon was thought to be resulted from the fact that during the photocatalytic H₂ evolution reactions, a gradual activation and decomposition of Ag₃PO₄ in Ag₃PO₄/Pd/LaPO₄ should occur. As a result, Ag nanoparticles should be released with a suitable quantity at a certain time like 8 h, which would achieve the best separation and transferring efficiencies of photogenerated electron-hole pairs of photocatalysts leading to the irregular enhancement of H₂ evolution. In addition, it was found that the XRD patterns (Fig. 4d) and urchin-like structure (Fig. 4e) of Ag₃PO₄/Pd/LaPO₄ could exhibit no obvious variation before and after the photocatalytic reactions, indicating that the nanocomposites could still remain the satisfactory crystal structure and initial morphology.

To investigate the possible photocatalytic mechanism, the energy band structures of Ag₃PO₄/Pd/LaPO₄ nanocomposites were investigated with the results shown in Table S2. Accordingly, the valence band potential (EᵥB) of LaPO₄ (2.68 eV) so calculated is more negative than that of Ag₃PO₄ (2.74 eV), which is in consistent with the conduction band potential (EᶜB) of LaPO₄ (–0.74 eV) versus EₑB of Ag₃PO₄ (0.45 eV). The data indicate that this well-matched band structures could probably form an expectant heterojunction between LaPO₄ and Ag₃PO₄ for effective separation and transfer of photoinduced electrons-holes pairs. On the basis of their energy band potentials and photocatalytic performances, a possible photocatalytic mechanism of Ag₃PO₄/Pd/LaPO₄ was thereby proposed in Fig. 4f. The photogenerated electrons from CB of Ag₃PO₄ move to Ag nanoparticles with low work function (4.3 eV) through the Schottky barrier due to the more positive Fermi level and outstanding conductivity of Ag metal [33,34]. Furthermore, the photogenerated electrons from Ag nanoparticles further migrate to the VB of LaPO₄ to recombine rapidly with electropositive holes. Subsequently, the detached photogenerated electrons on the CB of LaPO₄ are captured by Pd nanoparticles with high work function (5.1 eV) for transforming H₂O (O₂) into H₂ (–O₂⁻).

Therefore, the developed photocatalyst can feature the functions of Ag₃PO₄ (electron donors) and Pd (electron reduction) for the photocatalytic hydrogen evolution and organic pollutants degradation under sunlight. In addition, although the CB potential of Ag₃PO₄ is more positive than that of EᵥB (H₂/H₂) and EₑB (O₂/O₂⁻) [35], an enhanced H₂ production can still be acquired for the photocatalytic reactions (Fig. 4a), indicating that the photo-induced electrons might migrate from Ag₃PO₄ to LaPO₄ rather than from LaPO₄ to Ag₃PO₄. According to the description for other nanocomposites (i.e., Ag₃PO₄/In₂S₃ and Ag/AgBr/BlOBr) [29,36,37], the obtained results above inspired us to believe that the developed Ag₃PO₄/Pd/LaPO₄ might conduct the Z-scheme mechanism in the photocatalytic reactions. Accordingly, the generated Ag nanoparticles might serve as the bridges to establish the Z-scheme heterojunction at the interface of LaPO₄ and Ag₃PO₄, suggesting that the pathways of electron migration might be converted from the conventional “downstairs” to the novel “upstairs”. Hence, this manner can conspicuously enhance the reduction ability of photogenerated electrons toward the improve photocatalytic H₂ evolution.

To further verify the hypothesis above, DMOPO electron spin resonance (ESR) tests were performed to validate if the existence of ·O₂⁻ and ·OH in the photocatalytic reactions, aiming to testify the construction of Z-scheme manner [38-40]. As shown in Fig. 5a, no peaks were discovered in the darkness. However, four strong characteristic peaks of DMOPO··O₂⁻ could be perceived in methanol while Ag₃PO₄/Pd/LaPO₄ was illuminated by visible light after 10 min. Similarly, typical signal of DMPO··OH was observed in Fig. 5b, implying the ·OH could also be continually generated during the photocatalytic process. Hence, the results of ESR were in good agreement with the data of the capture experiments, suggesting that the developed nanocomposites could feature the Z-scheme system for the efficient photocatalytic reactions. In addition, the active species capture experiments were performed to further attest the establishment of Z-scheme manner as described elsewhere [20,34,35], with the data shown in Fig. 5c. Accordingly, the ·O₂⁻ (rather than ·OH) should serve as the dominant active substances for the photocatalytic reactions with Ag₃PO₄/Pd/LaPO₄, even though the CB potential of Ag₃PO₄ is more positive than that of LaPO₄, thus confirming the presence of Z-scheme heterojunction.

3.3. Enhanced photogenerated carriers properties of Ag₃PO₄/Pd/LaPO₄

In order to further explore the main reasons for the enhanced photocatalytic activities of Ag₃PO₄/Pd/LaPO₄ nanocomposites, the separation efficiencies of photo-induced electron-hole pairs were investigated by the photoluminescence (PL) spectra by taking LaPO₄ and Pd/LaPO₄ for the comparison (Fig. 6a). In principle, a weaker PL intensity of peak should correspond to a lower recombination rate of photo-induced charge carriers, rendering a more favorable photocatalytic activity [41]. Accordingly, the developed photocatalysts were excited by light energy to attain the PL spectra. It was evidently found from Fig. 6a that Ag₃PO₄/Pd/LaPO₄ nanocomposites could exhibit the weakest PL intensity than those of other products, indicating that the synergistic effects of Ag₃PO₄/Pd/LaPO₄ components could satisfactorily promote the separation efficiency of photo-induced electron-hole pairs toward the high capacity for the photocatalytic H₂ evolution.

Moreover, electrochemical impedance spectroscopy (EIS) measurements were comparably performed to explore the photo-induced charge transfer process (Fig. 6b), in which a smaller semicircle radius should signify a faster charge carriers transfer [42]. One can note from Fig. 6b that the arc radius of Ag₃PO₄/Pd/LaPO₄ exhibits the better electrical conductivity and smaller transfer resistance of charge carriers than those of LaPO₄ and Pd/LaPO₄ products, implying that the photo-generated charge carriers could transfer rapidly through the interface of distinct semiconductors in the photocatalytic system of Ag₃PO₄/Pd/LaPO₄. As a result, the transfer velocity of photogenerated charge carriers could be expedited obviously due to the efficient synergistic effects between LaPO₄ and Ag₃PO₄ materials in the photocatalytic nanocomposites.

4. Conclusion

In summary, urchin-like LaPO₄ photocatalyst with integrated Pd and Ag₃PO₄ have been successfully synthesized simply by using a controlled self-assembly route at the assistance of citric acid. Herein, Pd (electron acceptor) and Ag₃PO₄ (electron donor) as different functional components of active sites were introduced on the surface of LaPO₄, leading to the improved separation and transfer ability of photogenerated charge carriers for the photocatalytic reactions. Meanwhile, Ag nanoparticles decomposed from Ag₃PO₄ could serve as the bridges to feature the Z-scheme system of nanocomposites, so that the reduction ability of photogenerated electrons could be significantly enhanced. Comparable investigations indicate that the developed photocatalysts could exhibit > 3600 times higher rates of photocatalytic H₂ evolution than the commercial TiO₂. Moreover, urchin-like LaPO₄ carriers could endow the Pd and Ag₃PO₄ components so anchored with the strong steric hindrance, resulting in the high morphological stability to promise for repeated photocatalytic uses. Importantly, this controlled self-assembly route should not only facilitate the synthesis of urchin-like LaPO₄ carriers, but also circumvent the enhanced photogenerated carriers properties of different functional components integrated in the nanocomposites, as testified by PL and EIS analysis. It may open a new
door toward the efficient fabrication of multi-component photocatalyst with highly stable structure and especially novel Z-scheme heterojunction to promise for highly H₂ evolution under sunlight.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apsusc.2019.143771.

References


[34] L. Ye, J. Liu, G. Gong, L. Tian, T. Peng, L. Zan, Two different roles of metallic Ag on Ag/AgX/BiOX (X = Cl, Br) visible light photocatalysts: surface plasmon resonance and Z-scheme bridge, ACS Catal 2 (2012) 1677–1683.

[35] T. Yan, J. Tian, W. Guan, Z. Qiao, W. Li, J. You, B. Huang, Ultra-low loading of Ag3PO4 on hierarchical In2S3 microspheres to improve the photocatalytic performance: the cocrystal effect of Ag and Ag3PO4, Appl Catal B Environ 202 (2017) 84–94.


