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Facile synthesis of TiO₂/Ag₃PO₄ composites with co-exposed high-energy facets for efficient photodegradation of rhodamine B solution under visible light irradiation

In this study, TiO₂/Aq₃PO₄ composites based on anatase TiO₂ nanocrystals with co-exposed {101}, {010}/ {100}, {001} and [111]-facets and Ag₃PO₄ microcrystals with irregular and cubic-like polyhedron morphologies were successfully synthesized by combining hydrothermal and ion-exchange methods. The anatase TiO₂ nanocrystals with different high-energy facets were controllably prepared via hydrothermal treatment of the exfoliated $[Ti_4O_5]^2$ -/ $[Ti_2O_5]^2$ - nanosheet solutions at desired pH values. The Aq_3PO_4 microcrystal with different morphologies was prepared via the ion-exchange method in the presence of $AgNO_3$ and $NH_4H_2PO_4$ at room temperature, which was used as a substrate to load the asprepared anatase TiO₂ nanocrystals on its surface and to form TiO₂/Aq₃PO₄ heterostructures. The apparent rate constant of the pH 3.5-TiO₂/Ag₃PO₄ composite was the highest at 12.0×10^{-3} min⁻¹, which was approximately 1.1, 1.2, 1.4, 1.6, 13.3, and 24.0 fold higher than that of pH 0.5-TiO₂/Aq₃PO₄ $(10.5 \times 10^{-3} \text{ min}^{-1})$, pH 7.5-TiO₂/Ag₃PO₄ (10.2 $\times 10^{-3} \text{ min}^{-1})$, pH 11.5-TiO₂ (8.8 $\times 10^{-3} \text{ min}^{-1})$, Ag₃PO₄ $(7.7 \times 10^{-3} \text{ min}^{-1})$, blank sample $(0.9 \times 10^{-3} \text{ min}^{-1})$, and the commercial TiO₂ $(0.5 \times 10^{-3} \text{ min}^{-1})$, respectively. The pH 3.5-TiO₂/Ag₃PO₄ composite exhibited the highest visible-light photocatalytic activity which can be attributed to the synergistic effects of its heterostructure, relatively small crystal size, large specific surface area, good crystallinity, and co-exposed high-energy {001} and [111]-facets. The as-prepared TiO₂/Ag₃PO₄ composites still exhibited good photocatalytic activity after three successive experimental runs, indicating that they had remarkable stability. This study provides a new way for the preparation of TiO2/Ag3PO4 composite semiconductor photocatalysts with high energy crystal surfaces and high photocatalytic activity.

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1. Introduction

With the rapid development of industrialization, energy and environmental crises have become the key factors restricting the sustainable development of human society. Therefore, it is very urgent to search for suitable semiconductor photocatalysts to make full use of solar energy to split water into hydrogen, convert carbon dioxide into fuels, store energy, and degrade the organic wastewater discharged from the textile industry.¹⁻⁵ In recent decades, different types of semiconductor photocatalysts, such as carbon-cloth functionalized transition metal based electrocatalysts,6 quantum dot-based photocatalysts,⁷⁻⁹ iron (Fe)-doped ZrO₂,¹⁰ metal-organic framework (MOF)-based heterostructured catalysts,¹¹ and ZnO/Bi₂WO₆ nanohybrids12 have been reported. Among the well-known oxide semiconductor photocatalysts, titanium dioxide (TiO2) has been proven to be the best choice due not only to its excellent photooxidization ability and low cost but also its long-term photostability and chemical stability and innocuousness.13,14 However, the photocatalytic efficiency of TiO₂ still needs to be further improved for its practical application. The photocatalytic efficiency of TiO₂ is mainly dependent on the phase structure, crystallization, crystal size, specific surface area, and surface energy.^{15,16} However, based on the principle of surface energy minimization (0.44 J m⁻² for {101} facets < 0.53 J m⁻² for $\{010\}/\{100\}$ facets < 0.90 J m⁻² for $\{001\}$ facets < 1.09 J m⁻² for $\{110\}$ facets < 1.61 J m⁻² for $\{111\}$ facets), the proportion of highenergy crystal surfaces in the natural and synthetic anatase TiO₂ crystals under equilibrium condition is very small, resulting in

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the dominant exposed {101} crystal facets (more than 94%) on its surface.17,18 Since the pioneering work by Wen and coworkers on the synthesis of nanometer-sized anatase TiO₂ crystals with a large percentage of {101} facets by using the delaminated $[Ti_{1,73}O_4]^{1.07-}$ nanosheets as the precursor, there has been intensive interest in the flexible and controllable synthesis of anatase crystals with varied high-energy facets, such as {001}, {010}/{100}, {110} and {111} facets.¹⁹⁻²² Recently, we synthesized high-energy {010}, {001}, and [111]-faceted anatase TiO₂ nanocrystals by using the delaminated $[Ti_4O_9]^{2-1}$ and $[TiO_3]^{2-}$ nanosheets as the precursors in the presence and absence of capping agent, which displayed superior photocatalytic and photovoltaic performance.23-25 Although the exposed high-energy crystal surface of anatase TiO2 crystals will be conducive to improving the photocatalytic activity and dyesensitized solar energy performance, however, anatase TiO₂ crystals cannot suitable for applications under visible light irradiation due to its wide band gap (3.2 eV), resulting in the lower energy conversion efficiency in practical application.²⁶

In order to overcome above limitation, it is of great significance to extend the light absorption range of the anatase TiO₂ crystals to the visible light region.²⁷⁻²⁹ Silver orthophosphate (Ag₃PO₄) is a semiconductor photocatalyst with a narrow band gap of 2.45 eV, and is often to decompose organic contaminants and oxidize water to produce oxygen under visible light irradiation.³⁰ However, the narrow band gap energy and low valence band (VB) and conduction band (CB) position of Ag₃PO₄ result in high recombination rate and weak redox capacity of photogenerated electrons and holes, which severely weaken the photocatalytic activity of Ag₃PO₄.^{26,31} Therefore, it is an effective strategy to form a heterojunction by coupling anatase TiO₂ crystals with Ag₃PO₄ photocatalyst for improving the photocatalytic activity under visible-light irradiation.^{32,33} Zhang et al. synthesized one-dimensional heterostructured Ag₃PO₄/TiO₂ photocatalyst with improved photocatalytic activity for degradation of 4-nitrophenol in simulant wastewater under visible light.³⁴ An et al. reported that the floating HGMs-TiO₂/Ag₃PO₄ composites exhibited superior photocatalytic performance than that of pure Ag₃PO₄ and TiO₂/Ag₃PO₄ for degradation of methylene blue solution under visible light irradiation.3 Xu et al. reported that the magnetic Ag₃PO₄/TiO₂/Fe₃O₄ heterostructured nanocomposite showed enhanced photocatalytic performance for the degradation of acid orange 7 under visible light irradiation.35 Hamrouni et al. synthesized Ag doped TiO2-Ag3PO4 (Ag@TiO₂-Ag₃PO₄) composites by coupling sol-gel and precipitation methods, which significantly improved the photocatalytic activity than that of the TiO2-Ag3PO4 and the benchmark TiO₂ Evonik P25 for degradation of 4-nitrophenol solution under solar light irradiation.³⁶

In this study, anatase TiO_2 nanocrystals with different high energy facets were successful synthesized by using the exfoliated two-dimensional $[Ti_4O_9]^{2-}/[Ti_2O_5]^{2-}$ nanosheets, which were compounded with Ag_3PO_4 microcrystals to form a series of heterostructured TiO_2/Ag_3PO_4 composites. To our knowledge, this is the first time to study the TiO_2/Ag_3PO_4 photocatalysts formed by the combination of the anatase TiO_2 nanocrystals with high energy crystal surface and Ag_3PO_4 with different

morphologies. Various catalyst characterization of the synthesized TiO₂/Ag₃PO₄ composites confirmed that TiO₂ nanocrystals with co-exposed high-energy facets were successfully attached to the surface of Ag₃PO₄ microcrystals. In comparison to the commercial TiO₂ and the pure Ag₃PO₄ samples, the heterostructured TiO₂/Ag₃PO₄ composites exhibited good photocatalytic activity for the degradation of rhodamine B under visible light irradiation, which can be attributed to the separation of the e^- (in Ag₃PO₄ crystal) and h^+ (in TiO₂ nanocrystal) inhibits the charge recombination. For the as-prepared TiO₂/ Ag₃PO₄ composites, the pH 3.5-TiO₂/Ag₃PO₄ exhibited the highest photocatalytic activity, which can be attributed to the synergistic effects of its relative small crystal size, large specific surface area, good crystallinity, and co-exposed high-energy {001} and [111]-facets. However, although the as-prepared TiO₂/Ag₃PO₄ composites exhibited good stability, the photocatalytic performance needs to be further improved for their practical application.

2. Materials and methods

2.1 Synthesis of TiO₂ nanocrystals

The K₂Ti₄O₉/K₂Ti₂O₅·xH₂O composite was prepared via solidstate synthesis in the present of 14.5109 g K₂CO₃ (0.105 mol, Tianjin Bodi Chemical Co., Ltd., Tianjin, China) and 15.9800 g TiO₂ (0.200 mol, Tianjin Bodi Chemical Co., Ltd., Tianjin, China) at 900 °C for 24 h. The obtained K₂Ti₄O₉/K₂Ti₂O₅·xH₂O composite (10.0 g) was dissolved in 1 M HCl aqueous (1 L, Sichuan Xilong Chemical Co., Ltd., Chengdu, China) for three days under continuous magnetic stirring conditions to obtain $H_2Ti_4O_9 \cdot H_2O/H_2Ti_2O_5 \cdot H_2O$ composite. Then, 6.0 g $H_2Ti_4O_9 \cdot H_2O/H_2Ti_2O_5 \cdot H_2O$ composite, 7.0 g tetramethylammonium hydroxide (TMAOH, Shanghai Dibai Biological Technology Co., Ltd., Shanghai, China) and 50 mL deionized water were mixed uniformly, which were hydrothermally treated at 100 °C for 24 h in a homogenous reaction (KLJX-8A, Yantai Keli Chemical Equipment Co. Ltd., Yantai, China) under stirring conditions prepare TMA⁺-intercalated $H_2Ti_4O_9 \cdot H_2O/H_2Ti_2O_5 \cdot H_2O$ to compound. The resulting white TMA+-intercalated compound was dispersed in 500 mL of deionized water under stirring conditions for three days to obtain the nanosheets solutions containing of H2Ti4O9/H2Ti2O5 compound. The above nanosheets solutions were adjusted to desired pH values (0.5–11.5) at 180 °C for 24 h to prepared TiO₂ nanocrystals.

2.2 Synthesis of Ag₃PO₄ crystals

Silver orthophosphate (Ag₃PO₄) crystals were synthesized by using an ion-exchange method, using AgNO₃ (Beijing Beihua Fine Chemicals Co., Ltd., Beijing, China) and NH₄H₂PO₄ (Beijing Guangfu Technology Development Co., Ltd., Beijing, China) as the starting materials and NH₄F (Tianjin Bodi Chemical Co., Ltd., Tianjin, China) as a capping agent at room temperature. The Ag₃PO₄ sample was prepared according to the stoichiometry of AgNO₃ and NH₄H₂PO₄ to 3:1 (3AgNO₃ + NH₄H₂PO₄ = Ag₃PO₄ + NH₄NO₃ + 2HNO₃). In a typical synthesis, 3.8228 g (0.0225 mol) AgNO₃ and 0.8626 g (0.0075

mol) NH₄H₂PO₄ were dissolved in 150 mL of deionized water, respectively. Then, 1.0 g NH₄F (0.027 mol) was dissolved in the NH₄H₂PO₄ aqueous solution. After that, the AgNO₃ solution (0.15 mol L⁻¹) was transferred to pear-shaped separatory funnel and added to the NH₄H₂PO₄ aqueous solution (0.05 mol L⁻¹) drop by drop under continuous magnetic stirring. The yellow Ag₃PO₄ precipitate was obtained after 2 h, which was washed with lots of deionized water to remove unwanted ions, kept in the dark and dried at ambient temperatures.

2.3 Synthesis of TiO₂/Ag₃PO₄ composites

The well dispersed TiO₂ colloidal suspensions were obtained by dispersed 1.2 g as-prepared TiO₂ in 200 mL deionized water under stirring for 2 h. Then, 0.3 g Ag₃PO₄ precipitate was added to the above TiO₂ colloidal suspensions and kept under stirring for 2 h to generate TiO₂/Ag₃PO₄ composites (w(TiO₂) = 80%, w(Ag₃PO₄) = 20%). Finally, the composites were collected by filtering, which were washed several times, and dried at room temperature.

2.4 Characterization

The crystal structure of obtained samples were characterized by powder X-ray diffractometer (XRD) on a XRD-6100 (Shimadzu, Kyoto, Japan) with monochromated Cu K α radiation ($\lambda = 1.5406$ Å). The data were collected for scatting angles (2 θ) from 5 to 80° with a scanning speed of 8° min⁻¹. The morphology of the samples were investigated by using cold field emission scanning electron microscope (FESEM, JSM-7500F, Japan). The crystalline nanostructures were investigated using transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) (Tecnai G² F20 S-TWIN, FEI, America). The specific surface areas of the as-prepared samples were determined by using the Brunauer-Emmett-Teller (BET) method (Autosorb-IQ3, Quantachrome, America). UV-Vis-NIR spectra of the samples were obtained by using a Cary Series UV-Vis-NIR Spectrophotometer (Agilent Technologies, Cary 5000). The absorbance of rhodamine B solution was recorded within the wavelength range of 350-650 nm by using a TU-1901 UV-vis spectrophotometer (Beijing Purkinje General Instrument Co. Ltd).

2.5 Photocatalytic activity evaluations

The photocatalytic activities of the as-synthesized TiO_2/Ag_3PO_4 composites were evaluated by monitoring the degradation of rhodamine B (RhB). The irradiation source was provided by a 300 W xenon lamp equipped with a 400 nm cutoff light filter and the wavelength ranges from 400 nm to 600 nm. Typically, 75 mg TiO_2/Ag_3PO_4 composite was suspended in 150 mL RhB solution (10 ppm). Prior to illumination, the suspensions were magnetically stirred for 2 h in the dark to achieve adsorption-desorption equilibrium. At intervals of 15 min, 5 mL of suspensions were taken out and centrifuged at 2500 rpm for 10 min to remove the TiO_2/Ag_3PO_4 composites. The changes of RhB concentration during xenon light irradiation were determined by using a TU-1901 ultraviolet-visible spectrophotometer at the maximum absorption wavelength of RhB (554 nm) with

deionized water as the reference solution. For comparison, the commercial TiO₂ powder (\sim 70.9% anatase and \sim 29.1% rutile), and as-prepared Ag₃PO₄ powder were also used as the photo-catalytic references. The stability and recyclability of the TiO₂/Ag₃PO₄ composites were investigated by the degradation experiments of the 10 ppm RhB solution (150 mL).

3. Results

3.1 Structure and morphological characterization

The XRD patterns of the $K_2Ti_4O_9/K_2Ti_2O_5 \cdot xH_2O$ and H₂Ti₄O₉·H₂O/H₂Ti₂O₅·H₂O composites depicted characteristic structures. The diffraction peaks at 10.08°, 14.23°, 22.49°, 28.08°, 30.24°, 31.04°, 41.30°, 43.34° and 48.04° corresponded to the (200), (201), (-203), (310), (311), (004), (512), (205) and (020) crystal facets of K₂Ti₄O₉, which depicted the characteristic monoclinic structure of K₂Ti₄O₉ (JCPDS card no. 32-0861, space group: C2/m, lattice parameter: a = 19.968 Å, b = 3.746 Å, c =12.025 Å and $\beta = 114.01^{\circ}$ (Fig. 1(a)). The diffraction peaks at 11.10°, 32.96° and 33.78° corresponded to the (200), (10-2) and (201) crystal facets of $K_2Ti_2O_5 \cdot xH_2O_5$, which depicted the characteristic monoclinic structure of K₂Ti₂O₅·xH₂O (JCPDS card no. 46-0224, space group: C2/m, lattice parameter: a = 6.605 Å, b = 3.069 Å, c = 5.665 Å and $\beta = 99.98^{\circ}$) (Fig. 1(a)). Fig. 1(b) shows XRD patterns of proton exchanged phase, the diffraction peaks located at 9.70°, 17.70°, 22.49°, 30.04°, 37.48° and 43.72° are ascribed to (20-1), (40-1), (203), (403) and (80-5) crystal facets of $H_2Ti_4O_9 \cdot H_2O_1$, respectively, and the diffraction peaks located at 9.70°, 19.40° and 24.22° are ascribed to (200), (400) and (110) crystal facets of $H_2Ti_2O_5 \cdot H_2O_5$, respectively. The basal spacing was changed from 8.77 Å for $K_2Ti_4O_9$ (or 11.10 Å for



Fig. 1 XRD patterns of the layered (a) $K_2Ti_4O_9/K_2Ti_2O_5\cdot xH_2O$ composite and the protonic titanate (b) $H_2Ti_4O_9\cdot H_2O/H_2Ti_2O_5\cdot H_2O$ composite.



Fig. 2 XRD patterns of the (a) Ag_3PO_4 , (b) pH 0.5-TiO_2/Ag_3PO_4, (c) pH 1.5-TiO_2/Ag_3PO_4, (d) pH 3.5-TiO_2/Ag_3PO_4, (e) pH 5.5-TiO_2/Ag_3PO_4, (f) pH 7.5-TiO_2/Ag_3PO_4, (g) pH 9.5-TiO_2/Ag_3PO_4, and (h) pH 11.5-TiO_2/Ag_3PO_4 composites specimens obtained from the exfoliated H₂Ti₄O₉/H₂Ti₂O₅·H₂O nanosheets composites.

 $K_2Ti_2O_5 \cdot xH_2O$) to 9.11 Å for $H_2Ti_4O_9 \cdot H_2O$ (or 9.11 Å for $H_2Ti_2O_5 \cdot H_2O$), indicating the protonation of $K_2Ti_4O_9/K_2Ti_2O_5 \cdot xH_2O$ composite occur successfully. Based on the above

analysis, it can be seen that the $K_2 T i_4 O_9 / K_2 T i_2 O_5 \cdot x H_2 O$ composite and the protonated products $H_2 T i_4 O_9 \cdot H_2 O / H_2 T i_2 - O_5 \cdot H_2 O$ have been successfully prepared.

Fig. 2(a) presents the XRD pattern of the Ag₃PO₄ obtained by simple ion-exchange method. The diffraction peaks at 20.89°, 29.72°, 33.12°, 36.60°, 52.72°, 55.06°, 57.30°, 61.68° and 71.92° corresponded to the (110), (200), (210), (211), (222), (320), (321), (400) and (421) crystal facets of Ag_3PO_4 , which depicted the characteristic cubic structure of Ag₃PO₄ (JCPDS card no. 06-0505, space group: $P4\bar{3}n$, lattice parameter: a = 6.013 Å and $\beta =$ 90°) (Fig. 1(a)). After hydrothermal treatment of the exfoliated H₂Ti₄O₉/H₂Ti₂O₅·H₂O nanosheets composites, both composites transformed into anatase phase TiO_2 completely. The $TiO_2/$ Ag₃PO₄ composites were prepared by mixed the obtained anatase TiO_2 nanocrystals and Ag_3PO_4 in water. Fig. 2(b-h) shows the XRD patterns of the obtained TiO₂/Ag₃PO₄ composites, except for the characteristic diffraction peaks of the Ag₃PO₄ crystals, other diffraction peaks at around 25.32°, 37.84°, 38.60°, 48.06°, 53.98°, 55.04°, 62.84°, 68.82°, 70.34° and 75.24° corresponded to the (101), (004), (112), (200), (105), (211), (204), (116), (220) and (215) crystal facets of anatase TiO2 (JCPDS card no. 21-1272, crystal system: tetragonal, space group: I41/amd, lattice parameter: a = 3.7852 Å and c = 9.5139 Å). The diffraction peaks of TiO₂/Ag₃PO₄ composites are shifted slightly to the right, which can be attributed to the basic crystal plane spacing (d_{basic}) of the crystal plane varies slightly. The d_{basic} values of TiO₂(101) (Ag₃PO₄(110)) are 3.514 (4.244), 3.509 (4.236), 3.507 (4.234), 3.512 (4.247), 3.515 (4.250), 3.512 (4.244), and 3.512 Å (4.244 Å) for the pH 0.5-TiO₂/Ag₃PO₄, pH 1.5-TiO₂/Ag₃PO₄, pH 3.5-TiO₂/



Fig. 3 FESEM images of (a) pH 0.5-TiO₂/Ag₃PO₄, (b) pH 1.5-TiO₂/Ag₃PO₄, (c) pH 3.5-TiO₂/Ag₃PO₄, (d) pH 5.5-TiO₂/Ag₃PO₄, (e) pH 7.5-TiO₂/Ag₃PO₄, (f) pH 9.5-TiO₂/Ag₃PO₄, (g) pH 11.5-TiO₂/Ag₃PO₄, (h) pH 11.5-T

Ag₃PO₄, pH 5.5-TiO₂/Ag₃PO₄, pH 7.5-TiO₂/Ag₃PO₄, pH 9.5-TiO₂/ Ag₃PO₄, and pH 11.5-TiO₂/Ag₃PO₄, respectively. Moreover, for the as-prepared pH 5.5-TiO₂/Ag₃PO₄ composite, a weak impurity peak was observed at 18.04°. The intensities of anatase TiO₂ and Ag₃PO₄ crystals indicate that the TiO₂/Ag₃PO₄ composites are well crystallized and no diffraction peaks attributed to rutile or brookite are detected. It can be seen that with increasing pH value, the peak intensities of anatase TiO₂ increase and the width of the (101) crystal facets diffraction peak of anatase TiO₂ $(2\theta = 25.32^{\circ})$ become narrow, indicating the increase of the average crystalline sizes and relative crystallinity of the TiO₂/ Ag₃PO₄ composites. The diffraction peaks of TiO₂(101)/Ag₃PO₄ composites synthesized are relatively broad, which may be ascribed to the small size of TiO₂/Ag₃PO₄ composites. Based on the broadening of (101) peaks of the TiO₂/Ag₃PO₄ composites specimens (b–h) in Fig. 2, the average crystalline size of the specimens can be calculated as 23.0, 23.2, 23.5, 26.4, 28.0, 29.7, and 32.0 nm for pH 0.5-TiO₂/Ag₃PO₄, pH 1.5-TiO₂/Ag₃PO₄, pH 3.5-TiO₂/Ag₃PO₄, pH 5.5-TiO₂/Ag₃PO₄, pH 9.5-TiO₂/Ag₃PO₄, pH 11.5-TiO₂/Ag₃PO₄, pH 11.5-TiO₂/Ag₃

Morphology of the TiO_2/Ag_3PO_4 composites and the pure Ag_3PO_4 specimens was determined by FESEM. The FESEM



Fig. 4 FESEM images and the corresponding EDS with elemental mapping images of (a and b) pH $0.5-TiO_2/Ag_3PO_4$, (c and d) pH $3.5-TiO_2/Ag_3PO_4$, (c and d) pH $3.5-TiO_2/Ag_3PO_4$, (e and f) pH $7.5-TiO_2/Ag_3PO_4$, and (g and h) pH $11.5-TiO_2/Ag_3PO_4$ composites specimens.

images of the TiO₂/Ag₃PO₄ composites that were synthesized under different pH values conditions (pH 0.5-11.5) are shown in Fig. 3(a)-(g). Results show that there were no significant differences in the morphology of the TiO2/Ag3PO4 composites synthesized at pH 0.5-11.5, and all the nanocrystals are severely agglomerated together. When the pH is 0.5, many square rodshaped anatase nanocrystals with about 70-160 nm in length and 40-50 nm in width, a lot of cuboid-shaped anatase nanocrystals with 25-110 nm in length and 20-60 nm in width, lots of shuttle-like anatase nanocrystals with the size about 60-110 nm in length and 30-50 nm in width and a large number of egg-like anatase nanocrystals with about 30-60 nm in the central axis length and 15-30 nm in the central axis width are observed, as shown in Fig. 3(a). Fig. 3(b) shows the FESEM image of the pH 1.5-TiO₂/Ag₃PO₄ composite, it can seen that some square rodshaped anatase nanocrystals with about 60-140 nm in length and 30 nm in width, some cuboid-shaped anatase nanocrystals with 35-50 nm in length and 30-40 nm in width, several shuttlelike anatase nanocrystals with about 90-150 nm in length and 45 nm in width, and a large numbers of egg-like anatase nanocrystals with about 20-70 nm in length and 15-40 nm in width are observed. When the pH value rises to 3.5, many cuboidshaped anatase nanocrystals with 40-80 nm in length and 35-

70 nm in width, some shuttle-like anatase nanocrystals with 95-185 nm in length and 40-80 in width, lots of spheroidal anatase nanocrystals with 20-45 nm in diameter, and several diamondshaped anatase nanocrystals with 50-90 nm in length and 20-60 nm in width are observed, as shown in Fig. 3(c). Fig. 3(d) shows the representation FESEM image of the pH 5.5-TiO₂/ Ag₃PO₄ composite prepared by mixed the pH 5.5-TiO₂ and Ag_3PO_4 samples. As shown in Fig. 3(d), egg-like anatase nanocrystals with a size of 30-60 nm and 30-70 nm in length in high yield, some shuttle-like anatase nanocrystals with a size of about 20-50 nm in width and 60-150 nm in length, and cuboid-shaped anatase nanocrystals with a size of 30-70 nm in width and 55-90 nm in length are observed. The FESEM image in Fig. 3(e) shows that the pH 7.5-TiO₂/Ag₃PO₄ composite that has two main morphologies, shuttle-like anatase nanocrystals with 40-200 nm in length and 25-50 nm in width, and cuboid-shaped anatase nanocrystals with 40-95 nm in length and 30-55 nm in width. Fig. 3(f) and (g) show FESEM images of the pH 9.5-TiO₂/Ag₃PO₄ and pH 11.5-TiO₂/Ag₃PO₄ composites, respectively. It can be seen that the prepared composites have similar morphologies, square rod-like (or cuboid-shaped) anatase nanocrystals with a length of about 50-130 nm (or 25-90 nm) and a width of about 30-50 nm (25-70 nm), spheroidal anatase nanocrystals with 20-95 nm (or



Fig. 5 TEM and HRTEM images of (a-f) pH 0.5-TiO₂/Ag₃PO₄ and (g-j) pH 3.5-TiO₂/Ag₃PO₄ composites specimens.

20-95 nm) in diameter, and shuttle-like anatase nanocrystals with a length of about 30-210 (or 30-215 nm) nm and a width of about 20-65 (or 20-85 nm) nm for pH 9.5-TiO₂/Ag₃PO₄ (or pH 11.5-TiO₂/Ag₃PO₄) composites. FESEM images of Ag₃PO₄ microcrystals are shown in Fig. 3(h) and (i), it can be seen that welldispersed irregular Ag_3PO_4 polyhedrons with about 3–12 μ m in length and 2.5-9.0 µm in width (or thickness), and cubic-like particles with the size about 1.5-7.0 µm were obtained. And the surface of the Ag₃PO₄ crystals is rough, which is formed by the agglomeration of many nanoparticles with the size about 30-50 nm in diameter (Fig. 3(i)). Based on the above analysis, the Ag₃PO₄ crystals were not observed in the TiO₂/Ag₃PO₄ composites, which can be ascribed to the fact that the sizes of Ag₃PO₄ crystals were micrometer while the anatase TiO₂ crystals were nanometer, and TiO₂ nanocrystals were bound to the surface of Ag₃PO₄ microcrystals.

The FESEM images and the corresponding elemental distribution maps of TiO_2/Ag_3PO_4 composites were achieved by energy dispersive spectrometer (EDS). As shown in Fig. 4, the appearance of Ag and P elements in EDS further demonstrated successful impregnation of Ag_3PO_4 . The analysis of the results shows the atomic ratio of Ag to Ti is about 1 : 27.86, 1 : 71.55, 1 : 58.27, and 1 : 121 for pH 0.5-TiO_2/Ag_3PO_4, pH 3.5-TiO_2/Ag_3PO_4, pH 7.5-TiO_2/Ag_3PO_4, and pH 11.5-TiO_2/Ag_3PO_4 composites, respectively.

The TEM and HRTEM images further reveal the detailed surface morphology of the obtained TiO_2/Ag_3PO_4 composites products, as shown in Fig. 5 and 6. For pH 0.5-TiO_2/Ag_3PO_4, shuttle-like anatase nanocrystals with the length of about 30–85 nm and the width of about 15–25 nm, and square rod-shaped anatase nanocrystals with the length of about 25–140 nm and the width of about 15–50 nm are observed (Fig. 5(a)), which corresponds to the results of FESEM



Fig. 6 TEM and HRTEM images of (a-f) pH 7.5-TiO₂/Ag₃PO₄ and (g-o) pH 11.5-TiO₂/Ag₃PO₄ composites specimens.

(Fig. 3(a)). The square rod-shaped nanocrystals with a lattice of 0.353 nm (or 0.359 nm) can be indexed to the (101) planes of the anatase, and the egg-like nanoparticle with a lattice fringes of 0.359 nm also can be indexed to the (101) planes of the anatase (Fig. 5(b)-(f)). The lateral planes of square rod-shaped nanocrystals are parallel to (101) planes, indicating that the exposed facets are {101} facets (Fig. 5(b) and (c)). The lattice fringe has d-spacing values of 0.236 and 0.246 nm, corresponding to (004) and (103) planes of anatase TiO_2 , respectively (Fig. 5(c)). The long axis of the shuttle-like anatase nanocrystals is perpendicular to (004) planes, indicating that the exposed facets are {001} facets of the top and bottom planes (Fig. 5(c)). In Fig. 5(e), the lattice fringes of the irregular crystals with lattice spacings of 0.235 and 0.353 nm can be assigned to the (004) and (101) planes of the anatase TiO₂, respectively. And the angle between the (004) and (101) facets is 68° , implying that the irregular crystals expose {010} facets on its surface. The coexistence of various morphologies of the pH 3.5-TiO₂/Ag₃PO₄ composites was further investigated by TEM and HRTEM, as shown in Fig. 5(j-l). For the cuboid-shaped anatase nanocrystals, the TEM images depict the nanocrystals with 15-50 nm in length and 15-30 nm in width (Fig. 5(g)), and the lattice fringe has d-spacing values of 0.353 (or 0.360) and 0.353 nm, corresponding to (101) and (011) planes of anatase TiO₂, respectively (Fig. 5(h) and (l)). The interior angle between (101) and (011) planes of 82° is in good agreement with the theoretical value, which indicates that the preferentially exposed crystal facets of the cuboid-shaped anatase is perpendicular to [111] crystal zone axis (expressed as [111]-facets). For the shuttle-like anatase nanocrystals, the TEM images depict the nanocrystals with 15-120 nm in length and 10-45 nm in width (Fig. 5(g)), and the lattice fringe has d-spacing values of 0.360 nm, corresponding to (101) planes of anatase TiO_2 (Fig. 5(k)). For the diamond-shaped anatase nanocrystals, the TEM images depict the nanocrystals with 35–85 nm in length and 15–35 nm in width (Fig. 5(g)), and the lattice fringe has d-spacing values of 0.191 and 0.360 (or 0.364) nm, corresponding to (200) and (101) planes of anatase TiO₂, respectively (Fig. 5(h)-(j)). The lateral planes of the diamond-shaped anatase nanocrystals is parallel to (101) planes, indicating that the exposed facets are {101} facets of the lateral planes. For the square rodshaped anatase nanocrystals, the TEM images depict the nanocrystals with 40-135 nm in length and 20-30 nm in width (Fig. 5(g)), and the lattice fringe has d-spacing values of 0.360 nm, corresponding to (101) planes of anatase TiO_2 (Fig. 5(1)). The top and bottom planes of square rod-shaped anatase nanocrystals are parallel to (101) planes, indicating that the exposed facets are {101} facets.

Fig. 6(a)-(f) shows the TEM and HRTEM analysis results of the pH 7.5-TiO₂/Ag₃PO₄ composite. The size of cuboid-shaped anatase nanocrystals has a size about 30–60 nm in length and 20–35 nm in width, as shown in Fig. 6(a). The size of shuttle-like anatase nanocrystals is about 25–250 nm in length and 20– 75 nm in width (Fig. 6(a) and (d)), and the lattice fringe of 0.349, 0.476 and 0.360 nm corresponds to the distance between two adjacent (10-1), (002) and (101) planes of anatase TiO₂, and the intersection angles between (10-1) and (002), (101) and (002), and (101) and (10-1) planes are 68.3°, 68.3°, and 43.4°, respectively, as shown in Fig. 6(b). The high crystallized shuttle-like TiO₂ surfaces with the clear lattice fringes of the anatase

phase are also observed from Fig. 6(c) and (f). Two set of nonparallel lattice fringes with the *d*-spacing values of 0.349 and 0.238 nm, corresponding to (101) and (004) atomic planes of anatase phase (Fig. 6(c)). The lattice spacing of 0.352 and 0.476 nm of the truncated shuttle-like TiO_2 anatase TiO_2 , corresponding to the distance between two adjacent (101) or (002) planes, and the intersection angle between (101) and (002) planes is 68.3°, as shown in Fig. 6(e). Based on the above TEM and HRTEM analysis and the Wulff construction model, the shuttle-like anatase TiO2 nanocrystals preferentially expose the {010} facets, {101} facets, and {001} facets on the four lateral planes, the eight isosceles trapezoid planes, and the two top/ bottom surfaces, respectively, and the directional grown direction is along the [001]-direction. The size of shuttle-like (or cuboid-shaped) anatase nanocrystals is about 50-180 nm (or 25-100 nm) in length and 25-50 nm (or 20-80 nm) in width, as shown in Fig. 6(g, j and m). $\{010\}$ facets exposed TiO₂ exhibits a typical shuttle-like morphology with lattice fringes of 0.353 (or 0.360) and 0.174 (or 0.238, 0.482) nm attributed to (101) and (006) (or (004), (002)) crystallographic planes, respectively, and an interfacial angle of 68.3° between the {101} and {001} planes, as shown in Fig. 6(h, i and k). In addition, {010} facets exposed shuttle-like TiO2 nanocrystals also has d-spacing values of 0.173 (or 0.234, 0.189) and 0.482 (or 0.238, 0.238) nm, corresponding to (105) (or (112), (200)) and (002) (or (004), (004)) crystallographic planes, respectively, and an interfacial angle of 26.7° (or 60.6°, 90°) between the {105} (or (112), (200)) and {112} (or (004), (004)) planes, as shown in Fig. 6(k, l and o). Fig. 6(n) exhibits a typical TEM image of cuboid-shaped anatase nanocrystals, the fringe spacing of 0.191 nm corresponding to the (200) planes of anatase TiO₂, indicating that the exposed crystal facets of the top/bottom of the nanocrystals are {100} facets.

The morphology and microstructure of the Ag₃PO₄ crystals were further analyzed by TEM and HRTEM images, as shown in Fig. 7. As can be seen in Fig. 7(a), the obtained Ag₃PO₄ crystals contains some irregular polyhedrons with the lengths of 1.0-3.7 µm and a cubic-like crystals with the lengths of about 1.75 µm and the widths of about 1.45 µm, respectively, which is in agreement with the results observed by the SEM images (Fig. 3(h) and (i)). The lattice fringes of 0.269 (or 0.262) and 0.247 (or 0.239) nm match well with the (210) and (2-1-1) (or (211)) planes of irregular polyhedral Ag_3PO_4 crystals, respectively (Fig. 7(b)-(d)). And the angle between the (210) and (2-1) facets of 57° agrees well with the theoretical value 56.8°, according to calculated result from the lattice constants of Ag₃PO₄ (cubic, space group $P4\bar{3}n$, JCPDS 06-0505, and a = 6.013 Å). Based on the above TEM and HRTEM analysis, the Ag₃PO₄ specimens in the TiO₂/Ag₃PO₄ composites were not observed, which can be attributed to the deposition of nanoscale anatase TiO₂ crystals on the microsized Ag₃PO₄ crystals via an in situ precipitation process.

3.2 Growth mechanism of the TiO₂/Ag₃PO₄ composites

According to the results of the XRD, SEM and HR-TEM observation, the possible growth mechanism for the formation of TiO_2/Ag_3PO_4 hybrids can be expressed as follows. Firstly, the TMA^+ -intercalated $H_2Ti_4O_9/H_2Ti_2O_5$ compounds



Fig. 7 (a) TEM and (b–d) HRTEM images of Ag_3PO_4 specimens.

 $(TMA^+-H_2Ti_4O_9/H_2Ti_2O_5)$ were exfoliated into nanosheets solutions under stirring conditions.

$$TMA^{+}-H_{2}Ti_{4}O_{9} + H_{2}O \rightarrow TMA^{+} + [Ti_{4}O_{9}]^{2-} + H_{3}O^{+}$$
 (1)

$$TMA^{+}-H_{2}Ti_{2}O_{5} + H_{2}O \rightarrow TMA^{+} + [Ti_{2}O_{5}]^{2-} + H_{3}O^{+}$$
 (2)

The positive ions of TMA⁺ and H_3O^+ located on surface of $[Ti_4O_9]^{2-}/[Ti_2O_5]^{2-}$ nanosheets to balance the negative charge of $[Ti_4O_9]^{2-}/[Ti_2O_5]^{2-}$ so that the nanosheets remain electrically neutral. Then, the nanosheets solutions containing of $[Ti_4O_9]^{2-}/[Ti_2O_5]^{2-}$ compounds (pH = 0.5–11.5) were transformed to anatase TiO₂ nanocrystals under hydrothermal conditions by the following reaction.

$$[Ti_4O_9]^{2-} + 2H^+ \rightarrow 4TiO_2 + H_2O$$
 (3)

$$[Ti_2O_5]^{2-} + 2H^+ \rightarrow 2TiO_2 + H_2O$$
 (4)

$$[Ti_4O_9]^{2-} + H_2O \rightarrow 4TiO_2 + 2OH^-$$
 (5)

$$[Ti_2O_5]^{2-} + H_2O \rightarrow 2TiO_2 + 2OH^-$$
 (6)

Acidic condition is beneficial for reactions (3) and (4), neutral and basic conditions are favorable for reactions (5) and (6). In this process, the $[Ti_4O_9]^{2-}/[Ti_2O_5]^{2-}$ nanosheets were transformed firstly to nanosheet-like anatase TiO_2 crystals by an *in situ* topotactic dehydration reaction.³⁷ Then the nanosheet-like anatase TiO_2 crystals were split into anatase TiO_2 nanocrystals with various morphologies and different exposed facets by dissolution–recrystallization process along their different planes.

The micro-sized Ag_3PO_4 crystals were synthesized by using an ion-exchange method, using $AgNO_3$ and $NH_4H_2PO_4$ ($3Ag^+ + H_2PO_4^- = Ag_3PO_4 \downarrow + 2H^+$). The anatase TiO₂ nanocrystals with various morphologies and different exposed facets and Ag_3PO_4 precipitate were well dispersed into deionized water under stirring to form suspension solution. The micro-sized Ag_3PO_4 polyhedrons with larger particle surface, which could absorb more nano-sized anatase TiO₂ nanocrystals onto their surfaces *via* an *in situ* precipitation process to form the heterostructured TiO₂/Ag₃PO₄ composites.

3.3 UV-vis adsorption spectra of Ag_3PO_4 , TiO_2/Ag_3PO_4 and TiO_2

The UV-visible absorption spectrum was applied to examine the optical properties of pure Ag_3PO_4 , TiO_2 and TiO_2/Ag_3PO_4 composites. As observed in Fig. 8, the UV-Vis NIR spectrum of



Fig. 8 UV-Vis NIR Spectra of pure TiO₂, pure Ag₃PO₄, pH 0.5-TiO₂/Ag₃PO₄, pH 3.5-TiO₂/Ag₃PO₄, pH 7.5-TiO₂/Ag₃PO₄, and pH 11.5-TiO₂/Ag₃PO₄ composites.

pure TiO₂ sample only exhibits the fundamental absorption band edge (395 nm) in the UV light region, and the absorption band edge almost no more exists in the visible wavelength range. The pure Ag₃PO₄ sample shows strong adsorption with absorption band edge at around 500 nm, which is equivalent to the band gap energy of 2.45 eV, in an good agreement with the results reported previously.38 However, for the prepared TiO₂/ Ag₃PO₄ composites at different values of pH, except for adsorption band edge (less than 408 nm) in the UV light region, a feature band edge (510 nm) of pure Ag₃PO₄ appears in the visible light range based on the UV-Vis NIR spectrum. The absorption edges of TiO₂/Ag₃PO₄ composites are shifted slightly toward higher wavelength relative to pure Ag₃PO₄, indicating TiO₂ in the composites is coupled to Ag₃PO₄. The above analysis show that the as-prepared TiO₂/Ag₃PO₄ composites can be used for visible light photocatalytic reactions.

3.4 Photocatalytic activities for the degradation of rhodamine B solutions

Recently, different types of photocatalysts, such as Mn-doped ZrO_2 ,³⁹ carbon quantum dots,⁴⁰ MOFs,¹¹ BaTiO₃,⁴¹ were used to degrade the organic pollutants. In this study, the photocatalytic activities of the TiO₂/Ag₃PO₄ composites were evaluated by degradation of the carcinogenic textile dye rhodamine B (RhB, adsorption band: 554 nm). The degradation efficiency of all the specimens is expressed as $(c_0 - c_t)/c_0 \times 100\%$, where c_0 and c_t represent the initial and residual concentration of the

RhB, respectively. Prior to illumination, the suspensions were magnetically stirred in the dark for 2 h to make the RhB dyes reach achieve adsorption-desorption equilibrium on the surface of TiO₂/Ag₃PO₄ composites.⁴² The adsorption values $(mol(RhB) g(TiO_2/Ag_3PO_4)^{-1})$ of RhB on the surface of TiO_2/ Ag_3PO_4 composites were 4.0×10^{-6} , 7.0×10^{-6} , 5.5×10^{-6} , and $4.5 \times 10^{-6} \text{ mol g}^{-1}$ for pH 0.5-TiO₂/Ag₃PO₄, pH 3.5-TiO₂/ Ag₃PO₄, pH 7.5-TiO₂/Ag₃PO₄, and pH 11.5-TiO₂/Ag₃PO₄ samples, respectively. These results indicated that the enhancement order of adsorption binding of the RhB to the TiO₂/Ag₃PO₄ was pH 0.5-TiO₂/Ag₃PO₄ < pH 11.5-TiO₂/Ag₃PO₄ < pH 7.5-TiO₂/Ag₃PO₄ < pH 3.5-TiO₂/Ag₃PO₄, and that the strong anchoring of the RhB onto the surface of pH 3.5-TiO₂/Ag₃PO₄ could improve the photocatalytic activity. The commercial TiO₂ powder (\sim 70.9% anatase and \sim 29.1% rutile) and Ag₃PO₄ powder were used as the photocatalytic references. Fig. 9(a) shows the variation of the absorption of rhodamine B (RhB) in the presence of pH 0.5-TiO₂/Ag₃PO₄ composite under the Xe light irradiation for 120 min. The peak position at 554 nm gradually moved towards the short-wavelength direction (*i.e.*, hypsochromic shift) and the intensity gradually decreased, indicating the partial N-de-ethylation and the destruction of structure of the polycyclic aromatic hydrocarbon by the gradual decolorization of the RhB solution.43

After exposure to visible light for 120 min, the degradation of RhB was as follows: pH 3.5-TiO₂/Ag₃PO₄ (75.6%) > pH 0.5-TiO₂/Ag₃PO₄ (72.2%) > pH 7.5-TiO₂/Ag₃PO₄ (65.8%) > pH 11.5-TiO₂/Ag₃PO₄ (61.3%) > Ag₃PO₄ (56.0%) > blank (10.8%) > the



Fig. 9 (a) Temporal evolution of rhodamine B (RhB) over pH 0.5-TiO₂/Ag₃PO₄ composite, (b) photocatalytic degradation of RhB solution over blank, TiO₂, Ag₃PO₄, and TiO₂/Ag₃PO₄ composites under Xe light irradiation with a 400 nm cutoff filter, (c) the kinetic fit of the RhB degradation by blank, TiO₂, Ag₃PO₄, and TiO₂/Ag₃PO₄ composites, and (d) the corresponding apparent rate constants.



Fig. 10 Possible photocatalytic mechanism for the photodegradation of RhB over the TiO_2/Ag_3PO_4 composites under visible light irradiation.

commercial TiO_2 (5.8%), as shown in Fig. 9(b). Obviously, the as-prepared TiO₂/Ag₃PO₄ composites exhibit enhanced photocatalytic performance for the degradation of RhB compared to the commercial TiO₂ powder and Ag₃PO₄ powder. The enhanced photocatalytic performance can be attributed to the TiO₂/Ag₃PO₄ heterostructures, which can absorb more visible light and inhibit the recombination of photoelectrons and holes.³⁴ Fig. 10 shows a possible photocatalytic mechanism for the photodegradation of RhB over the TiO₂/Ag₃PO₄ heterostructures under visible light irradiation. The valence band (VB) potential (+2.90 eV vs. NHE) and conduction band (CB) potential (+0.45 eV vs. NHE) of Ag_3PO_4 are more positive than those of TiO_2 (VB potential: +2.70 eV, and CB potential: -0.30 eV), which imply that the photon generated electrons (e^{-}) of TiO₂ nanocrystal will be quickly transferred to the CB of Ag₃PO₄ crystal, whereas the photon generated holes (h⁺) of Ag₃PO₄ crystal will be migrated to the VB of TiO₂ nanocrystal under visible light irradiation.^{30,44} The separation of the e⁻ (in Ag₃PO₄ crystal) and h^+ (in TiO₂ nanocrystal) inhibits the charge recombination, which leads to the improvement of the photocatalytic activity of TiO_2/Ag_3PO_4 composites.³² The h⁺ and e⁻ have oxidation and reduction, respectively. Under visible light irradiation, the h⁺ in the VB of TiO₂ nanocrystal can directly oxidize the organic dye RhB and the water molecules adsorbed to the surface of TiO₂

photocatalyst to form RhB oxidation and 'OH radicals, respectively.³ At the same time, the e⁻ in the CB of Ag₃PO₄ crystal can directly reduce the oxygen molecules adsorbed to the surface of Ag₃PO₄ photocatalyst to form strong oxidizing capacity of hydrogen peroxide (H_2O_2) to oxidize and degradation RhB. Moreover, Ag_3PO_4 is reduced to Ag by e^- in the photocatalytic process. The 10 mg L^{-1} RhB solution (10 ppm) was not completely degraded due to the addition of more RhB solution (150 mL) and fewer catalysts (75 mg), and the liquid level of RhB solution was far away from the light source (25 cm). However, TiO₂ exhibited very low photocatalytic activity for the photodegradation of RhB, only 5.8% degradation efficiency, even lower than 10.8% for the blank without any photocatalysts under the Xe light irradiation for 120 min, implying that the TiO₂ actually had no any photocatalytic activity. Based on the discussion results of TiO₂ and the blank, it is reasonable that the presence of photocatalyst has a shielding effect on the degradation of RhB under the Xe light irradiation.45

Since the process of photodegradation of RhB solution followed the pseudo-first-order reaction kinetics model, the fitted pseudo-first-order reaction plots, the correlation coefficient and the corresponding apparent rate constant (k_{app}) are shown in Fig. 9(c) and (d), respectively. The correlation coefficients (R^2) are 0.968, 0.971, 0.943, 0.955, 0.997, 0.939, and 0.977 for the blank, TiO₂, Ag₃PO₄, pH 0.5-TiO₂/Ag₃PO₄, pH 3.5-TiO₂/Ag₃PO₄, pH 7.5-TiO₂/Ag₃PO₄, and pH 11.5-TiO₂/Ag₃PO₄, respectively. The pH 3.5-TiO₂/Ag₃PO₄ composite exhibited the highest k_{app} value $(12.0 \times 10^{-3} \text{ min}^{-1})$, which was approximately 24.0, 13.3, 1.6, 1.4, 1.2, and 1.1 times larger than those of the commercial TiO₂ ($0.5 \times 10^{-3} \text{ min}^{-1}$), blank ($0.9 \times 10^{-3} \text{ min}^{-1}$), Ag₃PO₄ (7.7 \times 10⁻³ min⁻¹), pH 11.5-TiO₂/Ag₃PO₄ (8.8 \times 10⁻³ min⁻¹), pH 7.5-TiO₂/Ag₃PO₄ (10.2 \times 10⁻³ min⁻¹), and pH 0.5-TiO₂/Ag₃PO₄ (10.5 \times 10 $^{-3}$ min $^{-1})$ samples, respectively. The pH 3.5-TiO_/ Ag_3PO_4 composite had the highest k_{app} value, indicating that the pH 3.5-TiO₂/Ag₃PO₄ composite had the highest photocatalytic activity.

The stability and recyclability of photocatalyst is one of the important parameters for its practical applications. Herein, the stability and recyclability of the pure Ag_3PO_4 and TiO_2/Ag_3PO_4 composites were evaluated by examining their recyclability in the photodegradation of RhB. Fig. 11 exhibited the repetitive photocatalytic degradation of RhB solution (10 mg L⁻¹, 150 mL)



Fig. 11 Recycling studies of the pure Ag_3PO_4 , pH 0.5-TiO₂/Ag₃PO₄, pH 3.5-TiO₂/Ag₃PO₄, pH 7.5-TiO₂/Ag₃PO₄, and pH 11.5-TiO₂/Ag₃PO₄ photocatalysts for the photocatalytic degradation of RhB solution.

during three sequential runs under identical conditions. After each run, TiO_2/Ag_3PO_4 and Ag_3PO_4 photocatalysts were collected by centrifugation and washed with deionized water for several times and the fresh RhB solutions with the same concentration (10 mg L⁻¹) were used for next run. The photocatalytic efficiency of the TiO_2/Ag_3PO_4 and Ag_3PO_4 photocatalysts remained almost unchanged after three successive experimental runs, indicating that the synthesized photocatalysts had remarkable stability.

As is well-known, the photocatalytic activity is not only related to the heterostructure of TiO₂ nanocrystals, but also influenced by other factors, such as crystalline phase, crystalline size, crystallinity, specific surface area, exposed facets, and so on.⁴⁶⁻⁴⁸ For the synthesized TiO₂/Ag₃PO₄ composites, the crystalline form (anatase) and proportion ($w(TiO_2) : w(Ag_2PO_4)$ = 4:1) of TiO₂ are the same, indicating that the influence of TiO₂ crystal form and proportion on photocatalytic activity in TiO_2/Ag_3PO_4 composites is negligible. In the TiO_2/Ag_3PO_4 composites, the average crystalline sizes of pH 0.5-TiO₂/Ag₃PO₄, pH 3.5-TiO₂/Ag₃PO₄, pH 7.5-TiO₂/Ag₃PO₄, and pH 11.5-TiO₂/ Ag₃PO₄ were 58.5, 68.5, 87.5 and 80.0 nm, respectively, by measuring 200 particles in the FESEM images with Particle Size Distribution Calculation Software (Fudan University, China). And the specific surface areas were 32.6, 27.8, 21.8, 24.4 m² g⁻¹ for pH 0.5-TiO₂/Ag₃PO₄, pH 3.5-TiO₂/Ag₃PO₄, pH 7.5-TiO₂/ Ag₃PO₄, and pH 11.5-TiO₂/Ag₃PO₄, respectively. It is known that smaller crystal size and larger specific surface (favorable for the RhB adsorption) contribute to the enhancement of photocatalytic activity in the photochemical reaction, which is attributed to its strong oxidation-reduction capability and more active sites.49,50 However, the pH 3.5-TiO₂/Ag₃PO₄ composite displayed the highest photocatalytic activity, although the crystal size (68.5 nm) is much bigger than that (58.5 nm) of the pH 0.5-TiO₂/Ag₃PO₄ composite, and the specific surface area $(27.8 \text{ m}^2 \text{ g}^{-1})$ slightly smaller than that $(32.6 \text{ m}^2 \text{ g}^{-1})$ of the pH 0.5-TiO₂/Ag₃PO₄ composite, indicating that it is also very significant to establish a balance between crystal size and specific surface area to improve the photocatalytic performance. On the other hand, the crystallinity of the pH 0.5-TiO₂/Ag₃PO₄ composite is better than that of pH 3.5-TiO₂/Ag₃PO₄ composite, which inhibits the recombination of photogenerated charge carriers (photogenerated electrons and holes), resulting in a relative good photoactivity.15

The surface energies of {101}, {010} (or {100}), {001}, {110} and [111]-facets of anatase TiO₂ are 0.44, 0.53, 0.90, 1.09, and 1.61 J m⁻², respectively.^{21,51} In generally, in the photocatalytic reaction, the crystal surface with high-energy crystal facets usually exhibits high photocatalytic activity. Based on the discussion above, the anatase TiO₂ nanocrystals preferentially co-exposed the {101}/{001}/{010} facets, {101}/{001}/[111]-facets, {101}/{010} facets, {101}/{001}/[111]-facets, {101}/{010} facets, {101}/{010} (or {100}) facets on their surfaces in the pH 0.5-TiO₂/Ag₃PO₄ pH 3.5-TiO₂/Ag₃PO₄, pH 7.5-TiO₂/Ag₃PO₄ can also be attributed to the coexistence of high-energy {001} and [111]-facets. According to the discussion above, the pH 0.5-TiO₂/Ag₃PO₄ composite possesses a relative small crystal

size, large specific surface area, good crystallinity, and coexposed high-energy {001} and [111]-facets, the synergistic effects resulting in the highest photocatalytic activity of the pH 3.5-TiO₂/Ag₃PO₄ composite.

4. Conclusions

In summary, TiO₂/Ag₃PO₄ composites composed of anatase TiO_2 nanocrystals with co-exposed {101}, {010}/{100}, {001} and [111]-facets and Ag₃PO₄ microcrystals with irregular polyhedrons and cubic-like crystals were successfully synthesized by combining hydrothermal and ion-exchange methods. The Ag₃PO₄ microcrystals were used as a substrate to load the anatase TiO₂ nanocrystals on their surface and to form TiO₂/ Ag₃PO₄ heterostructures. To investigate the photocatalytic performance, the carcinogenic RhB solution was selected as model pollutant because it widely used in the textile industry. Compared with the commercial TiO_2 and the pure Ag_3PO_4 microcrystals, the heterostructured TiO₂/Ag₃PO₄ composites exhibited excellent photocatalytic activity for the degradation of rhodamine B under visible light irradiation, which can be attributed to the separation of the e^- (in Ag₃PO₄ crystal) and h^+ (in TiO₂ nanocrystal) inhibits the charge recombination. For the as-prepared TiO₂/Ag₃PO₄ composites, the pH 3.5-TiO₂/Ag₃PO₄ composite exhibited the highest photocatalytic activity which mainly attributed to the synergistic effects of its relative small crystal size, large specific surface area, good crystallinity, and co-exposed high-energy {001} and [111]-facets. Moreover, this study provides new way for the preparation of TiO₂/Ag₃PO₄ composite semiconductor photocatalysts with high energy crystal surfaces. However, although the as-prepared TiO₂/ Ag₃PO₄ composites exhibited good stability, the photocatalytic performance needs to be further improved for their practical application.

Conflicts of interest

The authors declare no conflict of interest.

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References

- 1 T. Li, Z. L. Shen, Y. L. Shu, X. G. Li, C. J. Jiang and W. Chen, Facet-Dependent Evolution of Surface Defects in Anatase TiO_2 by Thermal Treatment: Implications for Environmental Applications of Photocatalysis, *Environ. Sci.*: *Nano*, 2019, **6**, 1740–1753.
- 2 G. Y. Zhang, X. M. Wei, X. Bai, C. M. Liu, B. Y. Wang and J. W. Liu, Ethanol-Water Ambient Precipitation of $\{111\}$ Facets Exposed Ag₃PO₄ Tetrahedra and Its Hybrid with Grapheme Oxide for Outstanding Photoactivity and Stability, *Inorg. Chem. Front.*, 2018, **5**, 951–961.
- 3 Y. An, P. W. Zheng and X. F. Ma, Preparation and Visible-Light Photocatalytic Properties of the Floating Hollow Glass Microspheres-TiO₂/Ag₃PO₄ Composites, *RSC Adv.*, 2019, **9**, 721–729.
- 4 E. Haque, Y. Yamauchi, V. Malgras, K. R. Reddy, J. W. Yi, M. S. A. Hossain and J. Kim, Nanoarchitectured Graphene-Organic Frameworks (GOFs): Synthetic Strategies, Properties, and Applications, *Chem. - Asian J.*, 2018, **13**, 3561–3574.
- 5 P. S. Basavarajappa, B. N. K. Seethya, N. Gangnagappa, K. B. Eshwaraswamy and R. R. Kakarla, Enhanced Photocatalytic Activity and Biosensing of Gadolinium Substituted BiFeO₃ Nanoparticles, *ChemistrySelect*, 2018, **3**, 9025–9033.
- 6 R. Koutavarapu, C. V. Reddy, B. Babu, K. R. Reddy, M. Cho and J. Shim, Carbon cloth/transition metals-based hybrids with controllable architectures for electrocatalytic hydrogen evolution - A review, *Int. J. Hydrogen Energy*, 2020, **45**, 7716– 7740.
- 7 E. Haque, J. Kim, V. Malgras, K. R. Reddy, A. C. Ward, J. You,
 Y. Bando, M. S. A. Hossain and Y. Yamauchi, Recent Advances in Graphene Quantum Dots: Synthesis, Properties, and Applications, *Small Methods*, 2018, 2, 1800050.
- 8 V. N. Rao, N. L. Reddy, M. M. Kumari, K. K. Cheralathan, P. Ravi, B. Neppolian, K. R. Reddy, N. P. Shetti, P. Prathap, T. M. Aminabhavi and M. V. Shankar, Sustainable Hydrogen Production for the Greener Environment by Quantum Dots-based Efficient Photocatalysis: A Review, *J. Environ. Manage.*, 2019, **248**, 109246.
- 9 N. R. Reddy, U. Bhargav, M. M. Kumari, K. K. Cheralathan, M. V. Shankar, K. R. Reddy, T. A. Saleh and T. M. Aminabhavi, Highly Efficient Solar Light-driven Photocatalytic Hydrogen Production Over Cu/FCNTs-titania Quantum Dots-based Heterostructures, *J. Environ. Manage.*, 2020, 254, 109747.
- 10 C. V. Reddy, I. N. Reddy, V. V. N. Harish, K. R. Reddy, N. P. Shetti, J. Shim and T. M. Aminabhavi, Efficient Removal of Toxic Organic Dyes and Photoelectrochemical Properties of Iron-doped Zirconia Nanoparticles, *Chemosphere*, 2020, 239, 124766.
- 11 C. V. Reddy, K. R. Reddy, V. V. N. Harish, J. Shim, M. V. Shankar, N. P. Shetti and T. M. Aminabjavi, Metalorganic Frameworks (MOFs)-based Efficient Heterogeneous

Photocatalysts: Synthesis, Properties and Its Applications in Photocatalytic Hydrogen Generation, CO_2 Reduction and Photodegradation of Organic Dyes, *Int. J. Hydrogen Energy*, 2020, **45**, 7656–7679.

- 12 R. Koutavarapu, B. Babu, C. V. Reddy, I. N. Reddy, K. R. Reddy, M. C. Rao, T. M. Aminabhavi, M. Cho, D. Kim and J. Shim, ZnO Nanosheets-decorated Bi₂WO₆ Nanolayer as Efficient Photocatalysts for the Removal of Toxic Environmental Pollutants and Photoelectrochemical Solar Water Oxidation, *J. Environ. Manage.*, 2020, **265**, 110504.
- 13 J. G. Yu, Y. R. Su, B. Cheng and M. H. Zhou, Effects of pH on the Microstructures and Photocatalytic Activity of Mesoporous Nanocrystalline Titania Powders Prepared via Hydrothermal Method, *J. Mol. Catal. A: Chem.*, 2006, **258**, 104–112.
- 14 Y. Zheng, K. L. Lv, Z. Y. Wang, K. J. Deng and M. Li, Microwave-Assisted Rapid Synthesis of Anatase TiO₂ Nanocrystals with Exposed {001} Facets, *J. Mol. Catal. A: Chem.*, 2012, **356**, 137–142.
- 15 J. G. Yu, G. H. Wang, B. Cheng and M. H. Zhou, Effects of Hydrothermal Temperature and Time on the Photocatalytic Activity and Microstructures of Bimodal Mesoporous TiO₂ Powders, *Appl. Catal.*, *B*, 2007, **69**, 171–180.
- 16 L. Yu, X. F. Yang, J. He and D. S. Wang, One-Step Hydrothermal Method to Prepare Nitroden and Lanthanum Co-doped TiO₂ Nanocrystals with Exposed {001} Facets and Study on their Photocatalytic Activities in Visible Light, *J. Alloys Compd.*, 2015, **637**, 308–314.
- 17 H. G. Yang, C. H. Sun, S. Z. Qiao, J. Zou, G. Liu, S. C. Smith, H. M. Cheng and G. Q. Lu, Anatase TiO_2 Single Crystals with a Large Percentage of Reactive Facets, *Nature*, 2008, **453**, 638–641.
- 18 H. G. Yang, Z. Li, C. H. Sun, H. G. Yang and C. Z. Li, Hydrothermal stability of $\{001\}$ facet anatase TiO₂, *Chem. Mater.*, 2011, 23, 3486–3494.
- 19 P. H. Wen, H. Itoh, W. P. Tang and Q. Feng, Single Nanocrystals of Anatase-Type TiO₂ Prepared from Layered Titanate Nanosheets: Formation Mechanism and Characterization of Surface Properties, *Langmuir*, 2007, 23, 11782–11790.
- 20 M. Liu, L. Y. Piao, L. Zhao, S. T. Ju, Z. J. Yan, T. He, C. L. Zhou and W. J. Wang, Anatase TiO_2 Single Crystals with Exposed {001} and {110} Facets: Facile Synthesis and Enhanced Photocatalysis, *Chem. Commun.*, 2010, **46**, 1664–1666.
- 21 H. Xu, P. Reunchan, S. X. Ouyang, H. Tong, N. Umezawa, T. Kako and J. H. Ye, Anatase TiO_2 Single Crystals Exposed with High-Reactive {111} Facets toward Efficient H₂ Evolution, *Chem. Mater.*, 2013, **25**, 405–411.
- 22 M. Zhang, X. Z. Xiao, X. W. Wang, M. Chen, Y. H. Lum, M. J. Lium and L. X. Chen, Excellent Catalysis of TiO₂ Nanosheets with High-Surface-Energy {001} Facets on Hydrogen Storage Properties of MgH₂, *Nanoscale*, 2019, **11**, 7465–7473.
- 23 Y.-E. Du, D. J. Du, Q. Feng and X. J. Yang, Delithiation, Exfoliation, and Transformation of Rock-Salt-Structured Li₂TiO₃ to Highly Exposed {010}-Faceted Anatase, ACS Appl. Mater. Interfaces, 2015, 7, 7995–8004.

- 24 Y.-E. Du, X. J. Niu, Y. Bai, H. X. Qi, Y. Q. Guo, Y. Q. Chen, P. F. Wang, X. J. Yang and Q. Feng, Synthesis of Anatase TiO₂ Nanocrystals with Defined Morphologies from Exfoliated Nanoribbons: Photocatalytic Performance and Application in Dye-Sensitized Solar Cell, *ChemistrySelect*, 2019, 4, 4443–4457.
- 25 Y.-E. Du, X. J. Niu, W. X. Li, J. An, Y. F. Liu, Y. Q. Chen, P. F. Wang, X. J. Yang and Q. Feng, Microwave-Assisted Synthesis of High-Energy Faceted TiO₂ Nanocrystals Derived from Exfoliated Porous Metatitanic Acid Nanosheets with Improved Photocatalytic and Photovoltaic Performance, *Materials*, 2019, **12**, 3614.
- 26 T. F. Li, H. R. We, H. Z. Jia, T. J. Xia, X. T. Guo, T. C. Wang and L. Y. Zhu, Mechanism for Highly Efficient Minerlization of Bisphenol A by Heterostructured Ag₃WO₄/ Ag₃PO₄ under Simulated Solar Light, ACS Sustainable Chem. Eng., 2019, 7, 4177–4185.
- 27 C. Cuarisco, G. Palmisano, G. Calogero, R. Ciriminna, G. Di Marco, V. Loddo, M. Pagliaro and F. Parrino, Visible-Light Driven Oxidation of Gaseous Aliphatic Alcohols to the Corresponding Carbonyls via TiO₂ Sensitized by a Perylene Derivative, *Environ. Sci. Pollut. Res.*, 2014, 21, 11135–11141.
- 28 N. L. Reddy, V. N. Rao, M. M. Kumari, R. R. Kakarla, P. Ravi, M. Sathish, M. Karthik, S. M. Venkatakrishnan and Inamuddin, Nanostructured Semiconducting Materials for Efficient Hydrogen Generation, *Environ. Chem. Lett.*, 2018, 16, 765–796.
- 29 P. S. Basavarajappa, S. B. Patil, N. Ganganagappa, K. R. Reddy, A. V. Raghu and C. V. Reddy, Recent Progress in Metal-doped TiO₂, Non-metal Doped/Codoped TiO₂ and TiO₂ Nanostructured Hybrids for Enhanced Photocatalysis, *Int. J. Hydrogen Energy*, 2020, **45**, 7764–7778.
- 30 Z. G. Yi, J. H. Ye, N. Kikugawa, T. Kako, S. X. Ouyang, H. Stuart-Williams, H. Yang, J. Y. Cao, W. J. Luo, Z. S. Li, Y. Liu and R. L. Withers, An Orthophosphate Semiconductor with Photooxidation Properties under Visible-Light Irradiation, *Nat. Mater.*, 2010, 9, 559–564.
- 31 Z. N. Liu, Y. C. Liu, P. P. Xu, Z. H. Ma, J. Y. Wang and H. Yuan, Rational Design of Wide Spectral-Responsive Heterostructures of Au Nanorod Coupled Ag₃PO₄ with Enhanced Photocatalytic Performance, *ACS Appl. Mater. Interfaces*, 2017, **9**, 20620–20629.
- 32 W. F. Yao, B. Zhang, C. P. Huang, C. Ma, X. L. Song and Q. J. Xu, Synthesis and Characterization of High Efficiency and Stable Ag₃PO₄/TiO₂ Visible Light Photocatalyst for the Degradation of Methylene Blue and Rhodamine B Solutions, *J. Mater. Chem.*, 2012, **22**, 4050–4055.
- 33 S. B. Rawal, S. D. Sung and W. I. Lee, Novel Ag₃PO₄/TiO₂ Composites for Efficient Decomposition of Gaseous 2-Propanol under Visible-Light Irradiation, *Catal. Commun.*, 2012, 17, 131–135.
- 34 M. Y. Zhang, L. Li and X. T. Zhang, One-dimensional Ag₃PO₄/ TiO₂ Heterostructure with Enhanced Photocatalytic Activity for the Degradation of 4-Nitrophenol, *RSC Adv.*, 2015, 5, 29693–29697.
- 35 J. W. Xu, Z. D. Gao, K. Han, Y. M. Liu and Y. Y. Song, Synthesis of Magnetically Separable Ag₃PO₄/TiO₂/Fe₃O₄

Heterostructure with Enhanced Photocatalytic Performance under Visible light for Photoinactivation of Bacteria, *ACS Appl. Mater. Interfaces*, 2014, **6**, 15122–15131.

- 36 A. Hamrouni, H. Azzouzi, A. Rates, L. Palmisano, R. Ceccato and F. Parrino, Enhanced Solar Light Photocatalytic Activity of Ag Dopoed TiO₂-Ag₃PO₄ Composites, *Nanomaterials*, 2020, 10, 795.
- 37 Q. Feng, M. Hirasawa and K. Yanagisawa, Synthesis of Crystal-Axis-Oriented BaTiO₃ and Anatase Platelike Particles by a Hydrothermal Soft Chemical Progress, *Chem. Mater.*, 2001, 13, 290–296.
- 38 B. Panigrahy and S. Srivastava, Minuscule Weight Percent of Graphene Oxide and Reduced Graphene Oxide Modified Ag₃PO₄: New Insight into Improved Photocatalytic Activity, *New J. Chem.*, 2016, **40**, 3370–3384.
- 39 C. V. Reddy, I. N. Reddy, B. Akkinepally, V. V. N. Harish, K. R. Reddy and S. Jaesool, Mn-doped ZrO₂ Nanoparticles Prepared by a Template-free Method for Electrochemical Energy Storage and Abatement of Dye Degradation, *Ceram. Int.*, 2019, **45**, 15298–15306.
- 40 A. Mehta, A. Mishra, S. Basu, N. P. Shetti, K. R. Reddy, T. A. Saleh and T. M. Aminabhavi, Band Gap Tuning and Surface Modification of Carbon Dots for Sustainable Environmental Remediation and Photocatalytic Hydrogen Production - A Review, *J. Environ. Manage.*, 2019, **250**, 109486.
- 41 K. V. Karthik, C. V. Reddy, K. R. Reddy, R. Ravishiankar, G. Sanjeev, R. V. Kulkarni, N. P. Shetti and A. V. Raghu, Brium Titanate Nanostructures for Photocatalytic Hydrogen Generation and Photodegradation of Chemical Pollutants, *J. Mater. Sci.: Mater. Electron.*, 2019, **30**, 20646– 20653.
- 42 S. J. Zhao, Y. L. Song, J. Guo, Z. Y. Zhang and J. R. Hou, Adsorption Induced Critical Shifts of Confined Fluids in Shale Nanopores, *Chem. Eng. J.*, 2020, **385**, 123837.
- 43 C. Carlucci, H. Xu, B. F. Scremin, C. Giannini, D. Altmura,
 E. Carlino, V. Videtta, F. Conciauro, G. Gihli and
 G. Ciccarella, Selective Synthesis of TiO₂ Nanocrystals with
 the Microwave-Solvothermal Method, *CrystEngComm*, 2014,
 16, 1817–1824.
- 44 Y. Xu and M. A. A. Schoonen, The Absolute Energy Positions of Conduction and Valence Bands of Selected Semiconducting Minerals, *Am. Mineral.*, 2000, **85**, 543–556.
- 45 D. R. Zhang, H. L. Liu, S. Y. Han and W. X. Piao, Synthesis of Sc and V-doped TiO₂ Nanoparticles and Potodegradation of Rhodamine-B, *J. Ind. Eng. Chem.*, 2013, **19**, 1838–1844.
- 46 J. G. Li, T. Ishigaki and X. D. Sun, Anatase, Brookite, and Rutile Nanocrystals via Redox Reactions under Mild Hydrothermal Conditions: Phase-Selective Synthesis and Physicochemical Properties, *J. Phys. Chem. C*, 2007, **111**, 4969–4976.
- 47 H. M. Zhang, P. R. Liu, F. Li, H. W. Liu, Y. Wang, S. Q. Zhang, M. X. Guo, H. M. Cheng and H. J. Zhao, Facile Fabrication of Anatase TiO₂ Microspheres on Solid Substrates and Surface Crystal Facet Transformation from {001} and {100}, *Chem. -Eur. J.*, 2011, 17, 5949–5957.

- 48 C. V. Reddy, I. N. Reddy, K. Ravindranadh, K. R. Reddy, N. P. Shetti, D. Kim, J. Shim and T. M. Aminabhavi, Copper-doped ZrO₂ Nanoparticles as High-performance Catalysts for Efficient Removal of Toxic Organic Pollutants and Solar Water Oxidation, *J. Environ. Manage.*, 2020, **260**, 110088.
- 49 S. Sitthisang, S. Komarneni, J. Tantirungrotechai, Y. D. Noh, H. H. Li, S. Yin, T. Sato and H. Katsuki, Microwave-Hydrothermal Synthesis of Extremely High Specific Surface Area Anatase for Decomposing NO_x, *Ceram. Int.*, 2012, 38, 6099–6105.
- 50 D. W. Hu, W. X. Zhang, Y. Tanaka, N. Kusunose, Y. Peng and Q. Feng, Mesocrystalline Nanocomposition of TiO₂ Polymorphs: Topochemical Mesocrystal Conversion, Characterization, and Photocatalytic Response, *Cryst. Growth Des.*, 2015, 15, 1214–1225.
- 51 X. G. Han, Q. Kuang, M. S. Jin, Z. X. Xie and L. S. Zheng, Synthesis of Titania Nanosheets with a High Percentage of Exposed {001} Facets and Related Photocatalytic Properties, *J. Am. Chem. Soc.*, 2009, 131, 3152–3153.