Supporting Information

Keplerate-type Polyoxometalate/Semiconductor Composite Electrode with Light-enhanced Conductivity towards High Efficient Photoelectronic Devices

Shasha Xu,‡[a] Yanhua Wang,‡[a] Yue Zhao,[c] Weilin Chen,*[a] Jiabo Wang,[a] Lifei He,[a] Zhongmin Su,[a] Enbo Wang*[a] and Zhenhui Kang*[b]

[a]Key laboratory of Polyoxometalate Science of Ministry of Education, Department of Chemistry, Northeast Normal University, Renmin Street No.5268, Changchun, Jilin, 130024, P. R. China. E-mail: chenwl@nenu.edu.cn, wangeb889@nenu.edu.cn, Tel: +86-431-85098787.

[b]Institute of Functional Nano and Soft Materials (FUNSOM) & Jiangsu Key Laboratory for Carbon-Based Functional Materials and Devices, Soochow University 199 Ren-Ai Road, Suzhou 215123, China. E-mail: zhkang@suda.edu.cn

[c]Department of Vascular Surgery, The China-Japan Union Hospital of Jilin University, Changchun, 130033, China

‡These two authors are equally contributed to this paper.

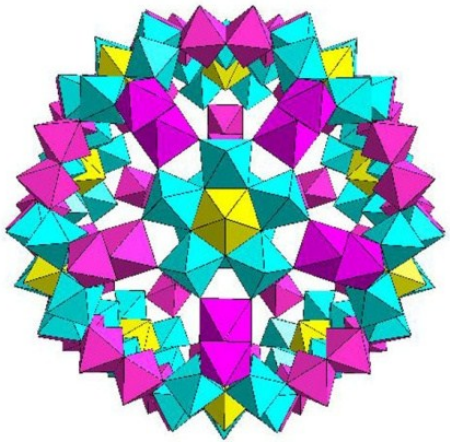

Fig. S1 The structure of $\{Mo_{132}\}$ with perspective view along *a* fivefold symmetry axis (yellow: MoO_7, blue: $\{MoO_6\}$ groups, purple: $\{Mo^V_2\}$).

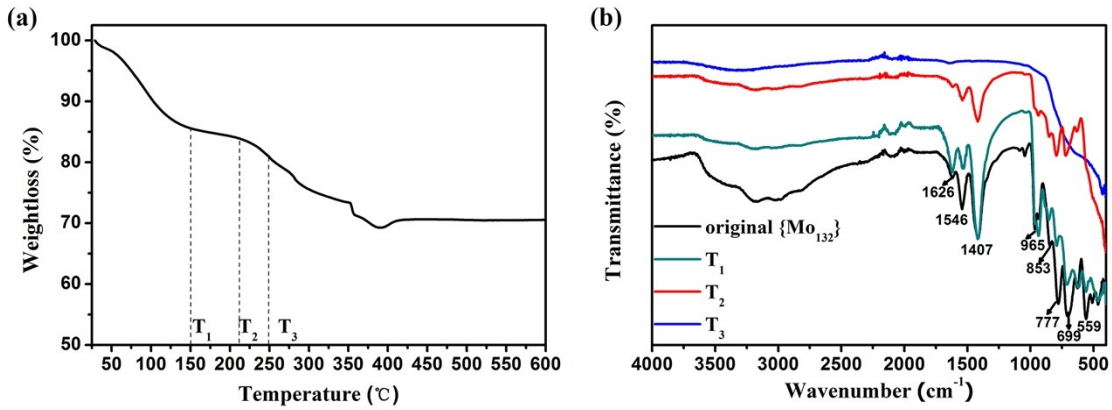

Fig. S2 (a) TG curve of $\{Mo_{132}\}$. (b) The IR spectra under different temperature (150, 210 and 250 °C for T_1, T_2 and T_3, respectively).

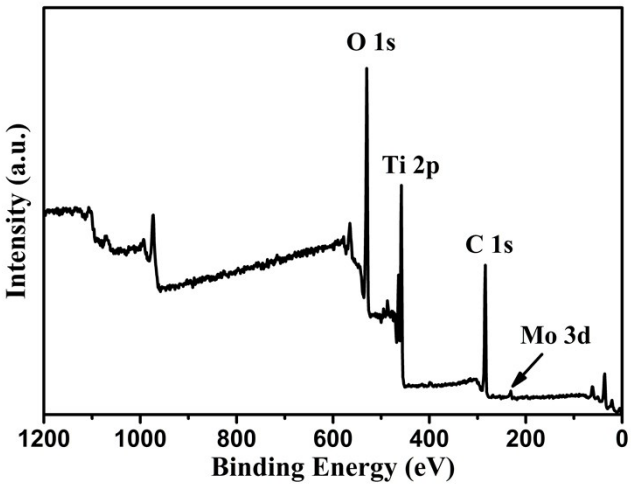

Fig. S3 The XPS survey spectrum of 5%$\{Mo_{132}\}$/TiO_2.

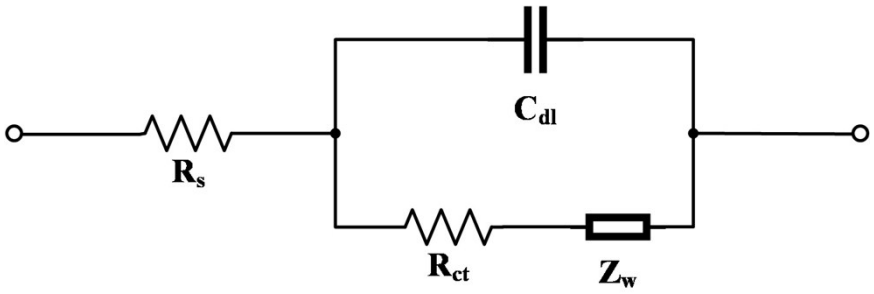

Fig. S4 Equivalent circuit used to fit the impedance measurements for the surface-modified electrode. (R_s is the solution resistance, R_{ct} is the charge transfer resistance, Z_w is the warburg element and C_{dl} is the double layer capacitance.)

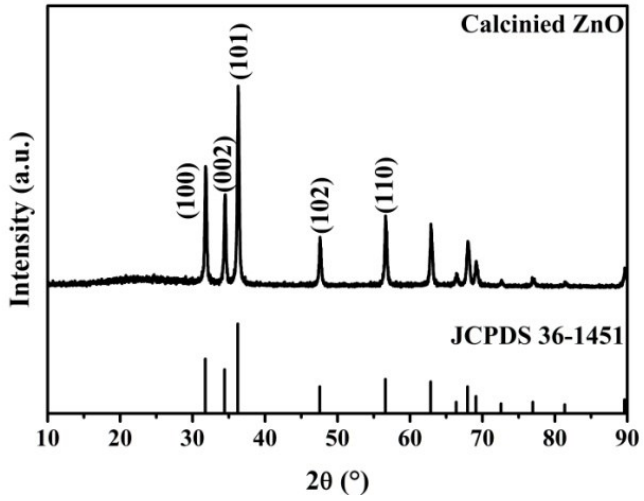

Fig. S5 XRD patterns of calcined ZnO.

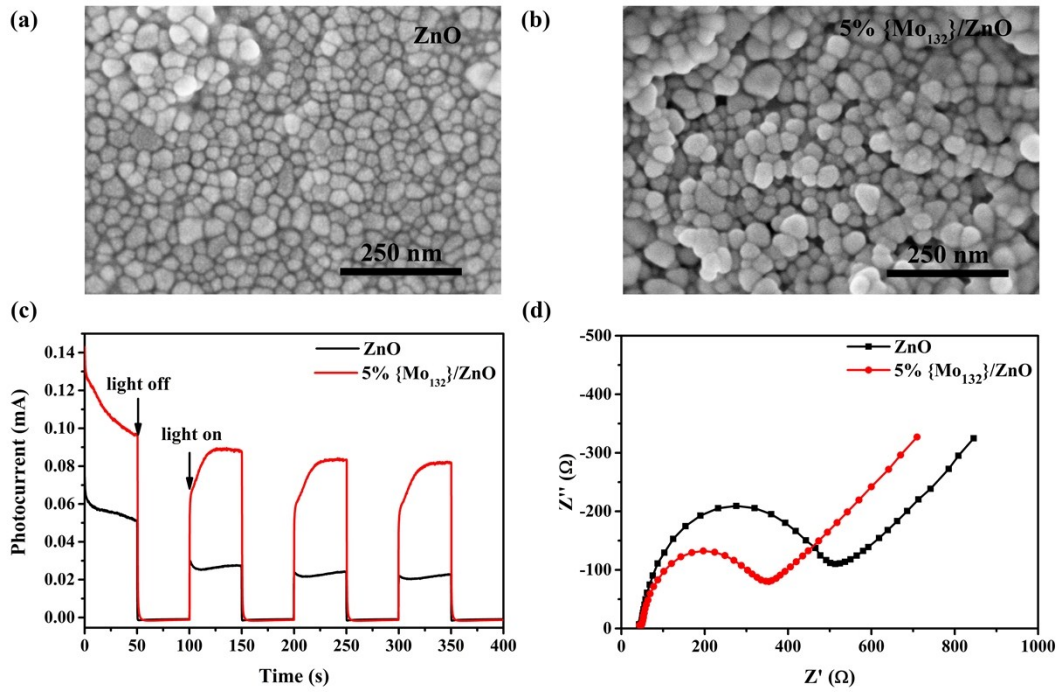

Fig. S6 (a) The SEM graph of ZnO. (b) The SEM graph of 5%{Mo_{132}}/ZnO film electrodes. (c) Photocurrent responses of ZnO and 5%{Mo_{132}}/ZnO. (d) Nyquist plots of ZnO and 5%{Mo_{132}}/ZnO. (red line: 5%{Mo_{132}}/ZnO, black line: ZnO)

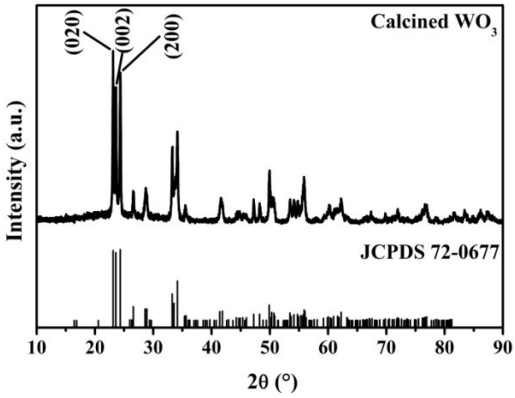

Fig. S7 XRD patterns of calcined WO_3.

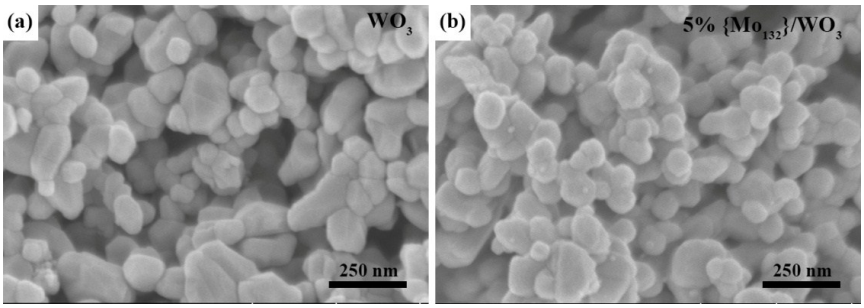

Fig. S8 SEM graphs of WO_3 and 5%{Mo_{132}}/WO_3 film electrodes.

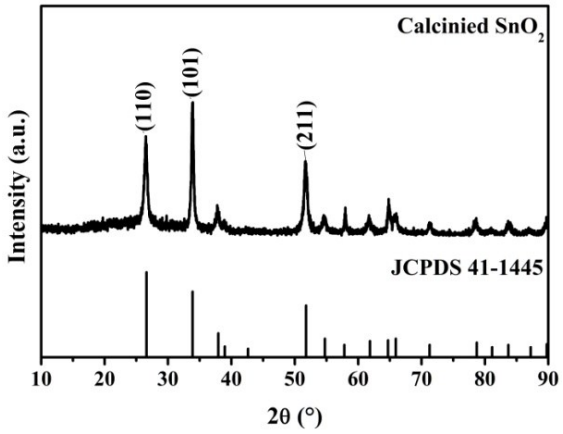

Fig. S9 XRD patterns of calcined SnO_2.

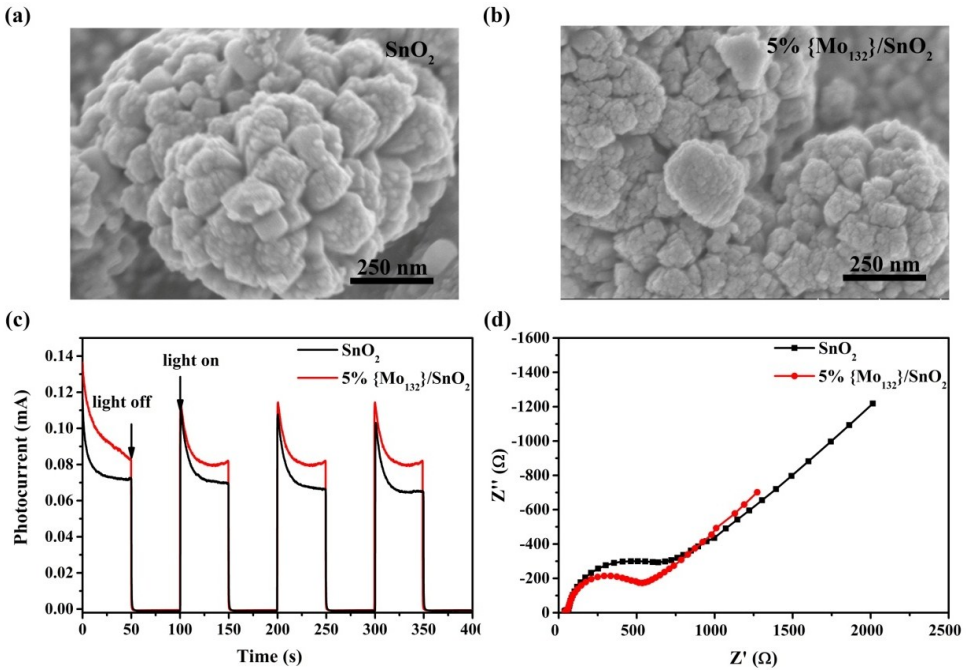

Fig. S10 (a) The SEM graph of SnO_2. (b) The SEM graph of 5%{Mo_{132}}/SnO_2 film electrodes. (c) Photocurrent responses of SnO_2 and 5%{Mo_{132}}/SnO_2. (d) Nyquist plots of SnO_2 and 5%{Mo_{132}}/SnO_2. (red line: 5%{Mo_{132}}/ SnO_2, black line: SnO_2)

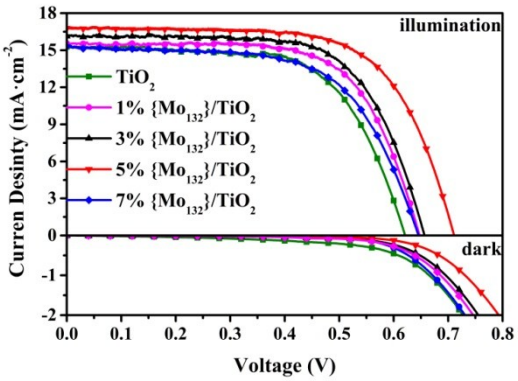

Fig. S11 *J-V* curves of the DSSCs with different proportions of $\{Mo_{132}\}/TiO_2$ and pure TiO_2 as the photoanodes. (green: pure TiO_2, pink: 1%$\{Mo_{132}\}/TiO_2$, black: 3%$\{Mo_{132}\}/TiO_2$, red: 5%$\{Mo_{132}\}/TiO_2$, blue: 7%$\{Mo_{132}\}/TiO_2$)

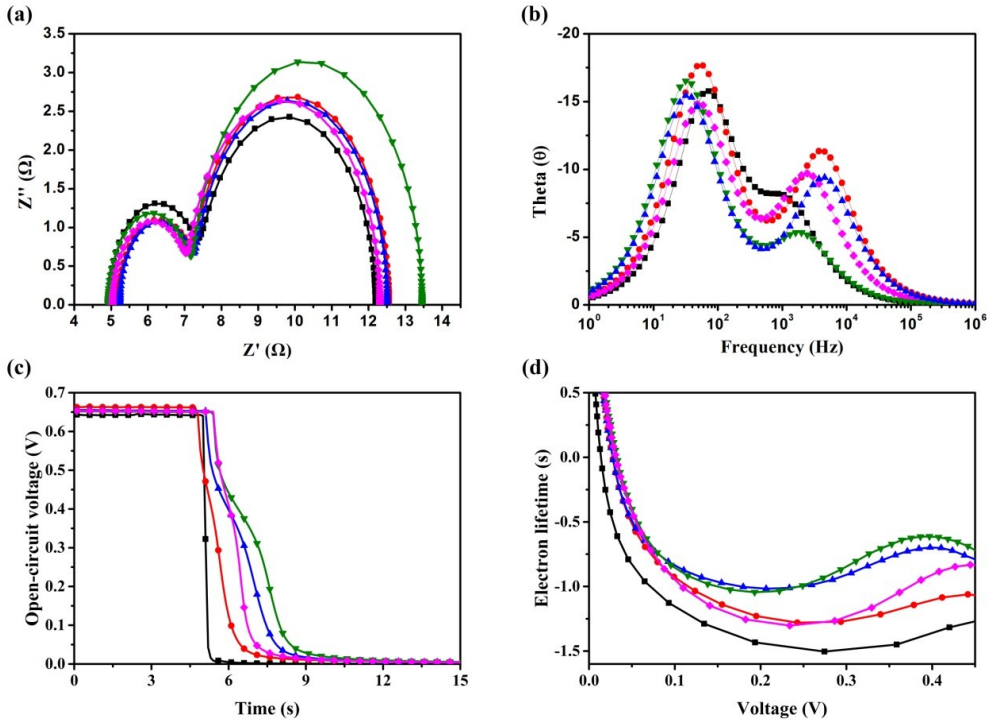

Fig. S12 (a) Nyquist plots. (b) Bode phase plots. (c) OCVD curves of different DSSCs. (d) Electron lifetime calculated from OCVD. (black: pure TiO_2, red: 1%$\{Mo_{132}\}/TiO_2$, blue: 3%$\{Mo_{132}\}/TiO_2$, green: 5%$\{Mo_{132}\}/TiO_2$, pink: 7%$\{Mo_{132}\}/TiO_2$)

Table S1 Photovoltaic parameters of different DSSCs.

Percentage	J_{sc}(mA cm^{-2})	V_{oc}(V)	*FF*	η(%)
0	15.28 ± 0. 01	0.621 ± 0.003	0.638 ± 0.020	6.06 ± 0.04
1	15.54 ± 0. 02	0.648 ± 0.004	0.669 ± 0.010	6.73 ± 0.02
3	16.14 ± 0. 01	0.657 ± 0.003	0.668 ± 0.030	7.08 ± 0.03
5	16.78 ± 0. 02	0.711 ± 0.002	0.666 ± 0.020	7.94 ± 0.01
7	15.33 ± 0. 02	0.646 ± 0.004	0.623 ± 0.010	6.17 ± 0.02

Table S2 The corresponding parameters of different DSSCs obtained from electrochemical impedance spectroscopy.

Percentage	R_1(Ω)	R_2(Ω)	f_{max} (Hz)	τ_e(ms)
0	2.23	4.86	72.20	2.21
1	2.14	5.32	52.82	3.02
3	2.18	5.61	33.14	4.81
5	2.07	6.26	31.10	5.12
7	2.28	5.04	48.06	3.32

Note: The mean electron lifetime (τ_e) can be got from the relation: $\tau_e = (2\pi f_{max})^{-1}$. f_{max} is the frequency at the top of the intermediate frequency arc.