Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supporting Informations

A photovoltaic system composed of the Keplerate-type polyoxometalate and the water-soluble poly(*p*-phenylenevinylene) derivative

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Experimental

Materials

$\{W_{72}V_{30}\}$ and P2 were prepared according to the literature method.[a,b] Poly(ethylenimine) solution (PEI, P3143) were purchased from Aldrich. Poly(sodium-p-styrenesulfonate) (PSS, Mw 70 000) were purchased from Acros. All the other reagents are of analytical grade and used as received without further purification. All the aqueous solutions were prepared with deionized water.

Preparation of the composite film

The fabrication of the multilayer film electrode was schematically illustrated in Fig. S1 and was carried out according to the following steps.

The substrate (ITO glass) were cleaned respectively in an 70℃ piranha solution [H_2SO_4 : H_2O_2 (7 : 3, v/v)] bath for 20 min. Then they were rinsed with copious deionized water and dried under an nitrogen stream. PEI (5×10^{-4}M) was adsorbed by immersing the substrates into the solution for 20 min, followed by rinsing with water and drying in nitrogen. Then the precursor film was alternately dipped into $\{W_{72}V_{30}\}$

(5×10^{-4}M, pH = 2.0), P2(5×10^{-4}M) aqueous solution for 10 min. After the deposition of each layer, the substrate was rinsed with deionized water and dried in nitrogen. This sequence can be repeated until the desired number of [$W_{72}V_{30}$/P2] layers is obtained. All the fabrication processes were performed at room temperature.

Thin film characterization

UV-Vis absorption spectra of the quartz-supported films were recorded on a 725PC UV-visible spectrophotometer after each layer deposition. X-ray photoelectron spectra (XPS) were measured on quartz wafers using an thermo ESCALAB 250 spectrometer (including X-ray photoelectron spectrometer) with Al Kα (1486.6eV) as X-ray source. The photoluminescent properties were measured on FLSP920 Edinburgh Fluorescence Spectrometer. Atomic force microscopy (AFM) measurements were performed in air with a SPI3800N Probe Station.

Photoelectrochemical measurements

All the electrochemical experiments were performed on a CS350 electrochemical workstation(Wuhan CorrTest Instrument Corporation, China). A 100W Xe arc lamp(XQ-500W, Beijing Changtuo Device, P.R.China) was used as an irradiation source under ambient conditions. A conventional three electrodes system was used, with the ITO electrode coated by the self-assembled film as the working electrode, SCE as the reference electrode and platinum foil as the counter electrode. All photocurrent transient experiments were carried out at a constant bias of 0V. The photoelectrochemical measurements were carried out in 0.1M Na2SO4 solution which

was exposed to air.

Linear sweep voltammetry

The *J-V* curves of the composite films were measured by linear sweep voltammetry. The experiments were performed under Xe lamp irradiation on a CS350 electrochemical workstation. The three electrodes system was used, with the ITO electrode coated by the composite films as the working electrode, SCE as the reference electrode and platinum foil as the counter electrode. The composite-film-coated electrode was immersed in 0.1M Na_2SO_4 solution, then scanned from 0 V to 0.5 V at scan rate of 50 mV s^{-1}. The structure of the device (the composite-film-coated electrode) was shown in Fig. S2.

a A. M. Todea, A. Merca, H. Bögge, T. Glaser, L. Engelhardt, R. Prozorov, M. Lubanc and A. Müller, Chem. Commun., 2009, 49, 3351-3353.

b Y. Gao, C. C. Wang, L. Wang and H. L. Wang, Langmuir, 2007, 23, 7760-7767.

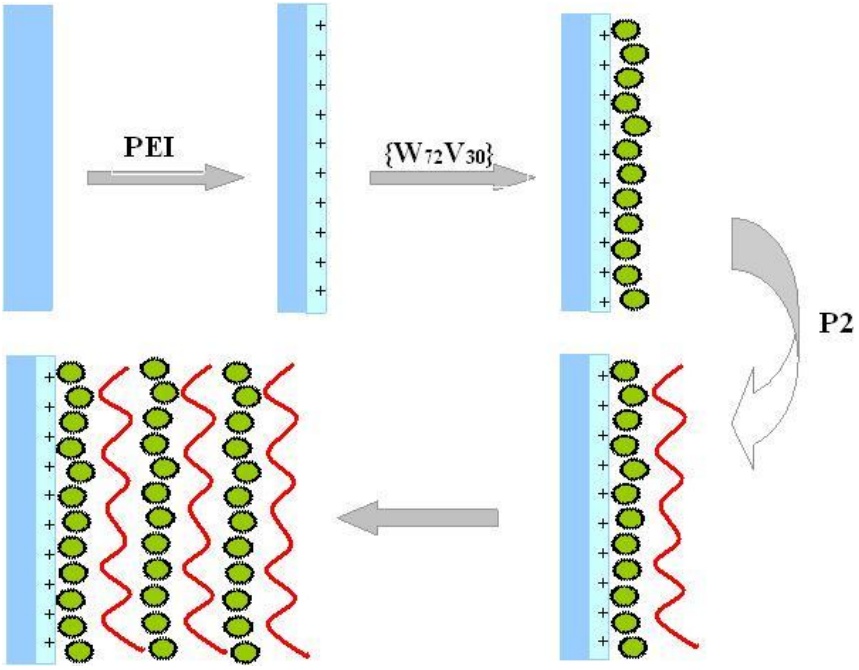

Fig. S1 Schematic of the self-assembly of the $(W_{72}V_{30}/P2)_n$ film.

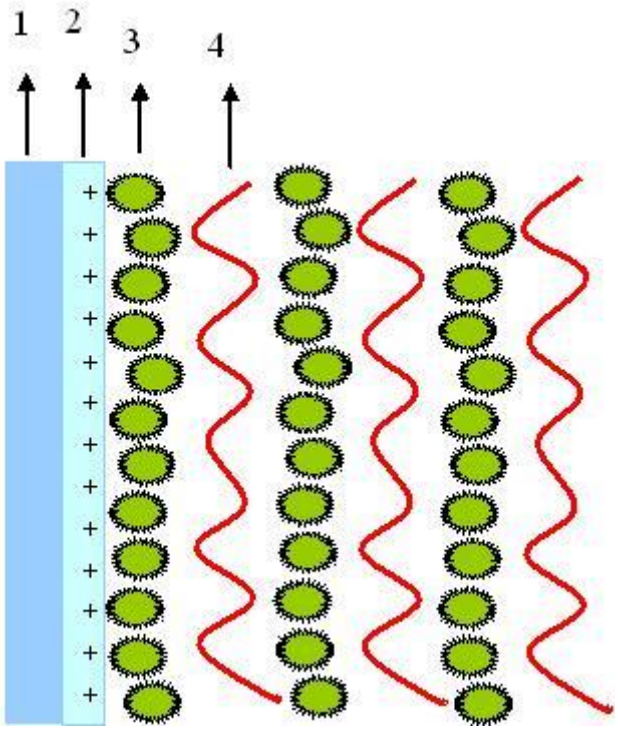

Fig. S2 Schematic of the internal layer structure of the $(W_{72}V_{30}/P2)_n$ film: (1) ITO glass; (2) PEI; (3)$\{W_{72}V_{30}\}$; (4)P2.

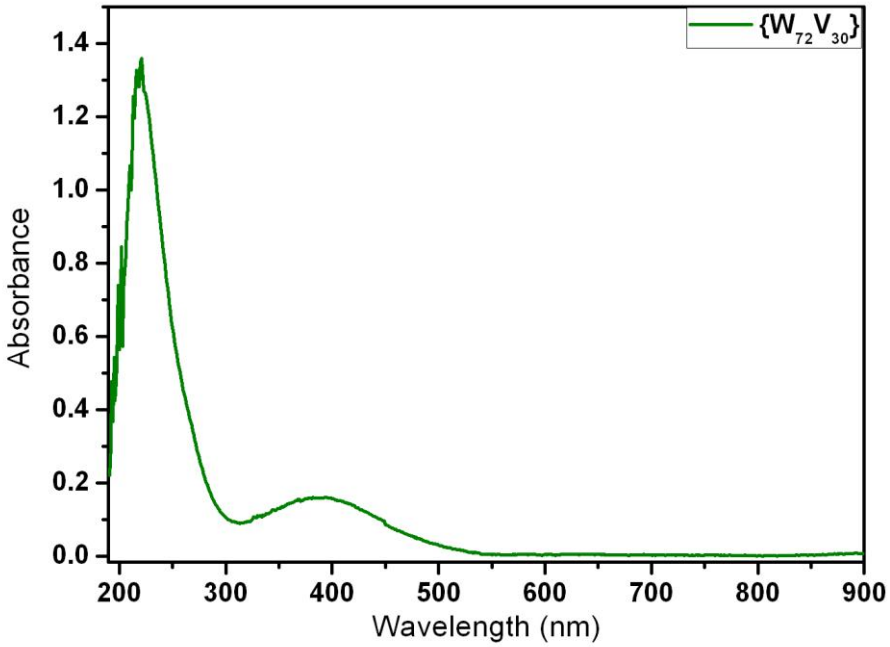

Fig. S3 UV-Vis spectra of $\{W_{72}V_{30}\}$

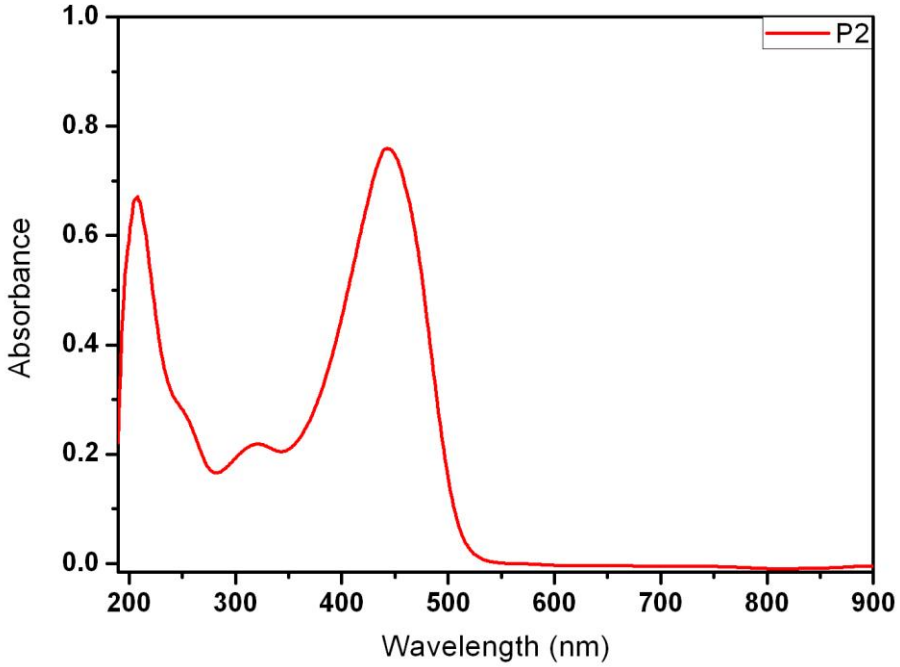

Fig. S4 UV-Vis spectra of P2

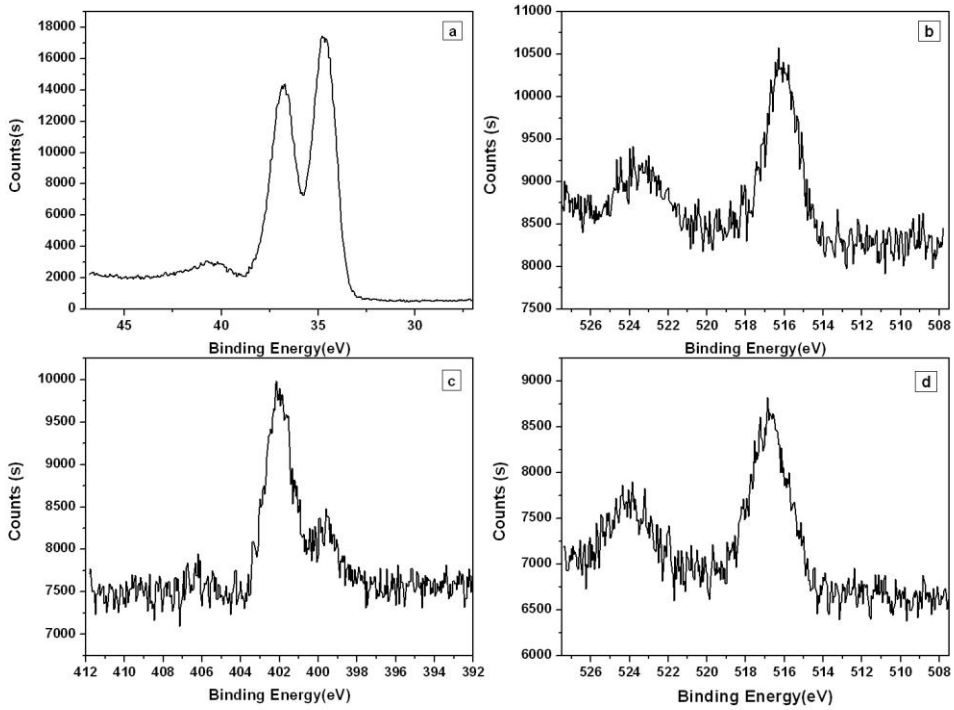

Fig. S5 XPS spectra of the $(W_{72}V_{30}/P2)_5$ film: (a) W 4f, (b) V 2p, (c) N 1s; and XPS spectra of $\{W_{72}V_{30}\}$: (d) V 2p.

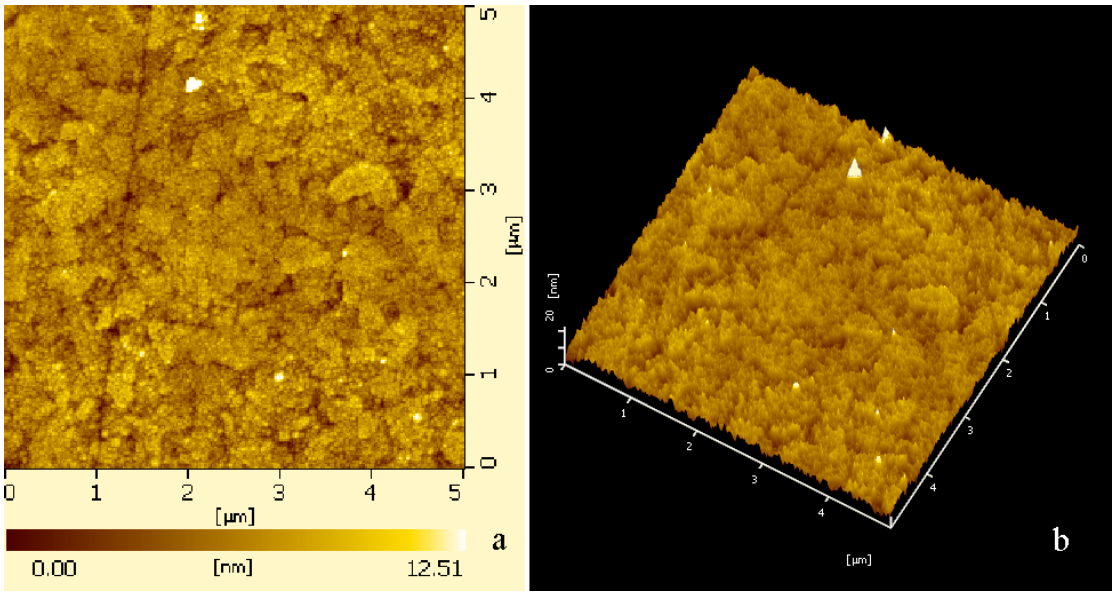

Fig. S6 AFM images of the $(W_{72}V_{30}/P2)_5$ film on ITO glass.

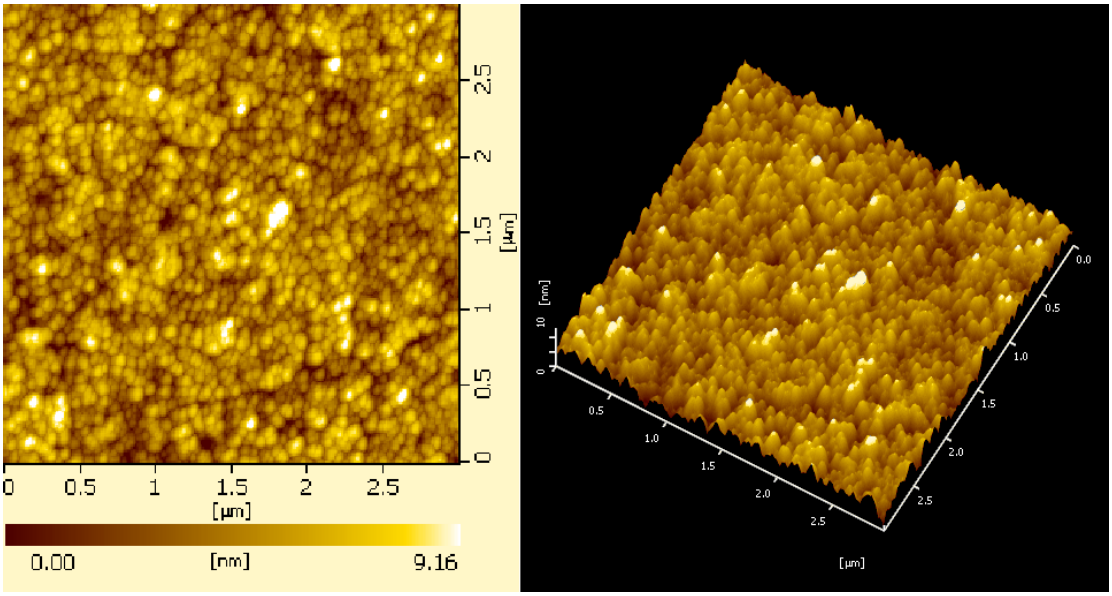

Fig. S7 AFM images of the precursor film-modified ITO.

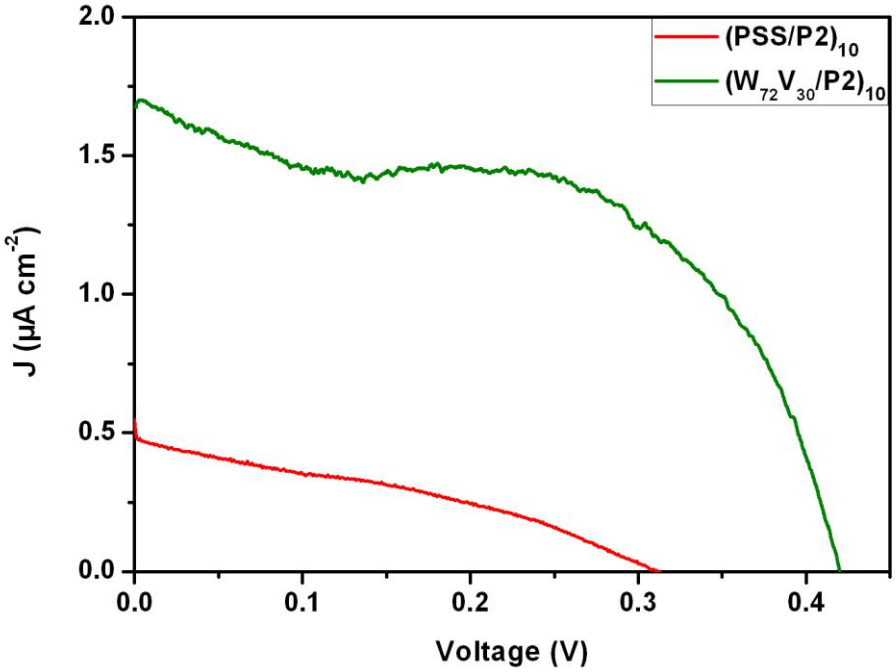

Fig. S8 Current-voltage curves of the $(W_{72}V_{30}/P2)_{10}$ film (green curve) and the $(PSS/P2)_{10}$ film (red curve).

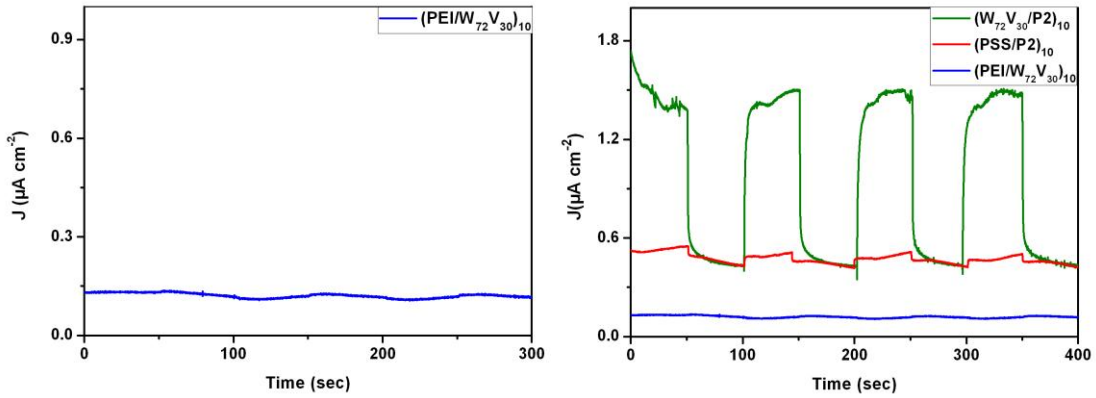

Fig. S9 Photoelectrochemical response of the $(PEI/W_{72}V_{30})_{10}$ film (blue curve) with on-off light illumination from a Xe arc lamp.

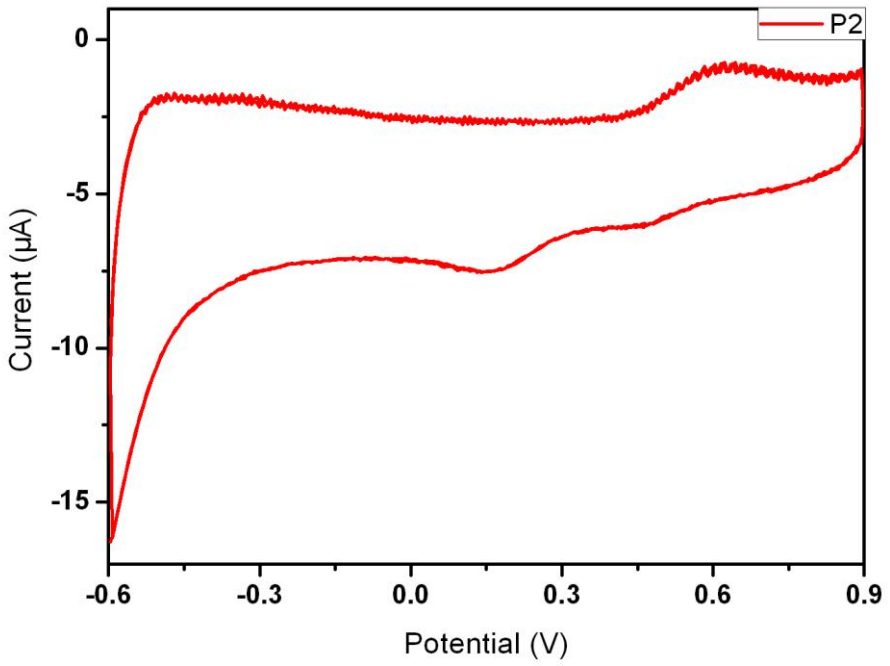

Fig. S10 Cyclic voltammetry curve of P2

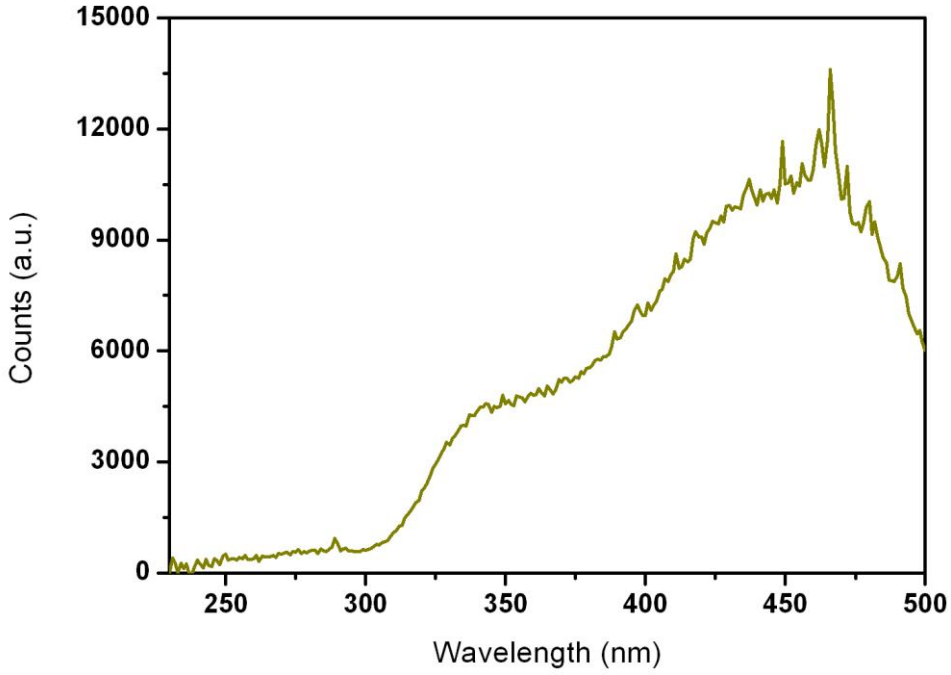

Fig. S11 Optical excitation spectrum of P2

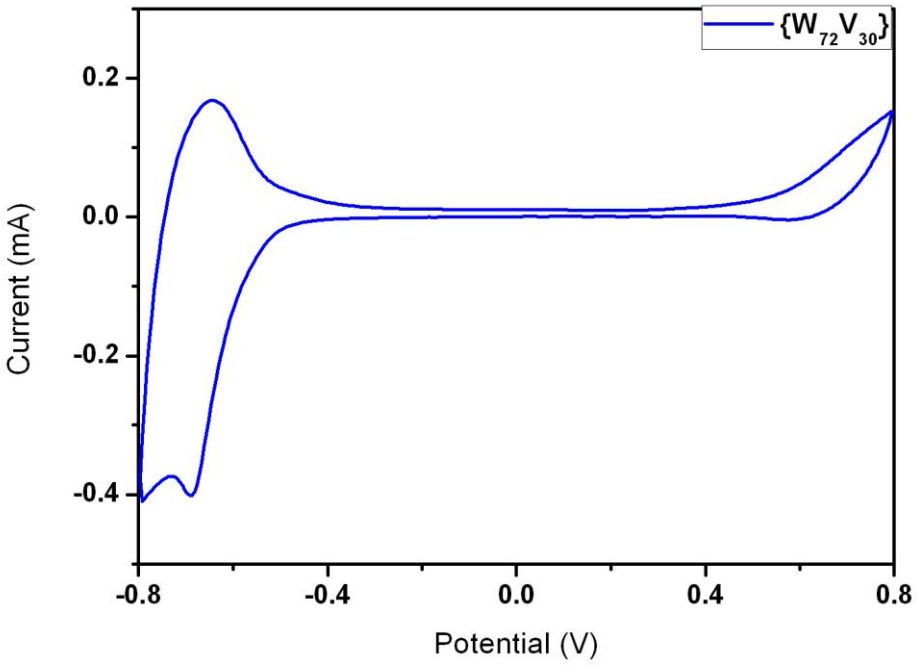

Fig. S12 Cyclic voltammetry curve of $\{W_{72}V_{30}\}$

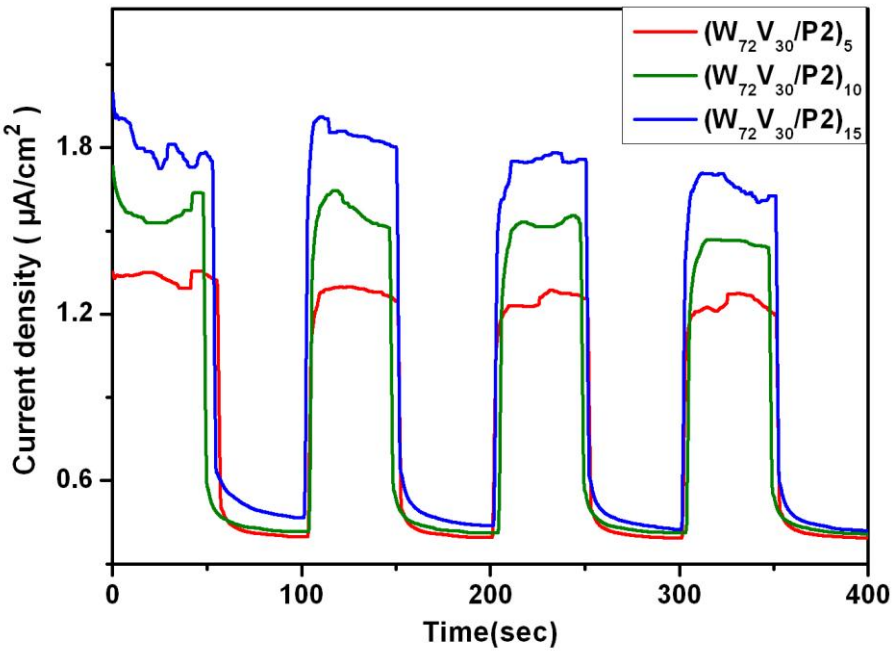

Fig. S13 Photoelectrochemical response of the $(W_{72}V_{30}/P2)_n$ films with different layers (n = 5, 10, 15)