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# **Supporting Information**

## Design, synthesis and electrocatalytic properties of a coaxial and layer-tunable

## MoS<sub>2</sub> nanofragments/TiO<sub>2</sub> nanorod arrays

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### **Preparation of TNAs on FTO substrates**

FTO substrates were ultrasonically cleaned sequentially in 2% Micro-90 solution, ethanol and deionized water for 10 min and were dried under airflow. All substrates were placed at an angle against the wall of Teflon liner with the conducting side facing down. Titanium tetrachloride of 600  $\mu$ L and diluted hydrochloric acid (deionized water/concentrated hydrochloric acid, V/V=75 mL/60 mL) were added to the above Teflon-lined autoclave at 180°C for 2 h. The white TNAs coating FTO substrates were taken out, rinsed with deionized water and dried in ambient air.

#### Preparation of TNAs@XL-MoS<sub>2</sub>

The ultrathin film with different layers of MoS<sub>2</sub> (TNAs@XL-MoS<sub>2</sub>, X=1, 2, 3, F (few=4~6), T (thin>6)) coating TNAs skeleton were prepared by a two-step route of dip-coating/chemical vapor deposition. Briefly, Mo-precursor decorated TNAs were obtained through dip-coating for 1 h using ammonium molybdate solution of 50 mg mL<sup>-1</sup> to form TNAs@Mo-precursor. When using deionized water of 15 mL each time to adjust the content of Mo-precursor under ultrasound within 20 s, the MoS<sub>2</sub> layers coating TNAs can be conveniently controlled by washing 0~3 times to form the few (4~6), triple, double and single layers of MoS<sub>2</sub>. After natural drying, TNAs@Mo-precursor substrates

and sulfur powder were placed into two ceramic boats in CVD system. The operation procedure was evacuated by a vacuum pump to keep a constant pressure of 30 Pa, and then ramped with a rate of  $12.5 \,^{\circ}$ C min<sup>-1</sup> to  $550 \,^{\circ}$ C under N<sub>2</sub> (99.99%) flow, and subsequently kept at  $550 \,^{\circ}$ C for 30 min. On the other hand, TNAs@TL-MoS<sub>2</sub> was prepared by a hydrothermal process. Ammonium molybdate tetrahydrate of 45 mg, thioacetamide of 90 mg and deionized water of 30 mL was put to the Teflon-lined autoclave at 200  $\,^{\circ}$ C for 24 h. After cooling, TNAs@TL-MoS<sub>2</sub> substrates were washed by deionized water and dried in ambient air.

#### **DSSC** assembly

The working electrode consisted of the mesoporous and scattering  $TiO_2$  films with a total thickness of about 13 µm using a screen-printing technique, and then was sensitized by Ru-dyes (N719). The redox shuttle electrolyte was composed of 1-methyl 3-propyl imidazolium iodide (0.8 M), 4-tert-butyl pyridine (0.5 M) and iodine (0.02 M) in acetonitrile solution. The sandwich-type cell is composed of the working electrode, electrolyte and counter electrode with a Surlyn film of 25 µm.

### Measurements

The morphologies were observed by scanning electron microscopy (SEM, FEI) with energydispersive spectroscopy (EDS) mapping profiles and transmission electron microscopy (TEM, JEM-2100). The crystal structure was investigated by X-ray diffraction (XRD) on a Rigaku Smartlab 3 using CuK $\alpha$  radiation ( $\lambda = 1.54$  Å). Raman spectra were collected on Horiba-JY HR 800 equipped with a 514.5-nm laser source. X-ray photoelectron spectroscopy (XPS) was performed using Thermo Scientific ESCALAB 250 equipped with Mg K $\alpha$  radiation (hv=253.6 eV) at a power of 250 W. Cyclic voltammetry (CV) was carried out on CHI760E electrochemical workstation at a scan rate of 50 mV s<sup>-1</sup> using three electrode systems: TNAs@XL-MoS<sub>2</sub> electrode, Ag/AgCl electrode and a platinum wire. The electrolyte was composed of 0.01 M LiClO<sub>4</sub>, 10 mM LiI, and 1 mM  $I_2$  in acetonitrile solution. Current-voltage (I-V) was measured by Keithley 2400 under Newport Oriel 91.192 simulated illumination (AM1.5, 100 mW cm<sup>-2</sup>).



Fig. S1 Schematic synthesis route of TNAs@FL-MoS2 on FTO substrates.



Fig. S2 (a) XRD patterns of the bare FTO substrate, TNAs on FTO, and TNAs@FL-MoS<sub>2</sub> on FTO.(b) Top view SEM images of TNAs (inset: cross-section). High magnification image from top: (c)

TNAs anf (d) TNAs@FL-MoS<sub>2</sub>.



Fig. S3 (a) EDS pattern of the TNAs@FL-MoS<sub>2</sub>. (b) SEM image of the TNAs@FL-MoS<sub>2</sub>. (c-e) The corresponding EDS mapping images of molybdenum, sulphur, titanium and oxygen elements.

Element	Weight (%)	Atom (%)
0	37.29	64.68
S	8.78	7.60
Ti	41.76	24.19
Мо	12.17	3.52

Table S1 Element contents of TNAs@FL-MoS<sub>2</sub> from EDS analysis.

The Mo 3d spectra consist of two peaks at 229.1 and 232.4 eV, referring to the doublet Mo<sup>4+</sup>  $3d_{5/2}$  and Mo<sup>4+</sup>  $3d_{3/2}$  of 2H MoS<sub>2</sub>, respectively. The peak at 226.7 eV can be corresponded to S 2s. The S 2p spectra include the spin-orbit S  $2p_{3/2}$  (162.1 eV) and S  $2p_{1/2}$  (163.9 eV). The tiny peak of 235.7 eV corresponds to Mo<sup>6+</sup>  $3d_{5/2}$  of MoO<sub>3</sub>, indicating that the oxidation of FL-MoS<sub>2</sub> is negligible.

The two peaks of Ti  $2p_{3/2}$  (458.8 eV)and Ti  $2p_{1/2}$  (464.5 eV) are consistent with the typical values pure rutile TiO<sub>2</sub>. The O 1s peaks at 530 and 532 eV correspond to Ti-O-Ti and Ti-OH, respectively. The results confirm that the as-synthesized FL-MoS<sub>2</sub> films have been coated on the rutile TNAs.



Fig. S4 XPS spectra of TNAs@FL-MoS<sub>2</sub>: (a) Mo 3d, (b) S 2p, (c) Ti 2p and (d) O 1s.



Fig. S5 Top view SEM images of (a) TNAs@TL-MoS<sub>2</sub> and (b) TNAs@TL-MoS<sub>2</sub> (High magnification). (c) Cross-sectional view SEM images of TNAs@TL-MoS<sub>2</sub>. (d) TEM images of TNAs@TL-MoS<sub>2</sub>.



Fig. S6 CVs of  $I^{-}/I_{3}^{-}$  for the different counter electrodes at a scan rate of 10 mV s<sup>-1</sup>.



Fig. S7 EIS plots of (a) bare TNAs, (b) Pt and various layers  $MoS_2$  coated TNAs, (c) the enlarged image of (b) with an insert of equivalent circuit fitted by EIS data. The symmetric cell with an active

area of 0.25 cm<sup>2</sup> was used to perform electrochemical impedance spectroscopy (EIS) in the frequency range from 0.01 to 10<sup>5</sup>Hz with an amplitude of 10 mV. The equivalent circuit based on fitting EIS analysis mainly consists of the following RC elements: a charge-transfer resistance ( $R_{ct}$ ), a series resistance ( $R_s$ ), a Warburg impedance ( $Z_N$ ) and a constant phase element (CPE).

CEs	$R_{s} \left(\Omega \ cm^{2}\right)$	$R_{ct} \left(\Omega \ cm^2\right)$
Pt	4.65	6.75
TNAs@1L-MoS <sub>2</sub>	4.76	60.75
TNAs@2L-MoS <sub>2</sub>	4.60	51.42
TNAs@3L-MoS <sub>2</sub>	4.38	37.21
TNAs@FL-MoS <sub>2</sub>	4.21	10.09
TNAs@TL-MoS <sub>2</sub>	4.84	36.72

Table S2 Resistance fitted by EIS data.

Table S3 Photovoltaic performance of DSSCs based on various CEs.

CEs	$J_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}(V)$	FF	η (%)
Pt	14.53	0.771	0.64	7.17
TNAs	1.40	0.295	0.09	0.04
TNAs@1L-MoS <sub>2</sub>	14.03	0.621	0.41	3.57
TNAs@2L-MoS <sub>2</sub>	14.60	0.717	0.45	4.71
TNAs@3L-MoS <sub>2</sub>	14.12	0.727	0.60	6.17
TNAs@FL-MoS <sub>2</sub>	14.45	0.751	0.66	7.16
TNAs@TL-MoS <sub>2</sub>	14.26	0.720	0.46	4.72



Fig. S8 The stability of the optimized TNAs@TL-MoS<sub>2</sub> solar cell during constant illumination at AM1.5, 100 mW cm<sup>-2</sup> and 45 C. Insert: IV curves of solar cells corresponding to Table S3.

Time (day)	$J_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}(V)$	FF	η (%)
0	14.45	0.751	0.66	7.16
2	14.43	0.751	0.66	7.14
4	14.40	0.750	0.66	7.13
6	14.39	0.749	0.65	7.01
8	14.36	0.751	0.65	7.00

Table S4 Photovoltaic performance of DSSC based on the optimized  $TNAs@FL-MoS_2$  CE during the different time period.

CEs	J <sub>sc</sub> (mA cm <sup>-2</sup> )	$V_{oc}(V)$	FF	η (%)	references
MoS <sub>2x</sub> Se <sub>2(1-x)</sub>	13.40	0.75	0.65	6.5	1
MoS <sub>2</sub> NPs	14.72	0.745	0.49	5.41	2
MWCNT@MoS <sub>2</sub>	13.69	0.73	0.65	6.45	3
MoS <sub>2</sub> /RGO	12.51	0.73	0.66	6.04	4
$2H MoS_2$	6.78	0.73	0.35	1.72	5
1T MoS <sub>2</sub>	18.76	0.73	0.52	7.08	5
MoS <sub>2</sub> NPs	13.08	0.68	0.65	6.11	6
MoS <sub>2</sub> /graphene	12.41	0.71	0.68	5.98	7
TNAs@FL-MoS <sub>2</sub>	14.45	0.751	0.66	7.16	This work

Table S5 Comparative photovoltaic performance of DSSCs assembled by various MoS<sub>2</sub>-based CEs.

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