## **Supporting Information**

## Electron transportation path build for superior photoelectrochemical performance of Ag<sub>3</sub>PO<sub>4</sub>/TiO<sub>2</sub>

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Fig. S1 Ag<sub>3</sub>PO<sub>4</sub>/TiO<sub>2</sub> composites (a) XRD images, (b) PL spectra

Powder X-ray diffraction (XRD) was performed on DX-2700 X-ray diffractometer (Dandong Fangyuan, China) with monochromatized Cu-K $\alpha$  radiation ( $\lambda = 1.5418$  Å) at 40 kV and 30 mA. The photoluminescence (PL) emission spectra could be used to investigate the efficiency of charge carrier trapping, immigration, transfer and to understand the fate of electron-hole pairs in semiconductors, since PL emission results from the recombination of free carriers either directly (band-band) or indirectly via a band gap state.<sup>[1]</sup> Photoluminescence (PL) spectra were obtained on a 7-PLSpec I (SOFN Instruments, China). All the spectra were taken at room temperature at excitation wavelength of 350 nm.

Both  $Ag_3PO_4/TiO_2$  and pure TNT samples XRD patterns exhibited the anatase characteristic peaks (Fig. S1a). The intense peak at 20 of 25.4° indicated a fine preferential growth of the pure TiO<sub>2</sub>. Absence of diffraction peaks corresponding to  $Ag_3PO_4$  phase might probably due to low concentration of  $Ag_3PO_4$  below the X-ray detection limit or its weak crystallization.

Obviously, a drastic decreasing of PL intensity of 8 cycles was observed, indicating that after depositing  $Ag_3PO_4$  on TNT (Fig. S1b), the recombination of photogenerated charge carriers was significantly reduced in the heterojunction. The small intense peaks at 476 nm and 490 nm were ascribed to excitonic signals originating from oxygen vacancies and defects on the catalyst surface.<sup>[2]</sup> The peak at 405 nm was assigned to emission of band gap transitions of anatase, which was in conformity with band gap (3.1 eV) at UV-vis spectra (Fig. 1c).



Fig. S2 XPS spectrum of  $Ag_3PO_4/TiO_2$  composites



Fig. S3 SEM images (a, b) and EDS (c) of  $Ag_3PO_4/TiO_2$ , 8 cycles



Fig. S4 Schematic diagram of photogenerated electron-hole pairs separation process



Fig. S5 Schematic diagram of photoelectrochemical test

## References

[1] J.-W. Xu, Z.-D. Gao, K. Han, Y. Liu, Y.-Y. Song, ACS Applied Materials & Interfaces 2014, 6, 15122.

[2] V. Jovic, Z. H. N. Al-Azri, W.-T. Chen, D. Sun-Waterhouse, H. Idriss, G. I. N. Waterhouse, Topics in Catalysis 2013, 56, 1139.