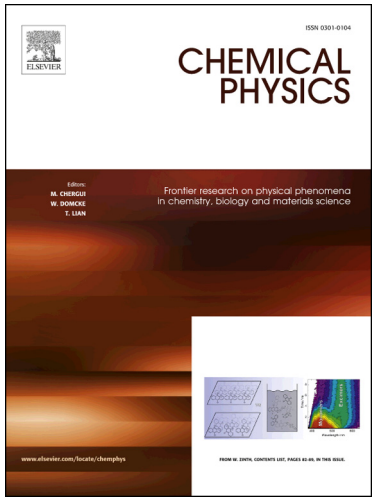

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Efficient visible-light-responsive photocatalyst: hybrid TiO_2-Ag_3PO_4 nanorods

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ABSTRACT

Herein, ordered TiO_2-Ag_3PO_4 nanorods are fabricated by loading Ag_3PO_4 nanoparticles on the as-prepared brookite TiO_2 nanorods. The amount of Ag_3PO_4 nanoparticles loaded on brookite TiO_2 nanorods can be rationally optimized. These hybrid TiO_2-Ag_3PO_4 nanorods could provide large surface area, extend the visible light absorption and facilitate the charge separation, leading to efficient visible-light-driven photocatalytic performance. When evaluated as photocatalysts under visible light illumination, all the hybrid TiO_2-Ag_3PO_4 nanorods exhibit high photocatalytic activity for degrading 2-propanol. Particularly, TiO_2-Ag_3PO_4-3 enables the best photocatalytic property, which yields high acetone production of 147 ppm at 3 h and CO_2 production of 424 ppm at 11 h.

Key Words: Nanocomposites; TiO_2-Ag_3PO_4; Visible-light-responsive; Solar energy materials

1. Introduction

Photocatalysts have attracted numerous interests ascribed to their potential applications for energy conversion and degradation of pollutants [1-2]. Titanium dioxide (TiO_2) as one of the most important photocatalysts exhibits excellent photocatalytic activity, good stability and abundant source, enabling the extensively research on exploring efficient photocatalyst. Furthermore, brookite TiO_2 has been confirmed to be superior in photo-degradation of organic containments [3-5]. Nevertheless, the brookite TiO_2 demonstrates photocatalytic response under UV-light instead of visible light irradiation, limiting the sufficient utilization of solar light. In order to extend the visible-light-driven photocatalytic response of brookite TiO_2, fabrication of heterostructures is highly proposed [6-8]. For instance, Peng et al. prepared g-C_3N_4 nanodots decorated brookite TiO_2 nanocubes with enhanced visible-light-driven photocatalytic activity [9]. Chen and co-authors constructed g-C_3N_4/anatase/brookite heterojunction structure with improved hydrogen production under visible light [10]. It is validated that the brookite TiO_2-based hetero-structured materials

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demonstrate efficient visible-light-driven photocatalytic performance. However, the research on brookite TiO_2-based heterojunctions is limited devoted to the difficult synthesis techniques.

Ag_3PO_4 [11,12] exhibit excellent visible light driven photocatalytic response ascribed to the narrow bandgap. However, the inherent fast charge recombination and poor photostability hinder the widely research and application of Ag_3PO_4 on photocatalysis. To address this issue, the strategy of coupling Ag_3PO_4 with other semiconductors was reported [13,14]. Herein, the well-defined brookite TiO_2 nanorods are obtained by a simple hydrothermal reaction. Subsequently, the precipitation method is adopted to yield Ag_3PO_4-brookite TiO_2 hybrid nanorods, which effectively extend the visible light absorption, enhance the surface area and promote charge separation. As expected, the TiO_2-Ag_3PO_4 heterostructured nanorods manifest distinct visible-light-driven photocatalytic performance for degrading 2-propanol. Moreover, the loading amount of Ag_3PO_4 can be rationally controlled and the highest photocatalytic activity can be obtained by TiO_2-Ag_3PO_4-3 with molar percentage of 13% for Ag_3PO_4.

Experimental section

All reagents are of analytic grade (Chongqing Chemical Company) and used without any further purification.

The brookite TiO_2 nanorods were synthesized by a facile hydrothermal method [15] using the titanium bis(ammonium lactate) dihydroxide (TALH) and urea as precursors. As typically, 5 mL TALH and 45 mL deionized water were added into urea (21.02 g), and then the solution was stirred for 2 hours. Aimed to yield regular brookite TiO_2 nanorods, the as-prepared solution was transferred into a Teflon cup (100 mL), which was kept at 230 ºC for 48 h. The white powder could be collected and washed after the product cooling down to the room temperature. In order to load Ag_3PO_4 on TiO_2, the as-prepared brookite TiO_2 (0.237 g) powder was dissolved in 50 mL deionized water, and then a certain amount of $AgNO_3$ (0.45 g) was added into the solution. After stirring for 10 min under dark, a solution of Na_2HPO_4 (50 mL, the molar ratio of $AgNO_3$ and Na_2HPO_4 is controlled at 3: 1) was added into the above solution drop by drop and then was stirred for 7 hours under dark. Moreover, the amount of $AgNO_3$ and Na_2HPO_4 was optimized with the molar percentage of 2.9%, 5.8%; 13%, 23% and 37.5% for Ag_3PO_4 in TiO_2-Ag_3PO_4 heterojunction. Correspondingly, the obtained hybrid samples are marked with TiO_2-Ag_3PO_4-1, TiO_2-Ag_3PO_4-2, TiO_2-Ag_3PO_4-3, TiO_2-Ag_3PO_4-4 and TiO_2-Ag_3PO_4-5. Finally, the well-defined TiO_2-Ag_3PO_4 composites can be obtained after filtration, washing and drying. For comparison, the pure Ag_3PO_4 nanoparticles were obtained by the same procedure except adding the TiO_2 nanorods.

The X-ray diffraction (XRD) instrument (MiniFlex II, Rigaku Co.) was utilized to characterize the crystal phases of products. The morphologies were investigated by scanning electron microscope (SEM). Furthermore, the UV-vis patterns were measured by the UV-vis spectrometer (UV-2500PC, Shimadzu). The Brunauer-Emmett-Teller (BET) surface area was characterized by Quantachrome Nova 4200e. The photocatalytic activities of samples were evaluated by degrading 2-propanol. The as-prepared powder (0.1 g) was uniformly dispread on a glass dish (2 cm^2), which was placed in a Tedlar bag with 125 mL 2-propanol (500 ppm). The absorption equilibrium was obtained by keeping the as-prepared bag in dark for 1 hour. Then the visible light (100 mW cm^{-2}) was gained by Xenon lamp equipped with a Yellow-44 filter and was used as the light source to measure the photocatalytic performance. During the photocatalytic process, the amount of acetone and CO_2 were evaluated by online gas chromatography (Agilent Technologies, 3000A micro-GC, TCD detector) equipped with OV1 and PLOT-Q columns.

3. Results and discussion

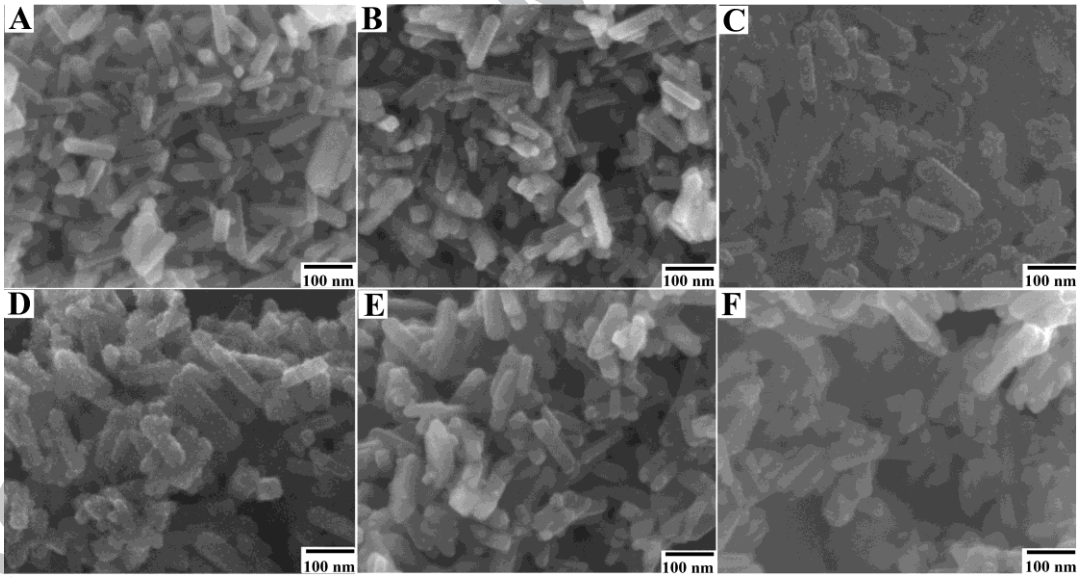

Figure 1. SEM images of (A) pristine brookite TiO_2 nanorods (B) TiO_2-Ag_3PO_4-1 (C) TiO_2-Ag_3PO_4-2 (D) TiO_2-Ag_3PO_4-3 (E) TiO_2-Ag_3PO_4-4 (F) TiO_2-Ag_3PO_4-5.

The morphologies and structures of as-prepared samples are characterized by SEM images. As can be seen from Figure 1A, the pristine brookite TiO_2 exhibits regular prismatic nanorod shape with smooth surface. Moreover, the nanorods display an average length of 100 nm and diameter of 20 nm. With modification of Ag_3PO_4, the nanoparticles were loaded on nanorods (Figure 1B-F). With the molar percentage of Ag_3PO_4

controlled at 2.9%, no obvious nanoparticle was detected on brookite TiO_2 nanorods (Figure 1B), which is suggested to be resulted from the uniform distribution of Ag_3PO_4 on brookite TiO_2 nanorods. Small particles can be observed in TiO_2-Ag_3PO_4-2 (Figure 1C) and TiO_2-Ag_3PO_4-3 (Figure 1D), and nanoparticles grow with increasing the amount of Ag_3PO_4. It is clearly that the aggregated nanoparticles distribute on brookite TiO_2 nanorods in SEM images of TiO_2-Ag_3PO_4-4 and TiO_2-Ag_3PO_4-5. Particularly, TiO_2-Ag_3PO_4-5 presents seriously agglomeration, and the nanorod configuration is difficult to identify (Figure 1F).

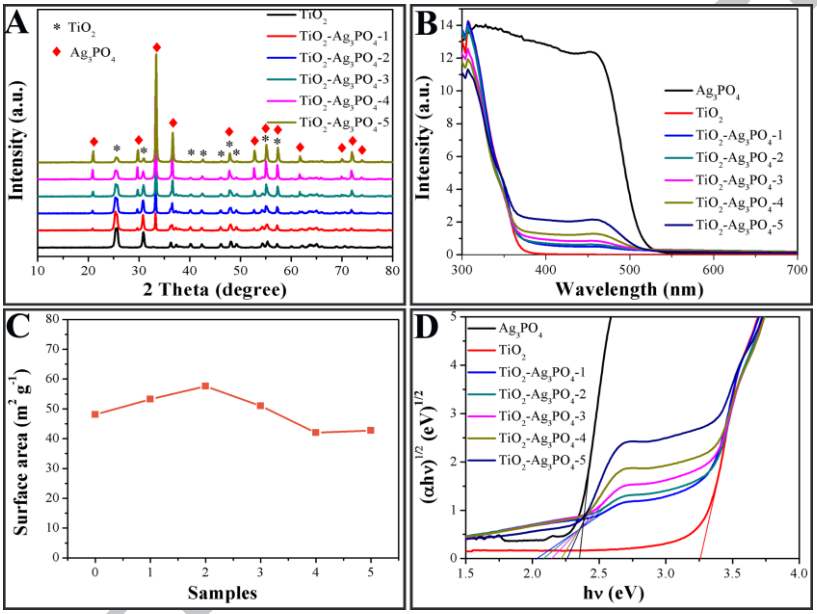

Figure 2. (A) XRD pattern (B) UV-vis spectra (C) BET surface area (D) band gaps of samples.

The XRD patterns exhibited in Figure 2A revealed the crystalline structure and crystal phases of samples. Obviously, all the diffraction peaks of nanorods could be well-indexed to brookite TiO_2 (JCPDS: 00-029-1360). As for the composites, the diffraction peaks of Ag_3PO_4 (JCPDS: 06-0505) [16] appear besides the peaks of brookite TiO_2. Furthermore, the intensities of peaks demonstrate increase and decrease for Ag_3PO_4 and TiO_2 with enhancing the amount of Ag_3PO_4. It is clearly that the diffraction peaks of brookite TiO_2 nanorods show weak intensity when the molar percentage of Ag_3PO_4 increased to 37.5%. In order to confirm the surface area of samples, the BET was carried out on pristine TiO_2 nanorods and TiO_2-Ag_3PO_4 heterojunction structures. Ascribed to the nanosize and uniform nanorod structure, the brookite TiO_2 possesses large surface area of 48.096 $m^2\ g^{-1}$. TiO_2-Ag_3PO_4-1, TiO_2-Ag_3PO_4-2 and TiO_2-Ag_3PO_4-3 exhibit surface area of 53.233 $m^2\ g^{-1}$, 57.581 $m^2\ g^{-1}$ and 51.011 $m^2\ g^{-1}$, which are higher than that of pure TiO_2 nanorods. However, the much more amount of Ag_3PO_4 would result in smaller surface area (41.994 $m^2\ g^{-1}$ and 42.768 $m^2\ g^{-1}$ forTiO_2-Ag_3PO_4-4 and TiO_2-Ag_3PO_4-5, respectively) with respect to TiO_2 and other hybrid samples attributed to the aggregated nanoparticles

[17].

The optical absorption properties of samples were investigated by the corresponding UV-vis spectra. As shown in Figure 2B, bare brookite TiO_2 nanorods display strong absorption in the UV light region. Interestingly, the samples exhibit visible light absorption when the Ag_3PO_4 nanoparticles are introduced into brookite TiO_2 nanorods. Moreover, the visible light absorption enhances with increasing the loading amount of Ag_3PO_4 on TiO_2 nanorods. It is worth to note that the absorption edges of TiO_2-Ag_3PO_4 hybrid nanorods exhibit red-shift with the increased amount of Ag_3PO_4. Calculated from the Tauc plots of samples shown in Figure 2D, the band gaps of Ag_3PO_4, TiO_2, TiO_2-Ag_3PO_4-1, TiO_2-Ag_3PO_4-2, TiO_2-Ag_3PO_4-3, TiO_2-Ag_3PO_4-4 and TiO_2-Ag_3PO_4-5 are 2.35, 3.25, 2.26, 2.22, 2.15, 2.08 and 2.02 eV, respectively. Based on the above results, it is suggested that the suitable amount of Ag_3PO_4 on TiO_2 nanorods could greatly enhance the visible light absorption and surface area [18,19].

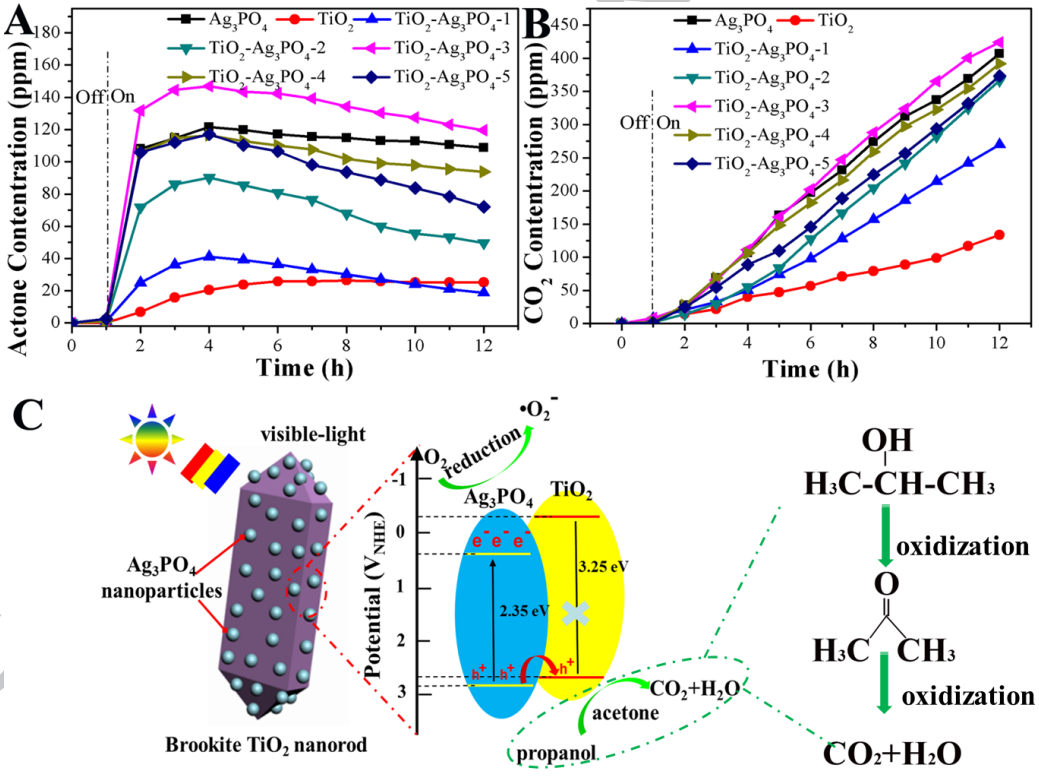

Figure 3. Acetone (A) and (B) CO_2 evolution through degradation of 2-propanol by photocatalysts (C) the scheme illustration for the photocatalytic process of TiO_2-Ag_3PO_4 hetero-nanorod.

The photocatalytic behavior of pure brookite TiO_2, Ag_3PO_4 and TiO_2-Ag_3PO_4 hybrid nanorods were evaluated by the concentrations of acetone and CO_2. For the hetero-nanorods, the concentration of acetone increases within 3 hours and then decreases with prolonged photo-irradiation time, suggesting the intermediate product character of acetone. When the amount of acetone reaches saturation, acetone was dramatically decomposed to

CO_2. The hybrid TiO_2-Ag_3PO_4 nanorods exhibit enhanced photocatalytic performance compared with pristine TiO_2 nanorods, validating the advantages of hybrid nanostructure. Furthermore, the photocatalytic efficiency improved with increasing the loading amount of Ag_3PO_4 on brookite TiO_2 nanorods, while too much amount of Ag_3PO_4 led to the decrease of photocatalytic performance. It is obviously that TiO_2-Ag_3PO_4-3 demonstrates the best photocatalytic property among these samples. The acetone production reaches 147 ppm at 3 h and CO_2 production reaches 424 ppm at 11 h irradiated by visible light, which is about 8 times and 3 times of that of brookite TiO_2 nanorods. Particularly, TiO_2-Ag_3PO_4-3 exhibits higher photocatalytic activity than that of pure Ag_3PO_4 nanoparticles, confirming the synergistic effect of TiO_2 and Ag_3PO_4. The introduction of Ag_3PO_4 into TiO_2 nanorods would greatly promote the visible light absorption and separation of photogenerated electrons-hole pairs. Ag_3PO_4 nanoparticles can be excited by visible light devoted to the band gap of 2.35 eV, while TiO_2 nanorods can't be excited by the visible light ascribed to the large band gap of 3.25 eV. More specifically, TiO_2 and Ag_3PO_4 demonstrate valence bands at 2.7 and 2.9 eV [20-21], respectively. The much higher valence band position of Ag_3PO_4 than that of TiO_2 enables the holes transformation from Ag_3PO_4 to TiO_2 as shown in Figure 3C, leaving the electrons on the conduction band of Ag_3PO_4. The holes on TiO_2 would be consumed by the oxidation of 2-propanol and the electrons on Ag_3PO_4 would be consumed by the reduction of oxygen, realizing the separation of reduction and oxidation reactions. However, the aggregated and too much amount of Ag_3PO_4 nanoparticles on TiO_2 nanorods would hinder the light harvesting, and increase the recombination efficiency of electrons and holes, resulting in the decreased photocatalytic activity. Above all, it is suggested that suitable amount of Ag_3PO_4 nanoparticles loaded on TiO_2 nanorods would provide large surface area as well as active sites for photocatalytic reactions, and promote the charge separation, resulting in the efficient visible-light-driven photocatalytic activity.

Conclusions

In conclusion, the well-defined TiO_2-Ag_3PO_4 heterostructured nanorods are constructed by a facile hydrothermal and co-precipitation method. The modification of TiO_2 brookite nanorods with Ag_3PO_4 nanoparticles allows visible light harvesting as well as visible-light-induced photocatalytic activity. Moreover, the suitable amount of Ag_3PO_4 nanoparticles loaded on brookite TiO_2 nanorods could greatly enhance the surface area, providing numerous active sites for photocatalytic reactions. When the molar percentage of Ag_3PO_4 is controlled at 13%, the TiO_2-Ag_3PO_4 nanorods exhibited the best photocatalytic performance for degrading 2-propanol. It is suggested that the combination of TiO_2 and Ag_3PO_4 could

promote the transfer of generated holes from valence band (VB) of Ag_3PO_4 to the VB of TiO_2, resulting in greatly improved charge separation. This work furnishes an effective strategy for exploration of visible-light-responsive photocatalysts with high photocatalytic properties.

Acknowledgements

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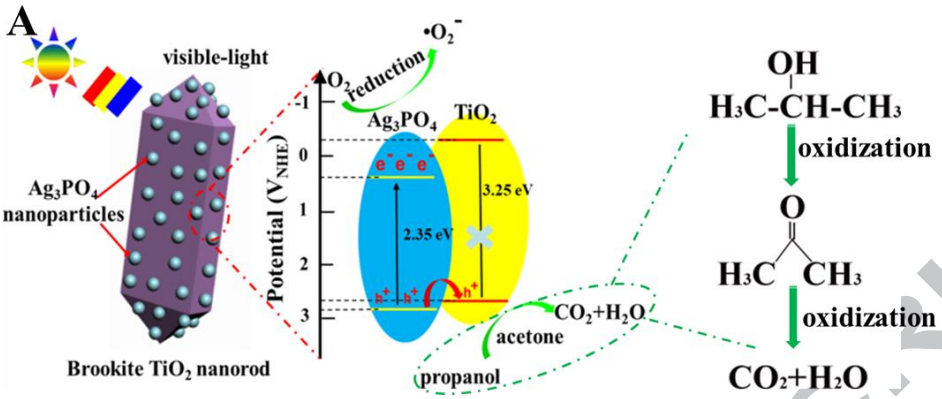

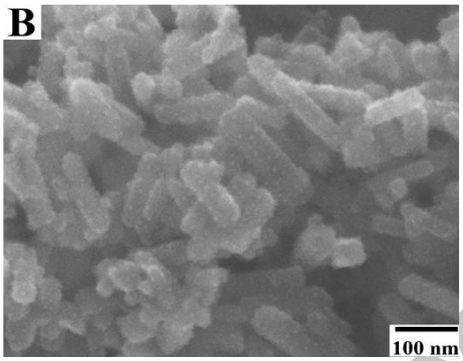

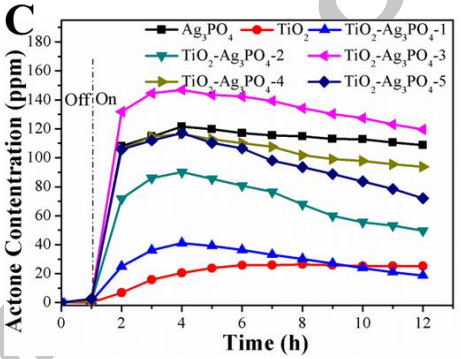

Highlights

- TiO_2-Ag_3PO_4 nanorods are fabricated by loading Ag_3PO_4 on brookite TiO_2 nanorods.
- The loading amount of Ag_3PO_4 nanoparticles is rationally optimized.
- Hybrid TiO_2-Ag_3PO_4 exhibits large surface area and enhanced visible light absorption.
- TiO_2-Ag_3PO_4 demonstrates efficient visible-light-driven photocatalytic performance.