

## Supplementary Information

### A long-term stable Pt counter electrode modified by POM-based multilayer film for high conversion efficiency dye-sensitized solar cells

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### *Experiment Section*

#### **Materials**

All the agents are of analytical grade and used without further purification. All the chemicals were purchased from Aladdin except that N719, electrolyte and electrodes were purchased from Heptachroma (Dalian, China).  $\alpha$ -K<sub>3</sub>H<sub>4</sub>[SiW<sub>9</sub>Al<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>O<sub>37</sub>]·7H<sub>2</sub>O was synthesized according literature method.<sup>1</sup> All the aqueous solutions were prepared with double distilled water.

1 L. Y. Qu, Y. G. Chen, J. Peng, Y. H. Lin and Z. L. Yu, *Chemical Journal of Chinese Universities*, 1991, **8**, 1009.

#### **Apparatus**

Electrochemical experiments were performed on CHI601D electrochemistry station (CH Instruments, Shanghai Chenhua Instrument Corporation, China). EIS was performed on Solartron 1255B 1470 Battery Test Unit Frequency Response Analyzer. The performance of the DSSCs were measured under 1 sun illumination (AM=1.5).

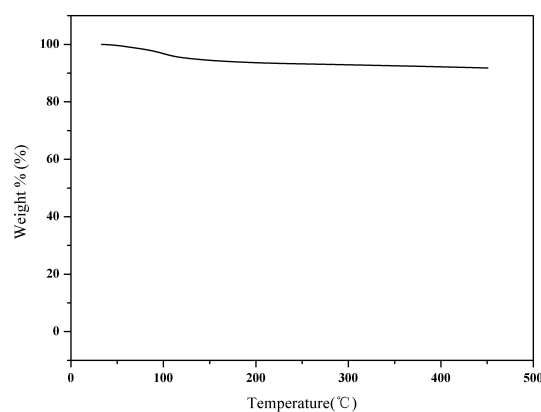
#### **Fabrication of the modified counter electrodes**

POM-modified Pt counter electrode was fabricated by electrochemical deposition. Cyclic voltammetry experiments were carried out in three electroanode system in which Pt counter was used as working electrode, Ag/AgCl was used as reference electrode and Pt wire was used as counter electrode. Pt electrode was washed with double distilled water, acetone, ethanol and double distilled water in turn before used. The electrolyte were SiW<sub>9</sub>Al<sub>3</sub> and poly(diallyldimethylammonium chloride) (denoted as PDDA) aqueous solution with a concentration of 2mg/ml, supporting

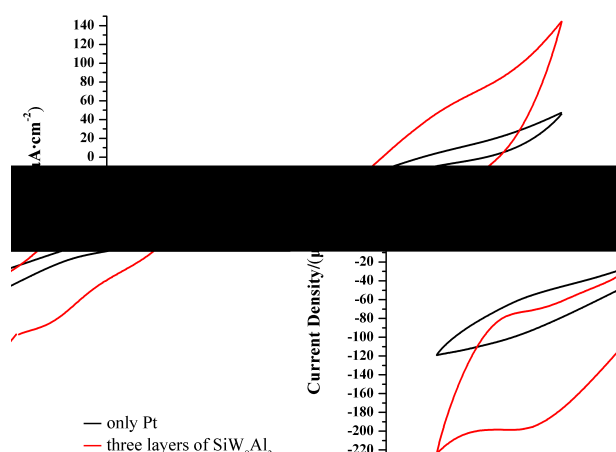
electrolyte was  $\text{Na}_2\text{SO}_4$  with the same concentration, pH value were 3.30 and 2.10 respectively. Voltage range were from -1V to 0.2 V, and -0.3V to 0.65V for POM solution and PDDA solution.

### Fabrication of solar cell using $\text{SiW}_9\text{Al}_3$ -modified electrode as counter electrode

Current-potential curves were obtained by using N719 sensitized  $\text{TiO}_2$  nanocrystal anode, typical electrolyte (0.1 M LiI, 0.05 M  $\text{I}_2$ , 0.6 M 2,3-dimethyl-1-propylimidazolium iodide, and 0.5M 4-tert-butylpyridine in 3-Methoxypropionitrile) and modified electrodes with three layers of  $\text{SiW}_9\text{Al}_3$ .



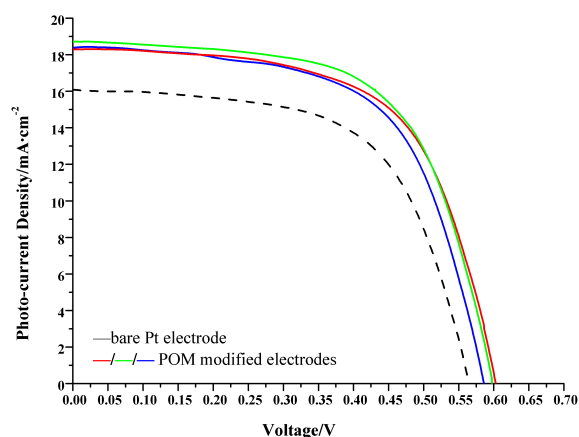
**Fig. S1** The TG curve of  $\text{K}_3\text{H}_4[\text{SiW}_9\text{Al}_3(\text{H}_2\text{O})_3\text{O}_{37}] \cdot 7\text{H}_2\text{O}$ .



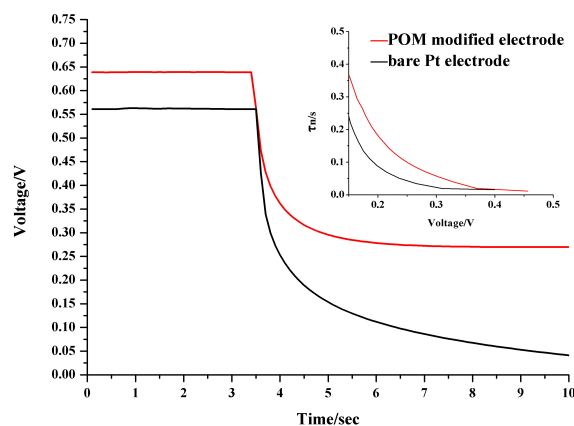
**Fig. S2** CVs of bare Pt electrodes and three layers of  $\text{SiW}_9\text{Al}_3$  modified electrodes. Electrolyte was  $\text{H}_2\text{SO}_4$  aqueous, and  $\text{Na}_2\text{SO}_4$  with a concentration of 2mg/ml as supporting electrolyte (pH = 3.30).

**Table S1** The data in the first row is derived from the DSSC using bare Pt electrode as counter electrode, and the subsequent three series of data are derived from the DSSCs using POM-modified electrodes as counter electrode.

	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (mV)	FF	$\eta$
1	16.1	564	0.62	5.62%
2	18.7	597	0.62	6.93%
3	18.3	602	0.62	6.79%
4	18.4	585	0.61	6.57%
Average of modified electrode	18.5	595	0.615	6.76%



**Fig. S3** Current-Voltage curves for DSSCs using different counter electrodes.



**Fig. S4** Open-circuit voltage experiments for DSSCs with bare Pt counter electrode and POM-modified counter electrode. The insert shows the relation between the life time ( $\tau_n$ ) of electrons and the voltage.