

# Cocatalytic Effect of SrTiO<sub>3</sub> on Ag<sub>3</sub>PO<sub>4</sub> toward Enhanced Photocatalytic Water Oxidation

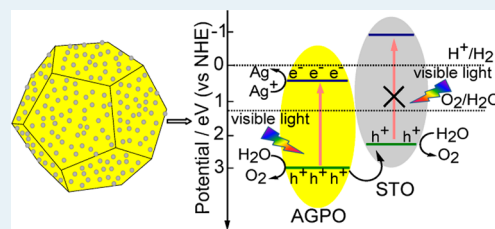
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## Supporting Information

**ABSTRACT:** Ag<sub>3</sub>PO<sub>4</sub> has been reported to be an excellent photocatalyst for O<sub>2</sub> evolution from aqueous solution, which makes it a promising candidate for designing a Z-scheme water-splitting system. In this work, in order to further improve the photocatalytic activity, a series of SrTiO<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub> composite photocatalysts was constructed by introducing SrTiO<sub>3</sub> (with a less positive valence band minimum) to Ag<sub>3</sub>PO<sub>4</sub> and was synthesized by two consecutive hydrothermal processes. The obtained photocatalysts were systematically characterized by XRD, SEM, BET, UV-vis, etc., showing that SrTiO<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub> composites were formed by coating SrTiO<sub>3</sub> onto a Ag<sub>3</sub>PO<sub>4</sub> polyhedron. Photocatalytic O<sub>2</sub> evolution results demonstrated that a small amount of SrTiO<sub>3</sub> brought about significant enhancement of photocatalytic activity of Ag<sub>3</sub>PO<sub>4</sub> and that the apparent quantum yield at 420 nm reached 16.2% with a molar ratio of SrTiO<sub>3</sub> to Ag<sub>3</sub>PO<sub>4</sub> equal to 1/20, which led to the fact that SrTiO<sub>3</sub> could serve as cocatalyst for water oxidation providing both accelerated electron-hole separation by band gap alignment and more active sites by enlarged surface area.

**KEYWORDS:** SrTiO<sub>3</sub>, Ag<sub>3</sub>PO<sub>4</sub>, cocatalysis, photocatalysis, O<sub>2</sub> evolution



## 1. INTRODUCTION

Photocatalytic water splitting assisted by a semiconductor has been considered to be one of the most promising approaches for solving both energy and environmental issues worldwide.<sup>1–4</sup> Water splitting can be separated to two half reactions, namely, hydrogen production and oxygen production.<sup>5–7</sup> As hydrogen production has been quite efficiently achieved during the past decade, fabrication of a robust photocatalyst for oxygen evolution still remains a challenge due to the more complicated four electron process.<sup>8–14</sup> Recently, Ag<sub>3</sub>PO<sub>4</sub> has been reported to be an excellent photocatalyst for water oxidation and thus drew tremendous attention.<sup>15</sup> Because of its highly dispersive conduction-band structure resulting from delocalized *d* states, a small effective mass of electron was obtained, which facilitated the immigration of photoexcited electrons and holes.<sup>16</sup> Tetrahedral Ag<sub>3</sub>PO<sub>4</sub> composed of {111} facets was synthesized by Martin et al. through a kinetic control method, and it performed greater activity in water photooxidation than those composed of {100} and {110} faceted crystals.<sup>17</sup> In our previous work, enhanced O<sub>2</sub> evolution activity was also achieved from the better crystallization and more regulated morphology by virtue of hydrothermal treatment, followed by optimization of reaction conditions such as temperature, pH, etc. for hydrothermal preparation of Ag<sub>3</sub>PO<sub>4</sub>.<sup>18</sup>

It is widely accepted that coupling semiconductor materials with matched band-edges could facilitate the immigration and separation of photogenerated electrons and holes, and indeed benefit the photocatalytic activity and stability.<sup>19</sup> Some composites of Ag<sub>3</sub>PO<sub>4</sub> (CQDs/Ag<sub>3</sub>PO<sub>4</sub>,<sup>20</sup> Ag<sub>3</sub>PO<sub>4</sub>/TiO<sub>2</sub>,<sup>21</sup> Ag<sub>3</sub>PO<sub>4</sub>/graphene(oxide),<sup>22–27</sup> Ag<sub>3</sub>PO<sub>4</sub>/CNTs,<sup>28</sup> and g-

C<sub>3</sub>N<sub>4</sub>/Ag<sub>3</sub>PO<sub>4</sub><sup>29</sup>) were also reported to give better activity for eliminating organic pollutants. As for O<sub>2</sub> evolution, few heterostructured photocatalysts based on Ag<sub>3</sub>PO<sub>4</sub> were evaluated.<sup>30</sup> SrTiO<sub>3</sub> is a stable semiconductor that has been widely studied as photocatalyst for water splitting,<sup>31–35</sup> whose minimum conduction band (CBM) and maximum valence band (VBM) are both negative compared to those of Ag<sub>3</sub>PO<sub>4</sub>. Guo et al. designed a heterojunction of Ag<sub>3</sub>PO<sub>4</sub> and Cr-SrTiO<sub>3</sub>, and proved the accelerated electron and hole transportation between them.<sup>36</sup> The designed heterojunction showed superior performance in IPA photodegradation than separated materials. However, low activity for O<sub>2</sub> evolution was obtained.

In this contribution, pure phase SrTiO<sub>3</sub> was introduced to Ag<sub>3</sub>PO<sub>4</sub>, in order to further enhance the photo oxidation activity of Ag<sub>3</sub>PO<sub>4</sub> by providing a cocatalytic effect. Several unique advantages of pure phase SrTiO<sub>3</sub> were taken into consideration. First, efficient charge separation could be achieved between SrTiO<sub>3</sub> and Ag<sub>3</sub>PO<sub>4</sub> due to their matched band-edges. Second, differing from the traditional noble metal cocatalyst, loading pure SrTiO<sub>3</sub> avoided obstructing visible light absorption of Ag<sub>3</sub>PO<sub>4</sub>. Third, unlike Cr-SrTiO<sub>3</sub>, pure SrTiO<sub>3</sub> was not excited under visible-light irradiation, which protected Ag<sub>3</sub>PO<sub>4</sub> from being reduced by photogenerated electrons of SrTiO<sub>3</sub> and facilitated the concentrating of research on the cocatalytic effect of SrTiO<sub>3</sub>. A series of SrTiO<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub> photocatalysts was synthesized by a two-consecutive hydro-

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thermal process. The properties of photocatalysts such as crystal structure, optical property, morphology, and photocatalytic activity were systematically characterized and evaluated, and the mechanism of the improved photocatalytic activity of SrTiO<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub> composite was proposed.

## 2. EXPERIMENTAL SECTION

**2.1. Materials and Sample Preparation.** All of the reagents were purchased from Sinopharm Reagent Company, China and used without further purification.

**2.1.1. Synthesis of Pure Phase SrTiO<sub>3</sub>.** Pure phase SrTiO<sub>3</sub>, with a particle size of 20–50 nm, was synthesized by a hydrothermal method. In a typical synthesis, 10 mmol Ti(C<sub>4</sub>H<sub>9</sub>O)<sub>4</sub> was dissolved in 20 mL of ethylene glycol (EG) to form a clear solution, to which 20 mL of 0.5 M Sr(NO<sub>3</sub>)<sub>2</sub> aqueous solution was then dropped in, and 10 mL of 5 M NaOH was finally added. After stirring for 30 min, the mixture was transferred into a Teflon-lined stainless autoclave and then heated at 200 °C for 24 h. The obtained products were washed with water and ethanol until the pH reached 7 and then dried overnight at 70 °C.

**2.1.2. Synthesis of SrTiO<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub> Composite.** The SrTiO<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub> composite was synthesized following the hydrothermal treatment procedure according to our previous report.<sup>18</sup> In a typical synthesis, 45.87 mg of SrTiO<sub>3</sub> was dispersed into 40 mL of distilled water and ultrasonically treated for 10 min. After that, 15 mmol AgNO<sub>3</sub> was quickly added and dissolved by stirring. Then, 40 mL of 0.125 M Na<sub>3</sub>PO<sub>4</sub> solution was dropped in, and a yellow precipitate appeared immediately. The obtained mixture was transferred into a Teflon-lined stainless autoclave and then heated at 100 °C for 24 h, followed by washing the product with distilled water three times and drying at 70 °C for 6 h. The collected product was designated as SA-1/20.

SrTiO<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub> composites with different molar ratios (1/50, 1/20, 1/10, 1/5, 1/2, and 1/1) were obtained by simply adjusting the usage of SrTiO<sub>3</sub> and were designated as SA-*x*, in which *x* refers to the molar ratio of SrTiO<sub>3</sub> and Ag<sub>3</sub>PO<sub>4</sub>.

**2.2. Characterization.** X-ray diffraction (XRD) patterns were identified by a PANalytical X'pert MPD Pro diffractometer using Ni-filtered Cu K $\alpha$  irradiation ( $\lambda = 1.5406$  Å, 40 kV, 40 mA) and a scan rate of 2°/min in the 2 $\theta$  range from 10° to 80°. UV–vis absorption spectra of the samples were recorded with a Hitachi U-4100 UV–vis–near-IR spectrophotometer using BaSO<sub>4</sub> as reference. FESEM images and energy dispersive spectra (EDS) of the samples were observed by JEOL JSM-7800F field emitting scanning electron microscope. The surface area measurement was carried out by the N<sub>2</sub> adsorption isotherms conducted in the Micromeritics ASAP 2020 plus instrument using the Brunauer–Emmett–Teller (BET) method. X-ray photoelectron spectroscopy (XPS) data were collected from a Kratos Axis-Ultra DLD instrument with a monochromatized Al K $\alpha$  line source (150 W), and all binding energies were referenced to the C 1s peak at 284.8 eV. Photoluminescence (PL) emission spectra were obtained on a PTI QM-4 fluorescence spectrophotometer at room temperature using an excitation wavelength of 325 nm.

**2.3. Evaluation of Photocatalytic Activity.** The photocatalytic activity for O<sub>2</sub> evolution under visible-light irradiation was performed in a Pyrex glass cell with a side window. A 300 W Xe arc lamp with a UV cutoff filter ( $\lambda > 420$  nm) was used as light source. Photocatalyst (0.2 g) was dispersed into 180 mL of 0.02 M AgNO<sub>3</sub> solution, in which AgNO<sub>3</sub> acted as the sacrificial

reagent. After purging with nitrogen gas to eliminate air, the dispersion was irradiated under light with a constant stirring velocity and at a constant temperature around 35 °C kept by thermostatic circulating water. The evolved O<sub>2</sub> was analyzed by a chromatography (Ar as carrier gas) with a NaX zeolite column and an online thermal conductivity detector (TCD).

Apparent quantum yield (A.Q.Y.) was measured using a 420 nm band-pass filter and an irradiate-meter, and calculated according to the following equation:

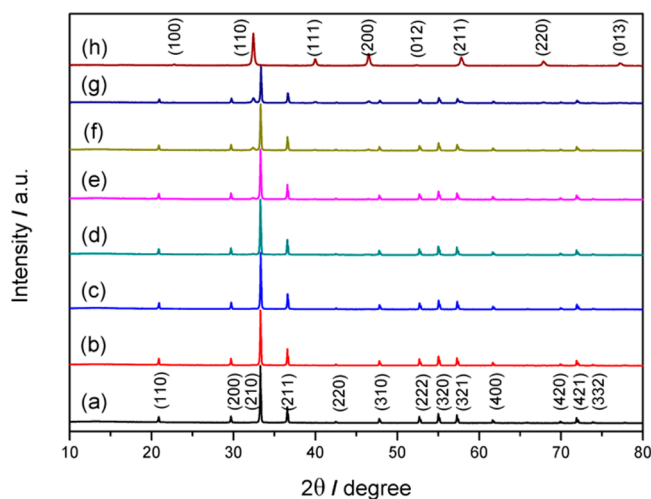
$$\begin{aligned} \text{A.Q.Y. (\%)} &= \frac{\text{the number of reacted electrons}}{\text{the number of incident photons}} \times 100 \\ &= \frac{\text{the number of evolved O}_2 \text{ molecules} \times 4}{\text{the number of incident photons}} \\ &\quad \times 100 \end{aligned}$$

The turnover number (T.O.N.) in terms of silver ions in the photocatalysts was calculated according to the following equation:

$$\text{T.O.N.} = \frac{\text{the number of reacted electrons}}{\text{the number of silver ions in the photocatalyst}}$$

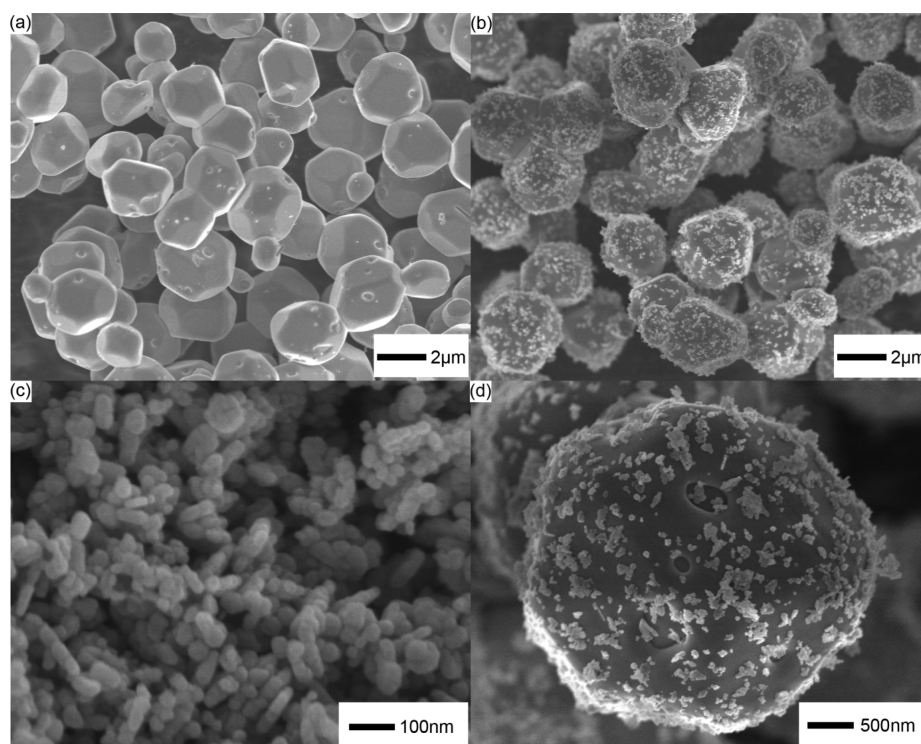
## 3. RESULTS AND DISCUSSION

**3.1. Characterization of As-Prepared Samples.** Composition and crystallographic structure of the as-prepared SrTiO<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub> photocatalysts were determined by XRD and are depicted in Figure 1. For comparison, pure SrTiO<sub>3</sub> was also



**Figure 1.** XRD pattern of SrTiO<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub> composites with different molar ratios: (a) Ag<sub>3</sub>PO<sub>4</sub>, (b) SA-1/50, (c) SA-1/20, (d) SA-1/10, (e) SA-1/5, (f) SA-1/2, (g) SA-1/1, and (h) SrTiO<sub>3</sub>.

included. As shown in Figure 1, all of the diffraction peaks of Ag<sub>3</sub>PO<sub>4</sub> were well matched with the body-centered cubic structure of Ag<sub>3</sub>PO<sub>4</sub> (JCPDS No. 01-084-0510; space group, *P* $\bar{4}3n$ ; *a* = 6.0110 Å), while those of SrTiO<sub>3</sub> corresponded to cubic phase SrTiO<sub>3</sub> (JCPDS No. 01-079-0176; space group, *Pm*-3*m*; *a* = 3.9046 Å). XRD patterns of SrTiO<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub> composites showed a combination of SrTiO<sub>3</sub> and Ag<sub>3</sub>PO<sub>4</sub>, and rule out the possibility of other impurity phases, indicating successful synthesis of composites. Hydrothermal treatment gave well-crystallized Ag<sub>3</sub>PO<sub>4</sub> powder with sharp diffraction peaks. Compared to Ag<sub>3</sub>PO<sub>4</sub>, peaks of SrTiO<sub>3</sub> were broader and less sharper, which may be resulting from the smaller



**Figure 2.** FESEM images of (a)  $\text{Ag}_3\text{PO}_4$ , (b) SA-1/20, (c)  $\text{SrTiO}_3$ , and (d) SA-1/20 in high magnification.

**Table 1.** BET Surface Area of  $\text{SrTiO}_3/\text{Ag}_3\text{PO}_4$  Composites

sample	$\text{Ag}_3\text{PO}_4$	SA-1/50	SA-1/20	SA-1/10	SA-1/5	SA-1/2	SA-1/1	$\text{SrTiO}_3$
surface area ( $\text{m}^2 \text{g}^{-1}$ )	0.43	1.02	1.74	1.89	2.12	5.21	8.15	27.96

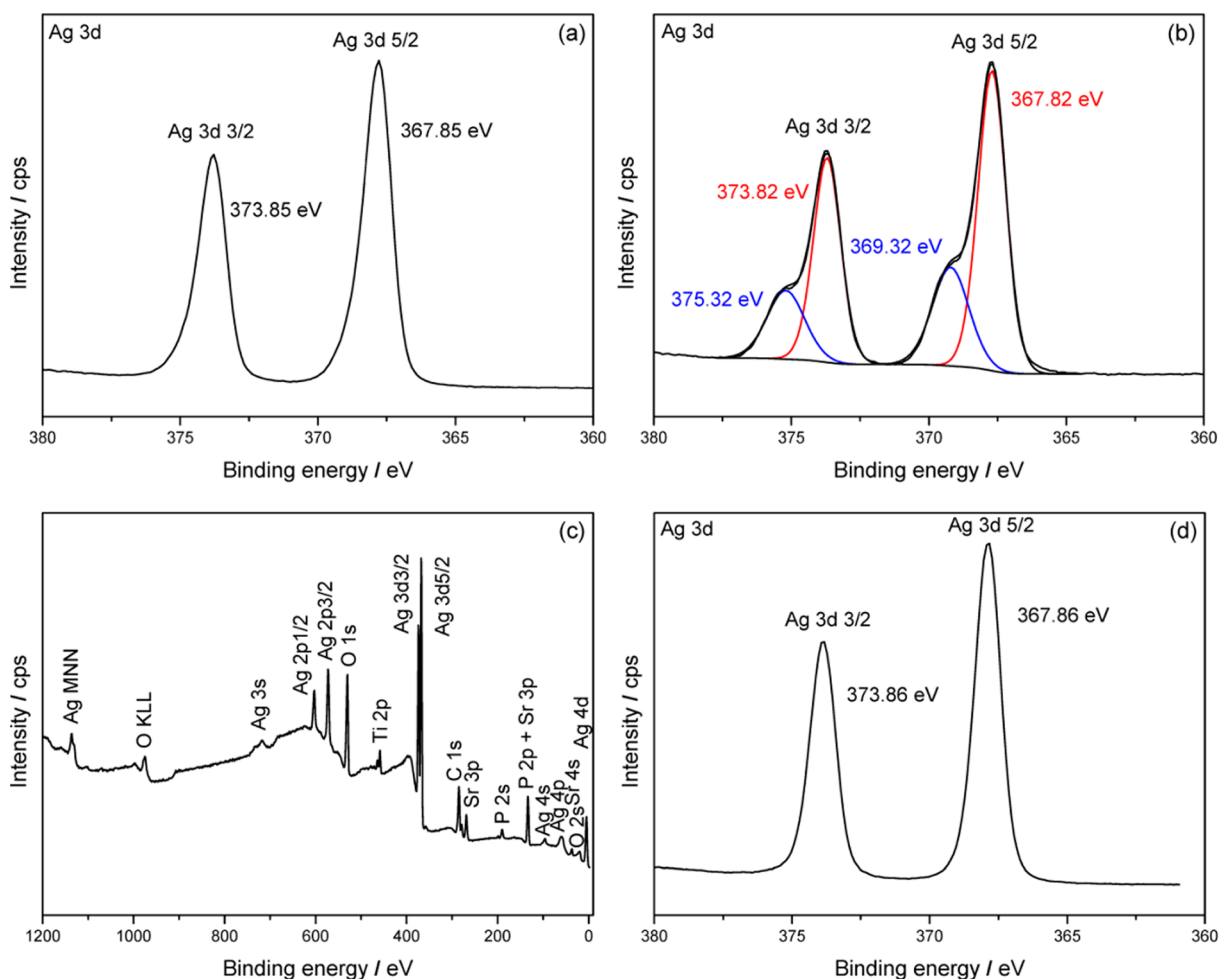
crystal size.<sup>37</sup> Moreover, as the molar ratio of  $\text{SrTiO}_3$  and  $\text{Ag}_3\text{PO}_4$  increased from 0 to 1/1, peaks of  $\text{SrTiO}_3$  became stronger, and the intensity ratio of (110) peaks in  $\text{SrTiO}_3$  to (210) peaks in  $\text{Ag}_3\text{PO}_4$  also increased in the XRD pattern of  $\text{SrTiO}_3/\text{Ag}_3\text{PO}_4$  composites.<sup>38</sup>

FESEM was used to investigate the morphology and particle size of as-prepared samples. Typical FESEM images of  $\text{SrTiO}_3$ ,  $\text{Ag}_3\text{PO}_4$ , and  $\text{SrTiO}_3/\text{Ag}_3\text{PO}_4$  composites are presented in Figure 2. Pure  $\text{SrTiO}_3$  were spherical particles with diameters in the range of 20–50 nm, while  $\text{Ag}_3\text{PO}_4$  possessed polyhedral morphology at the size of several micrometers with a smooth surface. As for  $\text{SrTiO}_3/\text{Ag}_3\text{PO}_4$  composites, it could be clearly seen that  $\text{SrTiO}_3$  particles were uniformly and tightly attached on the facet of  $\text{Ag}_3\text{PO}_4$ , which indicated an intimate contact between  $\text{SrTiO}_3$  and  $\text{Ag}_3\text{PO}_4$ .<sup>39</sup> As can be seen from Figure S1 (Supporting Information), a low molar ratio of  $\text{SrTiO}_3/\text{Ag}_3\text{PO}_4$  led to good dispersion of  $\text{SrTiO}_3$  onto the facet of  $\text{Ag}_3\text{PO}_4$ , and assembling of  $\text{SrTiO}_3$  occurred as the molar ratio increased, which reduced the effective area of contact between two materials.

The surface area of  $\text{SrTiO}_3/\text{Ag}_3\text{PO}_4$  composites was measured and listed in Table 1. BET surface area of as-synthesized  $\text{SrTiO}_3$  particles was  $27.96 \text{ m}^2 \text{g}^{-1}$ , which was much larger than that of  $\text{Ag}_3\text{PO}_4$  due to its small particle size. Therefore, with  $\text{SrTiO}_3$  content increasing, the surface area of the  $\text{SrTiO}_3/\text{Ag}_3\text{PO}_4$  composite was remarkably enlarged compared to that of pure  $\text{Ag}_3\text{PO}_4$ . Typically, the BET surface area of  $\text{SrTiO}_3/\text{Ag}_3\text{PO}_4$  (1/20) composite was 4-fold that of pure  $\text{Ag}_3\text{PO}_4$ .<sup>40–43</sup>

To investigate the elemental composition and chemical states of the as-prepared samples, XPS measurement was carried out, and the results are depicted in Figure 3. In Figure 3a, the two peaks in the spectra of  $\text{Ag}_3\text{PO}_4$  appearing at 373.85 and 367.85 eV could be ascribed to the binding energies of Ag 3d<sub>3/2</sub> and Ag 3d<sub>5/2</sub>. Peaks located in the same position were also found in the spectra of  $\text{SrTiO}_3/\text{Ag}_3\text{PO}_4$ , accompanied by peaks at 375.32 and 369.32 eV. The bands at 373.85 and 367.85 eV were attributed to  $\text{Ag}^+$ , and those at 375.32 and 369.32 eV were attributed to  $\text{Ag}^0$  species.<sup>44</sup> This result indicated the appearance of metallic Ag in  $\text{SrTiO}_3/\text{Ag}_3\text{PO}_4$ . Considering that neither the diffraction peaks in XRD nor the clues of Ag in FESEM images were observed, the detected metallic Ag should be tiny and well dispersed in the  $\text{SrTiO}_3/\text{Ag}_3\text{PO}_4$  composite.<sup>41</sup> The molar ratio of metallic Ag to  $\text{Ag}_3\text{PO}_4$  in SA-1/20 calculated from Figure 3b amounted to be 3/10. It has to be noted that this value was overestimated because XPS signals were mainly collected from the surface of the sample with depth less than 10 nm. XPS etching with  $\text{Ar}^+$  on SA-1/20 was then carried out, and signals of metallic Ag disappeared after etching for 20 s. Another calculation based on the EDS result showed that the molar ratio of Ag to  $\text{Ag}_3\text{PO}_4$  was 3.2%. XPS and EDS results confirmed that the metallic Ag was dispersed on the surface of  $\text{Ag}_3\text{PO}_4$  (see Figure S12, Figure S13, and Table S1 in Supporting Information). As mentioned in the Experimental Section,  $\text{Ag}_3\text{PO}_4$  precipitated rapidly when the  $\text{Na}_2(\text{PO}_4)_3$  solution was added to the  $\text{Ag}^+$  solution containing suspended  $\text{SrTiO}_3$ . It could be deduced that a trace amount of  $\text{Ag}^+$  on the surface of  $\text{Ag}_3\text{PO}_4$  was reduced by organic residuals adsorbed on  $\text{SrTiO}_3$  during the high temperature and high pressure hydrothermal



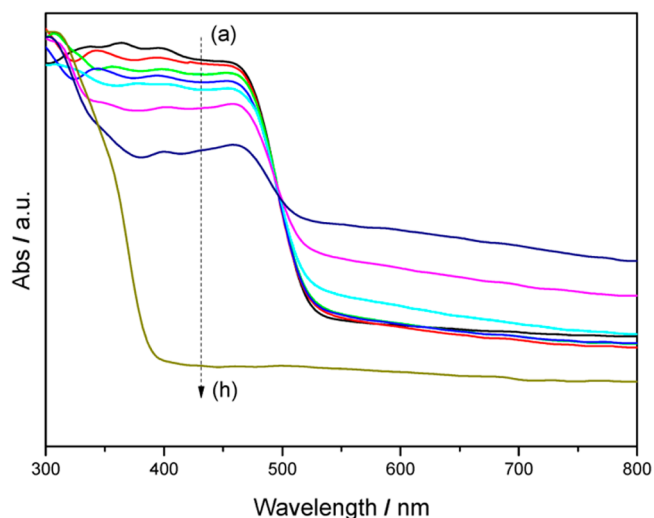


**Figure 3.** Typical XPS spectra of Ag 3d in  $\text{Ag}_3\text{PO}_4$  (a), SA-1/20 (b), SA-1/20 without Ag (d), and wide scan spectra of SA-1/20 (c).

process. To confirm this deduction,  $\text{SrTiO}_3$  was calcined at 800 °C to eliminate organic residuals, and the  $\text{SrTiO}_3/\text{Ag}_3\text{PO}_4$  composite was further synthesized. XPS spectra of Ag 3d in Figure 3d demonstrates that metal  $\text{Ag}^0$  species was thus avoided.

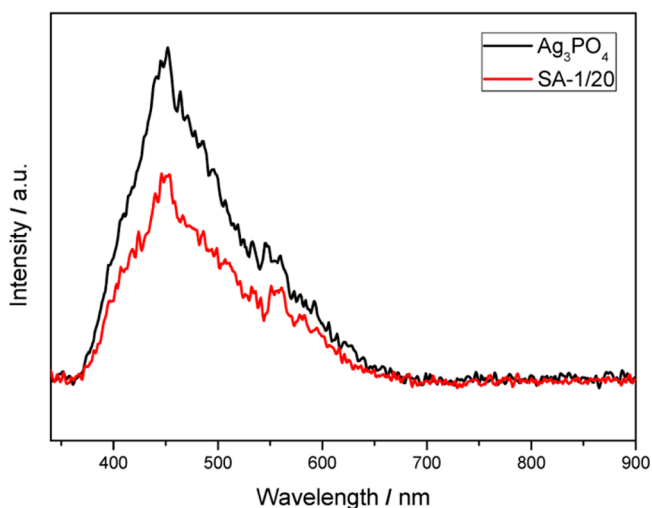
Figure 4 depicted the UV–vis absorption spectra of as-prepared samples. As shown in Figure 4,  $\text{SrTiO}_3$  performed a 380 nm absorption band-edge in the UV region, corresponding to a band gap energy of 3.24 eV, which agreed with the results previously reported.<sup>45</sup> Spectra of  $\text{Ag}_3\text{PO}_4$  indicated that it absorbed sunlight with wavelengths less than 530 nm, corresponding to a band gap energy of 2.42 eV. Band gap energy was calculated by the K-M method (see Figure S2 in Supporting Information). As  $\text{SrTiO}_3$  was introduced into  $\text{Ag}_3\text{PO}_4$ , light absorption less than 500 nm was slightly depressed, owing to the decreased relative content of  $\text{Ag}_3\text{PO}_4$ . It could be noticed that the absorption in the long-wavelength range was gradually elevated in samples of larger molar ratio, which was attributed to the existence of highly dispersed tiny  $\text{Ag}^0$  species.<sup>46</sup>

A room-temperature photoluminescence (PL) emission spectrum was recorded in order to investigate the migration and separation efficiency of photogenerated charge carriers in the as-prepared samples. Comparison of PL emission spectra for pure  $\text{Ag}_3\text{PO}_4$  and SA-1/20 is shown in Figure 5. As for pure  $\text{Ag}_3\text{PO}_4$ , a strong emission peak at 440 nm and a shoulder peak around 550 nm were observed. A similar PL spectrum was



**Figure 4.** UV–vis spectra of  $\text{SrTiO}_3/\text{Ag}_3\text{PO}_4$  composites with different molar ratios: (a)  $\text{Ag}_3\text{PO}_4$ , (b) SA-1/50, (c) SA-1/20, (d) SA-1/10, (e) SA-1/5, (f) SA-1/2, (g) SA-1/1, and (h)  $\text{SrTiO}_3$ .

obtained for SA-1/20, while the overall emission intensity was obviously reduced compared to that of pure  $\text{Ag}_3\text{PO}_4$ . Since PL emission is mainly due to the recombination of photogenerated electrons and holes, the weakened emission intensity in SA-1/20 thus indicates inhibition of recombination,



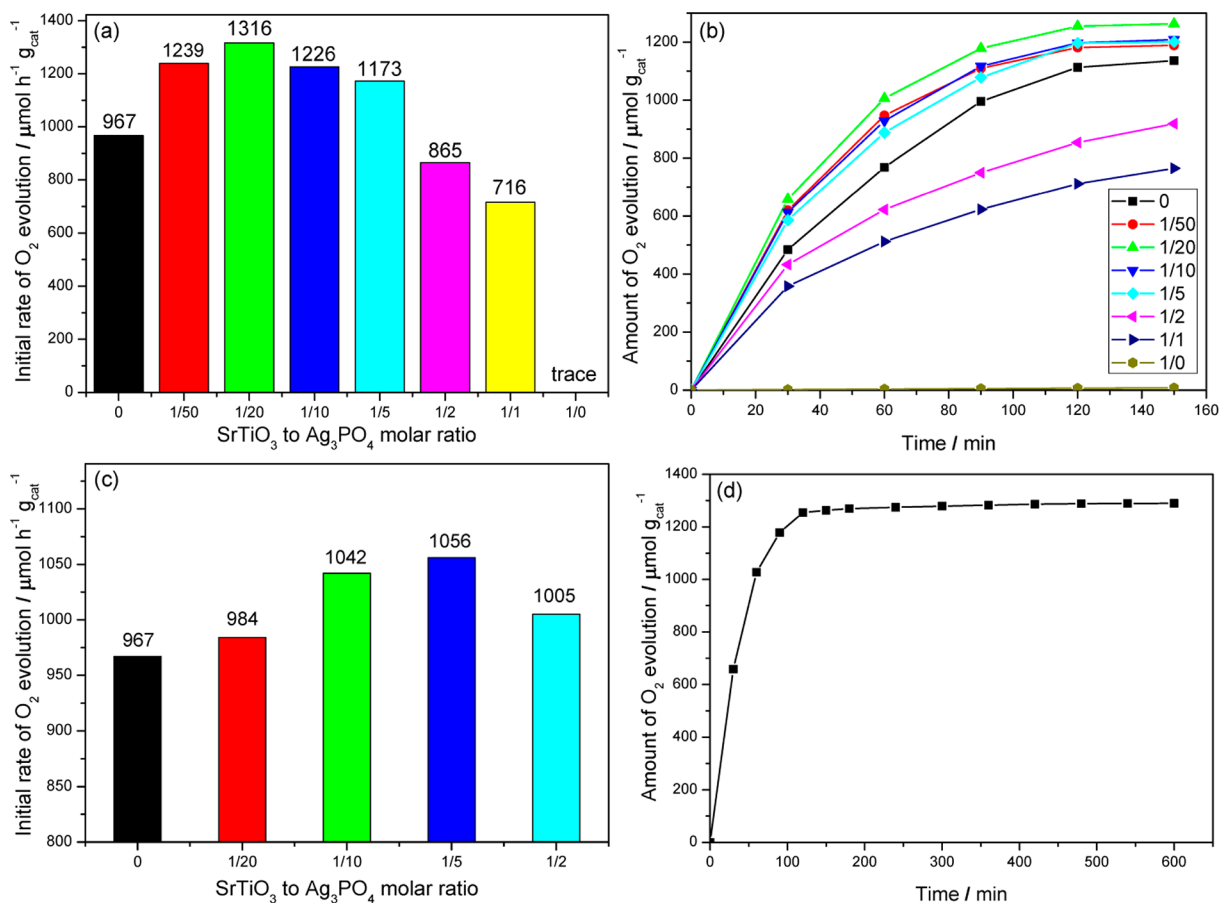
**Figure 5.** Photoluminescence spectra of as-prepared  $\text{Ag}_3\text{PO}_4$  and SA-1/20 samples.

which lengthens the lifetime of charge carriers and is beneficial for the improvement of photocatalytic activity.<sup>47,48</sup>

**3.2. Photocatalytic Activity.** Photocatalytic activities of  $\text{SrTiO}_3$ ,  $\text{Ag}_3\text{PO}_4$ , and  $\text{SrTiO}_3/\text{Ag}_3\text{PO}_4$  composites were evaluated by  $\text{O}_2$  evolution under visible-light irradiation ( $\lambda > 420$  nm), and the results are shown in Figure 6. No  $\text{O}_2$  was

detected in the absence of either photocatalyst or light irradiation, eliminating water oxidation by photolysis of sacrificial solution or mechanocatalysis. A trace of  $\text{O}_2$  was produced using pure phase  $\text{SrTiO}_3$  catalyst, whereas the pure  $\text{Ag}_3\text{PO}_4$  sample gave an excellent photocatalytic performance, with an initial rate of  $967 \mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$  and an A.Q.Y. of 12.4% at 420 nm. Introducing of  $\text{SrTiO}_3$  resulted in a remarkable enhancement of  $\text{O}_2$  evolution. As shown in Figure 6a,b, activity for  $\text{O}_2$  production first increased and then gradually decreased with further loading of  $\text{SrTiO}_3$ . It is worth noting that initial rate and A.Q.Y. for photocatalytic  $\text{O}_2$  evolution reached  $1316 \mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$  and 16.2%, respectively, with an optimal  $\text{SrTiO}_3/\text{Ag}_3\text{PO}_4$  molar ratio of 1/20.

For comparison, photocatalytic activities of the physical mixtures with different molar ratios are shown in Figure 6c. The  $\text{O}_2$  evolution was also enhanced but less efficiently, and the optimized molar ratio turned out to be 1/5. This is mainly ascribed to the poor contact and bad dispersion of  $\text{SrTiO}_3$  on  $\text{Ag}_3\text{PO}_4$  by simply physical mixing. These results indicate that loading of  $\text{SrTiO}_3$  and contact between the two materials play a crucial role in the enhanced activity of  $\text{Ag}_3\text{PO}_4$ . Figure 6d showed the time course of  $\text{O}_2$  evolution activity of SA-1/20 for 10 h. It could be recognized that the photocatalytic activity was linear at an early period and gradually decreased after irradiation for about 3 h. It should be noted that this phenomenon is not related to bad stability but is caused by the light shielding effect of photodeposited Ag particles, as has



**Figure 6.** Photocatalytic activity for  $\text{O}_2$  evolution of (a)  $\text{SrTiO}_3/\text{Ag}_3\text{PO}_4$  composites with different molar ratios, (b) time course of  $\text{SrTiO}_3/\text{Ag}_3\text{PO}_4$  composites with different molar ratios, (c) mixture of  $\text{SrTiO}_3$  and  $\text{Ag}_3\text{PO}_4$  with different molar ratios, and (d) SA-1/20 for 10 h, under visible-light irradiation ( $\lambda > 420$  nm).

been reported by pioneer studies.<sup>8,15,17</sup> Stable O<sub>2</sub> evolution from Fe<sup>3+</sup> sacrificial solution also verified this point from another aspect (see Figure S3 in Supporting Information). The turnover number (T.O.N.) in terms of silver ions in the photocatalysts was calculated by evaluating the O<sub>2</sub> production for 12 h using 0.1 g of photocatalyst (see Figure S5 in Supporting Information). T.O.N. values of 1.08 and 1.41 were obtained for pure Ag<sub>3</sub>PO<sub>4</sub> and SA-1/20 samples, respectively, meaning that this reaction is a photocatalytic process instead of a photochemical reaction. Herein, the T.O.N. was greatly underestimated because silver metal reduced from the sacrificial AgNO<sub>3</sub> would be deposited on the surface of the photocatalyst and prevent further water oxidation by blocking incident photon flux. Furthermore, XRD patterns of SA-1/20 were recorded both before and after the photocatalytic reaction and showed no significant change in composition except for the appearance of metal silver from photoreduction and deposition of sacrificial AgNO<sub>3</sub> (see Figure S6 in Supporting Information).

**3.3. Mechanism of Enhanced O<sub>2</sub> Evolution.** The enhancement of O<sub>2</sub> evolution for SrTiO<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub> composites compared to pure Ag<sub>3</sub>PO<sub>4</sub> photocatalyst could be ascribed to the following aspects: on the one hand, SrTiO<sub>3</sub> and Ag<sub>3</sub>PO<sub>4</sub> possessed interlaced band structure. The band-edge potentials of CB and VB, designated as  $E_{CB}$  and  $E_{VB}$ , could be calculated from the following equation:

$$E_{VB} = \chi - E_0 + 1/2E_g$$

$$E_{CB} = \chi - E_0 - 1/2E_g$$

in which  $\chi$  is the absolute electronegativity of the semiconductor, determined by the geometric mean of the absolute electronegativity of constituent atoms, which is defined as the arithmetic mean of the atomic electron affinity and the first ionization energy;  $E_0$  is the energy of free electrons on the hydrogen scale; and  $E_g$  is the band gap of the semiconductor.<sup>39,49,50</sup>  $E_{CB}$  and  $E_{VB}$  of SrTiO<sub>3</sub> were determined to be -0.79 and 2.45 eV, while those of Ag<sub>3</sub>PO<sub>4</sub> were 0.25 and 2.67 eV. On the basis of the alignment of their energy levels, an illustration of possible interface electron transfer behavior was proposed and shown in Figure 7. Ag<sub>3</sub>PO<sub>4</sub> was first excited under visible-light irradiation. Since the loaded SrTiO<sub>3</sub> was in intimate contact with Ag<sub>3</sub>PO<sub>4</sub>, photoexcited holes from VBM of Ag<sub>3</sub>PO<sub>4</sub> would be immigrated to the less positive VBM of SrTiO<sub>3</sub> and oxidize H<sub>2</sub>O to evolve O<sub>2</sub>. The loaded SrTiO<sub>3</sub> provided additional active sites for the photocatalytic reaction. Meanwhile, the photoexcited electrons were transferred to the

surface of Ag<sub>3</sub>PO<sub>4</sub>. It is known that metallic Ag<sup>0</sup> can serve as excellent acceptors and traps for photoexcited electrons; hence, the photoinduced electrons could be quickly transferred to Ag<sup>0</sup> species and consumed by the sacrificial Ag<sup>+</sup>, as depicted in Figure 7.<sup>15,36</sup> This entire process would facilitate charge separation and indeed improved photocatalytic activity. Further investigation of O<sub>2</sub> evolution activity for the SA-1/20 sample without metal Ag showed only a slight decrease compared to that with Ag on the surface of Ag<sub>3</sub>PO<sub>4</sub>; hence it illustrates that it was SrTiO<sub>3</sub> rather than Ag that played the core role in the process (see Figure S4 in Supporting Information). In addition, pure SrTiO<sub>3</sub> was not active under visible-light irradiation, thus protecting Ag<sub>3</sub>PO<sub>4</sub> from being reduced by photoexcited electrons of SrTiO<sub>3</sub>.

On the other hand, it has been widely reported that large surface area could greatly promote the photocatalytic reaction by offering more active sites.<sup>51,52</sup> The SrTiO<sub>3</sub> synthesized in this work possessed large surface area compared to that of the Ag<sub>3</sub>PO<sub>4</sub> polyhedron due to its small particle size. As is claimed above, the loaded SrTiO<sub>3</sub> serves as a hole acceptor for photocatalytic water oxidation. Consequently, the larger surface area obtained from SrTiO<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub> composites by introducing SrTiO<sub>3</sub> to Ag<sub>3</sub>PO<sub>4</sub> gave rise to more active sites for water oxidation, which improved photocatalytic O<sub>2</sub> evolution.

The characterization results and mechanism proposed above imply that SrTiO<sub>3</sub> can serve as an efficient cocatalyst for photocatalytic water oxidation, which not only provides active sites for redox reaction but also inhibits recombination by promoting charge separation.

When more SrTiO<sub>3</sub> was loaded (molar ratio = 1/2, 1/1), visible-light absorption of SrTiO<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub> composites were partly depressed. What's more, the assembling of SrTiO<sub>3</sub> particles resulted in less effective contact between two materials and meanwhile hindered the transference of both reactant and product. Therefore, activity of O<sub>2</sub> evolution decreased when the molar ratio of SrTiO<sub>3</sub> to Ag<sub>3</sub>PO<sub>4</sub> was further increased.

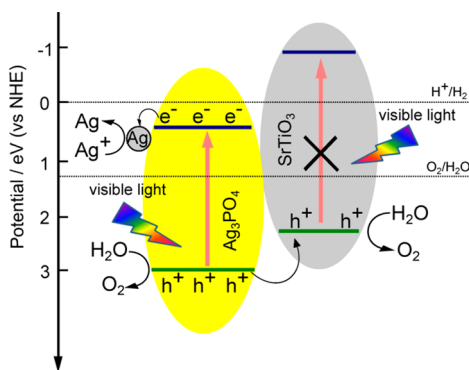
## 4. CONCLUSIONS

An efficient photocatalyst for water oxidation was fabricated by loading a small amount of SrTiO<sub>3</sub> onto Ag<sub>3</sub>PO<sub>4</sub> through a hydrothermal method. The as-synthesized SrTiO<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub> composite showed improved photocatalytic activity compared to that of Ag<sub>3</sub>PO<sub>4</sub>, which was ascribed to the cocatalytic effect of SrTiO<sub>3</sub> providing both accelerated charge separation by band gap alignment and enriched active sites by enlarged surface area. This work offers useful guidance for developing an efficient O<sub>2</sub> producing photocatalyst and designing an overall photocatalytic water splitting system.

## ■ ASSOCIATED CONTENT

### Supporting Information

FESEM images of SrTiO<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub> composites with different molar ratios; Bandgap determination of Ag<sub>3</sub>PO<sub>4</sub> and SrTiO<sub>3</sub> the by K-M method; photocatalytic O<sub>2</sub> evolution activity of SA-1/20 from Fe<sup>3+</sup> sacrificial solution; comparison of photocatalytic O<sub>2</sub> evolution activity of samples with and without metal Ag species; T.O.N. measurement of pure Ag<sub>3</sub>PO<sub>4</sub> and SA-1/20; XRD patterns of SA-1/20 before and after photocatalytic reaction; HRTEM images of as-prepared SrTiO<sub>3</sub>; comparison of photocatalytic O<sub>2</sub> evolution activity of SA-1/20 with both TiO<sub>2</sub>-Ag<sub>3</sub>PO<sub>4</sub> composites and TiO<sub>2</sub>; FESEM images of SrTiO<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub> (SA-1/20) synthesized with different times of the second hydrothermal process; schematic formation



**Figure 7.** Schematic diagram of band structure and expected charge separation of SrTiO<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub> composite under visible-light irradiation.

mechanism of SrTiO<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub>; XRD pattern of the as-prepared sample when using the method of first Ag<sub>3</sub>PO<sub>4</sub>, then SrTiO<sub>3</sub>; XPS etching profiles on SA-1/20; and EDS patterns and atomic content of existing elements in SA-1/20. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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