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Electron transportation path build for superior photoelectrochemical performance of $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ †

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TiO_2 is an attractive photoanode material with its large band gap, whilst its performance largely suffers from low efficiency on both charge separation and solar conversion. Herein, a self-organized TiO_2 nanotube arrays (TNT) is prepared by anodized Ti foil in ethylene glycol electrolyte to ameliorate charge transmission ability. Ag_3PO_4 is further synthesized on TNT substrate by dipping method. HRTEM images results indicate Ag_3PO_4 nanoparticles are successfully deposited on the surfaces of TNT. Photoelectrochemical tests show the $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ heterojunction has a higher photocurrent density of 2.34 mA cm^{-2} at 0 V than that of pure TNT (0.38 mA cm^{-2}). This is attributed to an Ag “pump” reduced on the interface of $\text{Ag}_3\text{PO}_4/\text{TiO}_2$, therefore electron transportation path is built between Ag_3PO_4 and TiO_2 leading to photogenerated electrons and holes effective separation. This high photocurrent density array films facilitates it a desirable photoelectrochemical material for water splitting.

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1 Introduction

Photoelectrochemical (PEC) water splitting is recognized as one of the most promising strategies in solar energy conversion. Titanium dioxide (TiO_2) has been specifically selected out among various PEC materials since Honda–Fujishima first found the ability of TiO_2 for photo-splitting water under ultraviolet light in 1972.¹ In 1976, Carey found that PCBs in TiO_2 suspension solution successfully dechlorinated under UV irradiation.² In 1991, Graetzel successfully developed a dye-sensitized solar cell by using TiO_2 nanoparticles.³ But TiO_2 suffers from its poor charge separation and high charge transmission resistance.^{4,5} One dimensional (1-D) nanostructure allows a short diffusion length for holes in radial direction, whereas the long axial direction of the structure becomes the preferred electron channel that provides enough length of light attenuation as well.^{6,7} Besides these above, 1-D nanostructures also provide excellent photovoltaic, photocatalytic, and PEC properties relative to random-shaped particles.^{8–12} Therefore, the 1-D self-organized TiO_2 nanotube array (TNT) is expected to design. In 2001, Grimes and co-workers successfully prepared TNT by anodization in hydrofluoric acid electrolyte.¹³ Further, Macak synthesized TNT by anodizing in glycerol electrolyte containing 0.5% NH_4F , the morphology more smooth than that obtained in aqueous electrolyte, and the length of nanotube

reached above $10 \mu\text{m}$.¹⁴ Also, TNT exhibits more attractive PEC performance and larger specific surface area than TiO_2 nanoparticles or nanosheets.^{15,16} However, band gap of TiO_2 at 3.0–3.2 eV can only absorb ultraviolet light corresponding for 5% of sunlight, which means the solar utilization efficiency is less than satisfactory.

Ag_3PO_4 a n-type semiconductor can absorb visible light wavelengths less than 520 nm (indirect band gap of 2.4 eV), and the quantum yield reaches more than 90%, which aroused attention of many researchers;^{17–19} but its conduction band (CB) is at 0.45 V vs. NHE, so Ag^+ of Ag_3PO_4 will be easily reduced to elemental Ag under visible light irradiation.^{10,20–26} Wang *et al.* studied $\text{Ag}_3\text{PO}_4/\text{AgBr}/\text{Ag}$ degradation of organic matter, due to better stability of AgBr and plasma effect of Ag nanoparticles, which improved Ag_3PO_4 stability and photocatalytic capacity.²⁷ Teng found that $\text{Ag}/\text{Ag}_3\text{PO}_4/\text{TiO}_2$ can photodegrade chlorophenol efficiently, and Ag nanoparticles can effectively prevent the occurrence of Ag_3PO_4 light corrosion, and photocurrent density at 0.28 mA cm^{-2} .²⁸ Xu *et al.* reported $\text{Ag}_3\text{PO}_4/\text{TiO}_2/\text{Fe}_3\text{O}_4$ photodegraded benzene sulfonate and had a great bactericidal effect.²⁹ Photodegradation properties on Ag_3PO_4 or its composites can be found in many research, but seldom on PEC properties, which is closely relative to photo-water-splitting. Moreover, all of works is not enough to achieve high performance because electrons randomly flow after the electron–hole separation resulting in fast electron–hole recombination.

In this study, Ag_3PO_4 nanoparticles were chemically deposited on 1-D TNT. A heterojunction of $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ was formed and linear sweep voltammetry test showed photocurrent was about 6 times bigger than pure TNT and the band flat potentials

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of $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ positively shifted, which meant solar absorption range of TiO_2 was significantly broadened. Ag was also synthesized on the interface between Ag_3PO_4 and TiO_2 due to light illumination, which formed an efficient system for separation of photo-generated charges and improvement of PEC properties.

2 Experimental

2.1 Sample $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ preparation

Ti foil of 1 cm^2 was provided with anodization in ethylene glycol electrolyte containing 4 wt% H_2O and 0.25 wt% NH_4F for 1 h under constant potential (50 V) at room temperature.^{14,30} The samples were washed with distilled water and dried at $60\text{ }^\circ\text{C}$. The as-prepared TiO_2 was thermally treated at $450\text{ }^\circ\text{C}$ for 2 h under atmospheric conditions.

Ag_3PO_4 nanoparticles were deposited into the crystallized TiO_2 nanotubes by sequential chemical bath deposition method. Typically, the sample was successively immersed in four different beakers for 3 minutes in each beaker. One beaker contained 5 mM AgNO_3 aqueous solution, another contained 5 mM NaH_2PO_4 , and the other two contained distilled water to rinse the samples from the excess of each precursor solution. Such an immersion cycle was repeated several times, typically between 2 and 8 cycles.

2.2 Characterization

The surface morphology was observed through a field-emission scanning electron microscope (Hitachi S-4800, Japan). Transmission electron microscopy (TEM) images were taken with

JEOL JEM-2100 transmission electron microscope at 200 kV. The absorbance was measured with UV-vis spectrophotometer (Hitachi U-3900, Japan). The elemental chemical status was measured by X-ray photoelectron spectroscopy (Thermo ESCA-LAB 250Xi), equipped with Al $K\alpha$ radiation. All energies were calibrated to spurious carbon at 284.8 eV.

The PEC properties of samples were investigated by a three-electrode configuration electrochemical workstation (CHI 760E), employing the samples, Ag/AgCl and Pt mesh as working, reference and counter electrode, respectively (Fig. S4†). The supporting electrolyte used was 1 M KOH (pH = 14) aqueous solution. Mott–Schottky plots were measured at 1000 Hz. Electrochemical impedance spectroscopic (EIS) measurements were performed between 10^5 Hz and 10^{-2} Hz dark. The working electrode was illuminated with a 300 W xenon lamp. The photocurrent was recorded concurrently with the light switching on and off without applied voltage.

3 Results and discussion

3.1 Electron transportation analysis

After deposited Ag_3PO_4 , a heterojunction of $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ first formed and promoted separation of the photogenerated carriers.^{25,31,32} Additionally, Ag^+ of Ag_3PO_4 was proved photo-reduced and decomposed to weakly active Ag under photo-illumination,^{31–35} which could obviously enhance visible light absorbance above 700 nm (Fig. 1c) and accelerate photo-generated carrier separation due to its surface plasma resonance (SPR).^{28,36} As reported by many researchers, SPR in Ag can

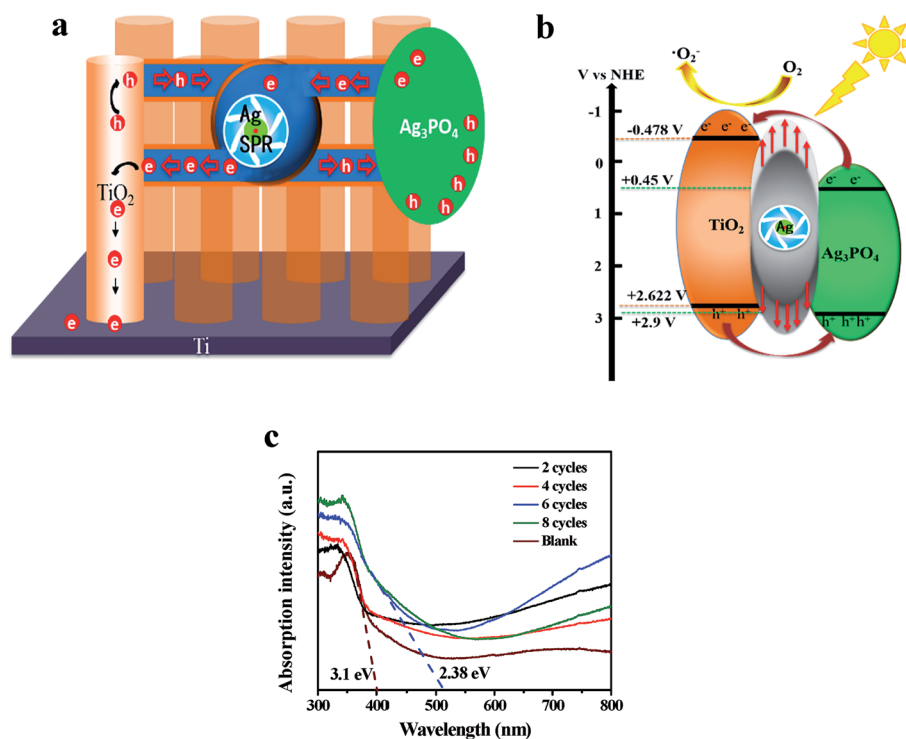


Fig. 1 Schematic diagram of bidirectional photo-induced electron transportation (a), photogenerated electron–hole pairs separation process (b) and UV-vis spectra (c).



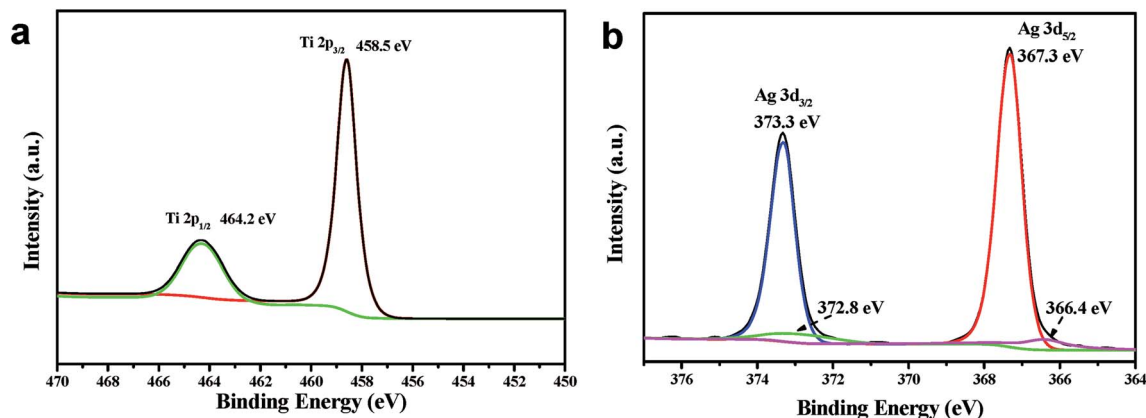


Fig. 2 High resolution XPS spectra of (a) Ti 2p and (b) Ag 3d of $\text{Ag}_3\text{PO}_4/\text{TiO}_2$.

be directly excited under visible light illumination to generate and inject hot carriers into the CB of semiconductors.^{37,38} This role is just like a “pump” (Fig. 1a and b), electrons in Ag_3PO_4 are absorbed by Ag and then “pumped” into higher energy level, the CB of TiO_2 , due to lower conductivity of Ag_3PO_4 and SPR of Ag which assisted electrons to get over the barrier of $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ junction. Then electrons transported from the CB of TiO_2 to Ti base along 1-D electron channel of TNT. Equally, holes were injected from the valence band (VB) of TiO_2 into the VB of Ag_3PO_4 , and then participated in oxidation reaction. The transfer route of electron can be $E_{\text{CB}}(\text{Ag}_3\text{PO}_4) \rightarrow E_{\text{f}}(\text{Ag}) \rightarrow E_{\text{CB}}(\text{TiO}_2)$. If without the SPR of Ag, charges transportation route are shown in Fig. S4,[†] the light induced electrons transported from higher conductor band (-0.612 V vs. NHE) of TiO_2 to lower conductor band ($+0.45 \text{ V vs. NHE}$) of Ag_3PO_4 , and the holes were accumulated in the valence band of TiO_2 , which is inconsistent with experimental results of electron transportation from TiO_2 to Ti foil.

3.2 XPS analysis

$\text{Ag}_3\text{PO}_4/\text{TiO}_2$ sample was examined by X-ray photoelectron spectroscopy (XPS), and the results are shown in Fig. 2. The binding energies of the XPS spectra were calibrated by C 1s (284.8 eV). The carbon peak is due to the adventitious hydrocarbon from the XPS instrument itself (Fig. S2[†]). In Fig. 2a, the characteristic peak at 458.5 eV and 464.2 eV assigned to Ti^{4+} in

TiO_2 are depicted.³⁹ Two binds at 367.7 and 373.7 eV, are ascribed to Ag 3d_{5/2} and Ag 3d_{3/2} bonding energies in Fig. 2b. These bands could be further deconvoluted into two peaks, respectively, at 366.4, 367.3 eV and 372.8, 373.7 eV, where the bands at 366.4 and 372.8 eV are ascribed to the Ag^+ of Ag_3PO_4 , and those at 367.3 and 373.7 eV are attributed to the metallic Ag^0 . As some papers have reported,^{40,41} these results verify the existence of metallic Ag^0 on $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ photocatalysts after the reaction.

3.3 Morphology characterization

Diameter of the self-organized pure TNT prepared by anodizing method is about 60 to 90 nm (Fig. 3a and b). Fig. 3b showed SEM images of the sample for 4 cycles deposited Ag_3PO_4 on TNT, and the nanoparticles of Ag_3PO_4 covered the surface with a diameter of about 10 nm. Also, some particles with a diameter of 40 to 50 nm were formed because of severe agglomeration for 8 cycles, shown in Fig. S3.[†] Illustration of EDS indicated that the atomic proportion of Ag and P is 2.44 to 1, close to stoichiometric ratio of 3 to 1 (Fig. 3c).

TEM images of the sample for 4 cycles deposited Ag_3PO_4 on TNT were shown in Fig. 4a and b. Ag_3PO_4 nanoparticles located at both surface TNT and inside of nanotubes at a diameter of 10–20 nm. To further confirm the existence of Ag_3PO_4 , HRTEM (Fig. 4c) showed the lattice fringe of 0.35 nm was consistent with

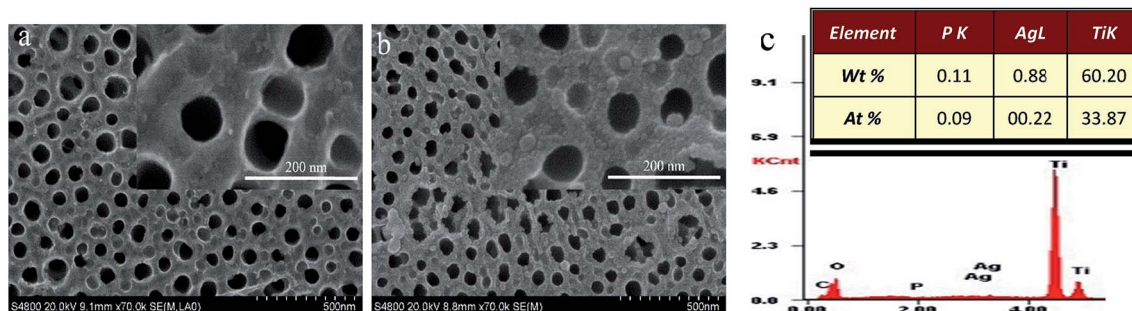


Fig. 3 SEM images of pure TiO_2 (a), $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ 4 cycles (b), insert is partial enlarged view of (a) and (b), EDS of 4 cycles (c).



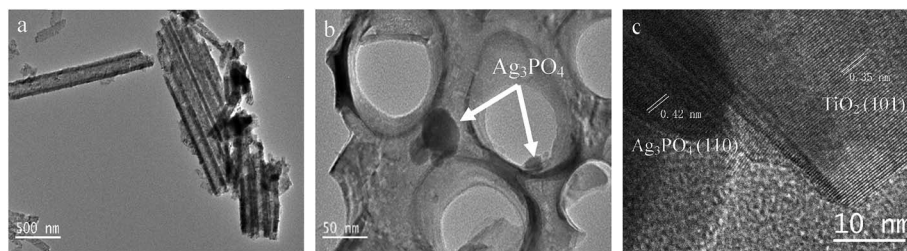


Fig. 4 TEM (a, b) and HRTEM (c) images of $\text{Ag}_3\text{PO}_4/\text{TiO}_2$, 4 cycles.

(101) facet of anatase TiO_2 , while the lattice fringe of 0.42 nm was assigned to the (110) facet of Ag_3PO_4 .

3.4 Photoelectrochemical properties

Under scanning potential from -0.9 V to 0.3 V vs. Ag/AgCl , the current density of TNT deposited Ag_3PO_4 were bigger than that of the pure TNT (Fig. 5a), only 0.387 mA cm^{-2} at 0 V vs. Ag/AgCl , whereas the current density of 4 cycles deposition was almost 5 times higher, reached to 2.340 mA cm^{-2} . It reported that maximum photocurrent of $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ nanowire array heterostructure photoelectrodes was about 0.7 mA cm^{-2} at an applied bias 0.23 V vs. Ag/AgCl .⁴² The improvement of photocurrent could be ascribed to Ag “pump”, preferred electron transportation direction along TNT and large absorption spectrum of Ag_3PO_4 .^{29,43} UV-vis spectra (Fig. 1c) proved the band gap of pure TNT and Ag_3PO_4 at 3.1 eV and 2.38 eV, respectively. And the recombination of photogenerated charge carriers was significantly reduced in the heterojunction (Fig. S1b†). Under intermittent light irradiation, time-dependent photocurrent generation is presented in Fig. 5b. The photocurrents respond exactly to the presence of solar light was interrupted every 50 s (light on/off) under 0 V vs. Ag/AgCl , and the steady state behavior of each photoanode follows the same trend as that of the I - V curves (Fig. 5a). Furthermore, the loading amounts of Ag_3PO_4 on TNT increase with the increasing of cycle time (Fig. 3c and S3c†). Whatever I - V curves or I - t curves showed photocurrent increased initially and then decreased with increase loading amount of Ag_3PO_4 . Therefore appropriate loading amounts of Ag_3PO_4 is fatal to enhance PEC

performance of TNT. In addition, there are no appreciable dark currents, demonstrating the photochemical stability of all of photoanodes in the alkaline solution. The steady-state photocurrents do not show any significant degradation with time.⁴⁴

Fig. 6a represented Nyquist diagrams from electrochemical impedance spectroscopy (EIS) for samples tested in dark. The equivalent circuit for this cell system was depicted in inset of Fig. 6a. R_b was the bulk resistance of the electrolyte. C_{sc} and R_{sc} were the capacitance and the resistance of the solid-state interfacial layer which was formed at the highly charged state due to the passivation reaction between the electrolyte and the surface of the electrode. C_{dl} and R_{ct} were the double layer capacitance and the charge transfer resistance. W was the Warburg resistance result from the diffusion resistance of redox couple.

The Mott-Schottky plots of $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ are used to analyze the flat band potential and carrier concentrations of semiconductor (Fig. 6b). Under the applied voltage, the Fermi level can be changed and bended the energy band, and flat band potential V_{fb} refers the applied potential which makes the inner electric field intensity of semiconductor approach zero. The carrier concentrations of semiconductor N_D and the slope of linear part of Mott-Schottky plots have the relation as follow:

$$N_D = \frac{2}{e\epsilon\epsilon_0 m} \quad (1)$$

where, e is the elementary charge (1.602×10^{-19} C), ϵ is the dielectric constant of sample and the dielectric constant of anatase is 48, ϵ_0 is the vacuum dielectric constant ($8.854 \times$

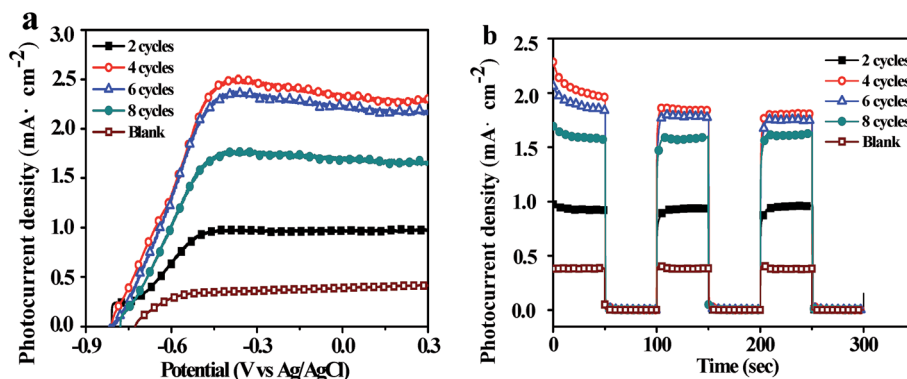


Fig. 5 $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ composites linear sweeps voltammetry (a), i - t curve (b), UV-vis spectra.



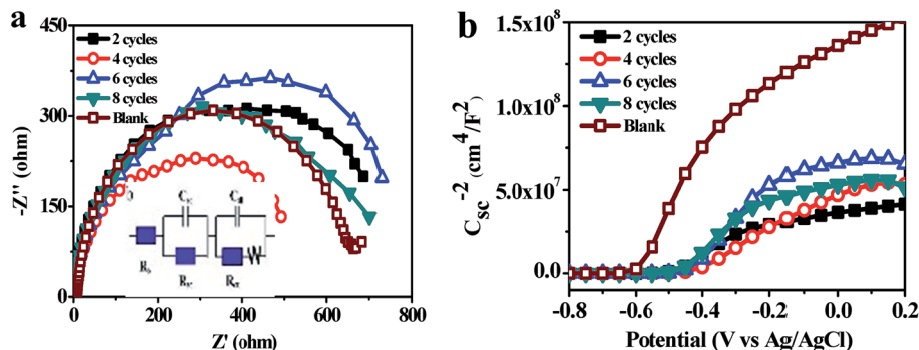


Fig. 6 $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ Nyquist diagrams (a), insert is equivalent circuit fitting the EIS and Mott–Schottky plots (b).

$10^{-14} \text{ F cm}^{-1}$), m is the slope of the linear part of Mott–Schottky plots. The flat band potential V_{fb} , C_{SC} and carrier concentrations N_{D} have a relationship, below:

$$C_{\text{SC}}^{-2} = \left(\frac{2}{\varepsilon_0 \varepsilon e N_{\text{D}}} \right) \left(V - V_{\text{fb}} - \frac{k_{\text{B}} T}{e} \right) \quad (2)$$

where, C_{SC} is the space charge capacitance, ε_0 , ε and e are constant, N_{D} is carrier concentrations, V and V_{fb} is respectively the applied potential and the flat band potential (vs. the potential of the reference electrode), $(k_{\text{B}} T)/e$ is 25.8 mV at room temperature.

The parameters obtained from EIS and Mott–Schottky plots are shown in Table 1. The charge transfer resistances R_{ct} of 4 cycles deposition Ag_3PO_4 minimal only $404.7 \text{ ohm cm}^{-2}$, since the carrier concentration N_{D} of it was 2.6 times higher than that of the pure TiO_2 about $4.85 \times 10^{22} \text{ cm}^{-3}$. Moreover, the carrier concentration of $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ samples was obviously higher than that of the pure TiO_2 . And valence bands of two semiconductors were very close,^{29,33,43,45,46} which inferred the heterojunction formed by depositing Ag_3PO_4 nanoparticles on TNT (Fig. 1b). Potentials of both conduction band (-0.612 V vs. NHE) and valence band ($+2.588 \text{ V vs. NHE}$) of TiO_2 are more negative than those of Ag_3PO_4 (conduction band potential: $+0.45 \text{ V vs. NHE}$, valence band potential: $+2.9 \text{ V vs. NHE}$).³³ It benefits for transfer of photogenerated carriers and separation of photogenerated electron–hole pairs, also increases the carrier concentrations. The flat band potential (V_{fb}) is close to the conduction band which makes the curving band of space charge layer straight. The V_{fb} of TNT was -0.612 V , after deposition Ag_3PO_4 of 4 cycles V_{fb} lowered to -0.410 V . The reason for lower V_{fb} was the photogenerated electrons were “pumped” into CB of TiO_2 by SPR of Ag. It

meant the range of absorption spectrum broaden and photocatalytic properties enhancement. As shown in Fig. 1c, the absorbance of $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ was significantly increased than pure TiO_2 , implying Ag_3PO_4 is a very promising material for building fast electron transportation path to improve PEC performance of TiO_2 .

4 Conclusion

A preferred electron transportation path was designed to improve the photoelectrocatalytic activity through deposition Ag_3PO_4 nanoparticles to the self-organized TiO_2 nanotube arrays. $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ effectively reduced the recombination of photogenerated electron–hole pairs due to unique 1-D nanostructure, as well as SPR of photoreduced Ag from Ag_3PO_4 . The charge carrier concentration of $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ increased 2.6 times than that of pure TNT. The photocurrents of $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ were significantly improved by 5 times. Therefore, fabrication of $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ nanotube arrays is a highly efficient method to build a noteworthy photoelectrode for PEC water splitting.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Table 1 Physics parameters of $\text{Ag}_3\text{PO}_4/\text{TiO}_2$

Sample	R_{ct} (ohm cm^{-2})	N_{D} (cm^{-3})	V_{fb} (V)
2 cycles	667.5	4.40×10^{22}	−0.478
4 cycles	404.7	4.85×10^{22}	−0.410
6 cycles	698.8	2.42×10^{22}	−0.433
8 cycles	621.4	3.16×10^{22}	−0.468
Blank	594.8	1.35×10^{22}	−0.612



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