Supporting Information

Improving TiO₂ photoanode through silver-polyoxotungstate nanohybrids: Toward photovoltaic and photoelectrocatalytic application

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Materials

Preparation of K₆P₂W₁₈O₆₂: Na₂WO₄·2H₂O (100g) was added to 350ml of water, and the solution was heated to boiling. Then 150ml of 85% H₃PO₄ 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 K₃P₂W₁₈O₆₂ using the ITO as a working electrode, the Ag/AgCl electrode as a reference electrode, a platinum foil as the counter electrode in HNO₃ (pH 1.5) electrolyte.
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 ~80°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.

![UV-vis absorption spectra of K$_2$P$_2$W$_{18}$O$_{62}$.](image1)

**Fig. S2 UV-vis absorption spectra of K$_2$P$_2$W$_{18}$O$_{62}$.**

![XRD pattern of TiO$_2$ colloids.](image2)

**Fig. S3.** XRD pattern of TiO$_2$ colloids.
**Fig. S4.** TEM image of TiO$_2$ colloids.

**Fig. S5.** UV-vis absorption spectra of multilayer films (Ag-POT/TiO$_2$)$_n$ on quartz substrates with $n=1$-$3$. The dashed line represents spectra after Ag-POT deposition, the solid line represents spectra after TiO$_2$ deposition. (Inset) relationship of absorbance at 248nm after TiO$_2$ deposition vs. the number of layers.
**Fig. S5.** UV–Vis absorption spectra of multilayer films (PSS/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 TiO$_2$ deposition.

**Fig. S6.** UV–Vis absorption spectra of multilayer films (POT/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 TiO$_2$ deposition.