

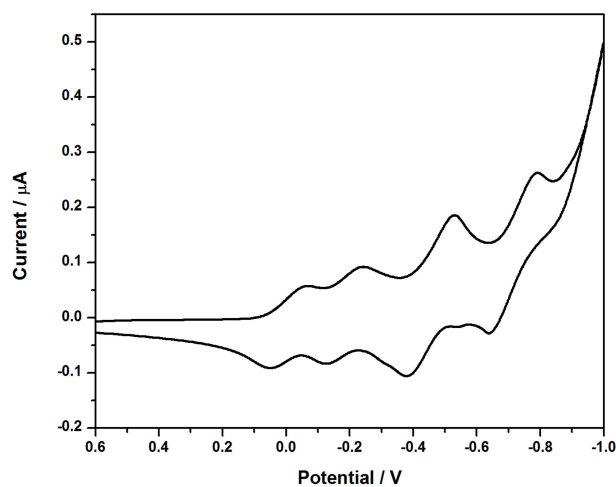
## Supporting Information

### Improving TiO<sub>2</sub> photoanode through silver-polyoxotungstate nanohybrids: Toward photovoltaic and photoelectrocatalytic application

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#### Materials

**Preparation of K<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>:** Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O (100g) was added to 350ml of water, and the solution was heated to boiling. Then 150ml of 85% H<sub>3</sub>PO<sub>4</sub> was slowly added to the boiling solution, and the resulting yellow-green solution was refluxed for 5-13h. The solution was cooled, and the product was precipitated by addition of 100g of solid KCl. The light green precipitate was collected, redissolved in a minimum amount of hot water, and allowed to crystallize at 5°C overnight. Cyclic voltammetry and UV-vis adsorption spectra were used to identify the product, which were shown in Fig. S1 and Fig. S2.



**Fig. S1** Cyclic voltammograms of K<sub>2</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> using the ITO as a working electrode, the Ag/AgCl electrode as a reference electrode, a platinum foil as the counter electrode in HNO<sub>3</sub> (pH 1.5) electrolyte.

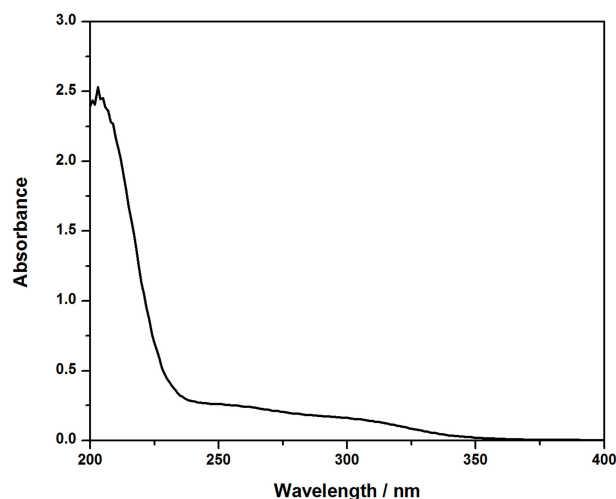


Fig. S2 UV-vis absorption spectra of  $K_2P_2W_{18}O_{62}$ .

**Preparation of  $TiO_2$ :**  $TiO_2$  colloid solutions were prepared by hydrolysis of titanium isopropoxide,  $Ti(OCH(CH_3)_2)_4$ , as follows: 25ml  $Ti(OCH(CH_3)_2)_4$  was added to dropping funnel containing 0.4ml of 2-propanol. The mixture was added slowly to 15ml deionized water, stirring vigorously. During the hydrolysis, 0.1ml of 70%  $HNO_3$  was added. The mixture was then stirred for 8h at  $\sim 80^\circ C$ . As shown in Fig. S3 and Fig. S4, they were described by X-ray diffraction (XRD) analysis and Transmission electron microscopy (TEM) image. The TEM image exhibited that the mean size of the particles were ca. 8 nm.

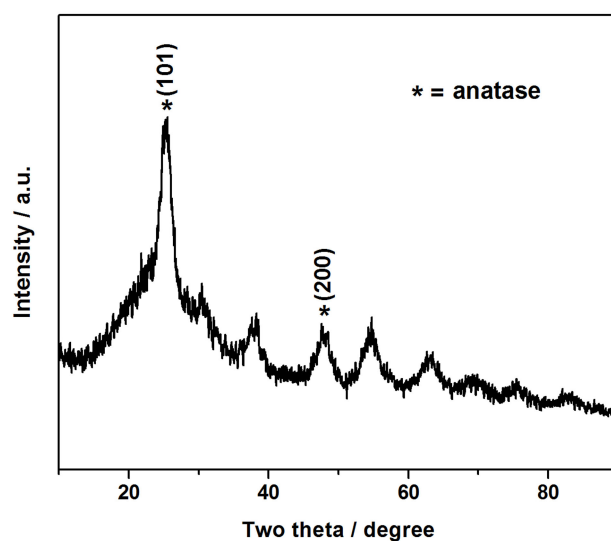
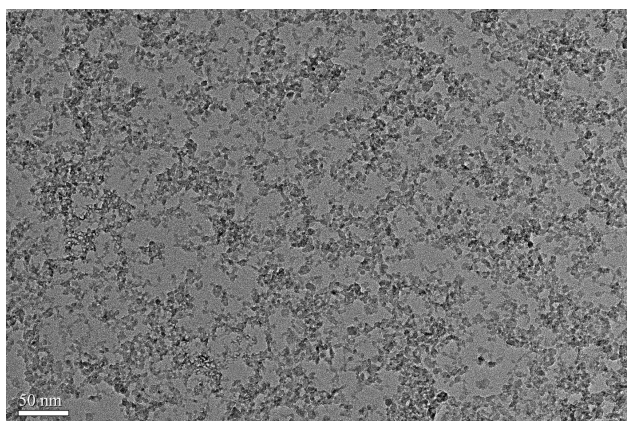
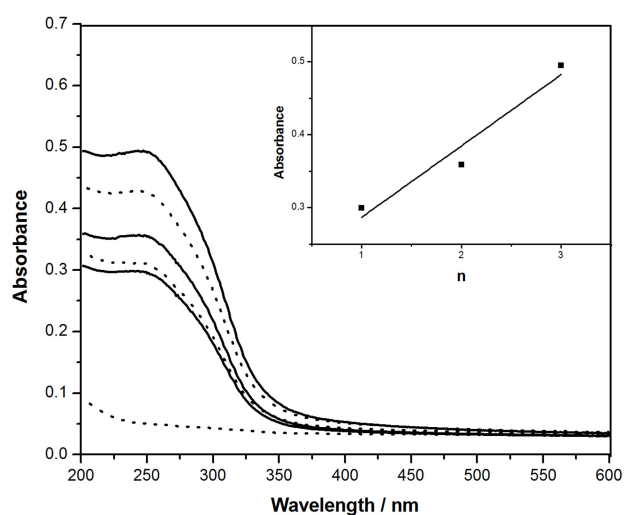


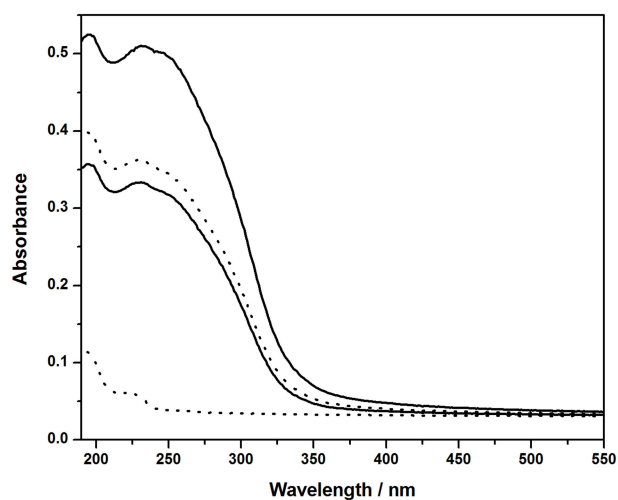
Fig. S3. XRD pattern of  $TiO_2$  colloids.



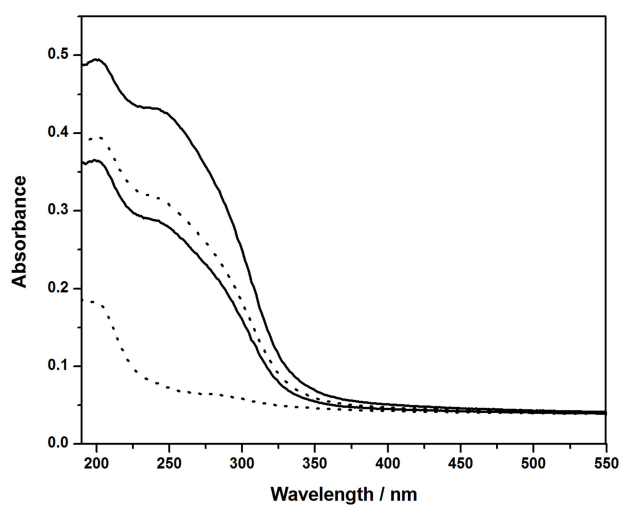
**Fig. S4.** TEM image of TiO<sub>2</sub> colloids.



**Fig. S5.** UV-vis absorption spectra of multilayer films (Ag-POT/TiO<sub>2</sub>)<sub>n</sub> on quartz substrates with n=1-3. The dashed line represents spectra after Ag-POT deposition, the solid line represents spectra after TiO<sub>2</sub> deposition. (Inset) relationship of absorbance at 248nm after TiO<sub>2</sub> deposition vs. the number of layers



**Fig. S5.** UV–Vis absorption spectra of multilayer films  $(\text{PSS}/\text{TiO}_2)_2$  on quartz substrates (from lower to upper curves). The dashed line represents spectra after PSS deposition, the solid line represents spectra after  $\text{TiO}_2$  deposition



**Fig. S6.** UV–Vis absorption spectra of multilayer films  $(\text{POT}/\text{TiO}_2)_2$  on quartz substrates (from lower to upper curves). The dashed line represents spectra after POT deposition, the solid line represents spectra after  $\text{TiO}_2$  deposition