

Electronic Supplementary Information for

**Facile preparation of cobalt disulfide/reduced graphene oxide composite film as an efficient counter electrode for dye-sensitized solar cells**

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## Experimental Section

### 1. Layer by layer assembly of FTO/GO thin films

In a typical experiment, graphite oxide was synthesized from natural graphite powder by a modified Hummers method.<sup>1</sup> The as-synthesized graphite oxide was dispersed in deionized water under ultrasonication for 10 min to prepare graphene oxide (GO) solution (1mg/mL) used for layer by layer assembly (LBL). The GO thin films were assembled on the fluorine-doped tin oxide (FTO) glass substrate via a typical LBL procedure<sup>2</sup> (Fig. 1(a)). After ultrasonic washing in acetone and ethanol for several times, the cleaned FTO substrates were immersed in a positively charged Poly diallyldimethylammoniumchloride) (PDDA, MW=8000) aqueous solution (0.2 wt%) for 20 min to get a positively charged surface and subsequently the FTO substrates were rinsed with deionized water and dried in a nitrogen gas flow. In order to get the thin film of FTO/GO, the FTO substrates with positively charged surface were dipped into the negatively charged GO (GO<sup>-</sup>) aqueous solution (1mg/mL) for 20 min, the multilayer films of GO can be obtained via repeating the LBL cycles as illustrated in Fig.1(a).

### 2. The preparation of FTO/RGO/CoS<sub>2</sub> composite thin film

Cobalt disulfide precursor solution was prepared by dissolving 1mmol CoCl<sub>2</sub>·6H<sub>2</sub>O and 4mmol thioacetamide in acetone. After stirring the mixture for 10 min, a blue precursor solution was obtained. The precursor solution was dropped onto the GO films, dried at room temperature and the composite thin films were annealed at 400 °C for 30 min in the Ar<sub>2</sub> atmosphere. After thermal reduction, some oxide-containing functional groups in GO were removed and CoS<sub>2</sub> formed from the precursor solution, a composite materials CoS<sub>2</sub>/RGO (CSG) was obtained.

### 3. Device fabrication

The Pt counter electrode was prepared by thermal decomposition of 2mg/mL solution of H<sub>2</sub>PtCl<sub>6</sub> (Sigma) in isopropyl alcohol on FTO (15Ω/square, NSG) substrate, and heating at 400°C for 30 min. The photoanodes were fabricated by immerse the TiO<sub>2</sub> films (OPV. Tech, Yingkou, China) into a 0.3 mM solution of Z907Na (Solaronix SA, Switzerland) in acetonitrile/tert-butyl alcohol (1:1 volume ratio) for 16 h. The photoanode and counter electrode were assembled in a sandwich configuration using a 30 μm thickness Surlyn ring. The liquid electrolyte, which consists of 0.02 M I<sub>2</sub>, 0.05 M LiI, 1 M 1, 2-dimethyl-3-propylimidazolium iodide, 0.1M guanidine thiocyanate and 0.5 M 4-tert-butyl-pyridine in acetonitrile was injected into the aperture of counter electrodes via vacuum back filling method.

### 4. Physical characterization and electrochemistry measurements

The crystal structure was detected on a PANalytical diffractometer, using CuKα radiation at 40 kV, 40 mA with a scanning rate of 2° min<sup>-1</sup>. The morphology and structure characterization of representative samples were examined by a field emission scanning electron microscope (FESEM, Hitachi S-8010) coupled with an energy-dispersive X-ray (EDX, Oxford Instrument) spectrometer and transmission electron microscopy (TEM, FEI Tecnai G<sup>2</sup> F30). The film growth was detected by UV-visible spectroscopy (UV-2450, SHIMADZU, Japan) and the thickness of monolayer GO film was examined with an atomic force microscope (Agilent 5500 AFM). The EIS experiments of the symmetrical cells were carried out using Electrochemical System (PARSTAT 2273, USA) in the dark under open circuit voltage condition. The cells were measured at a frequency ranged from 0.1 Hz to 100 kHz. The analyses of impedance spectra were made with the soft-ware

ZSimpWin version 3.1. The current density–voltage performance of the DSSCs was measured in 1 sun illumination (AM 1.5G, 100 mW cm<sup>-2</sup>) with a Newport (USA) solar simulator (300 W Xe source) and digital source meter (Keithley 2400, USA), at room temperature.

## 5. The EIS measurement of the CSG electrodes with different deposition cycle of GO

To confirm the electrochemical characteristics of the CSG electrodes with different deposition cycle number, electrochemical impedance spectroscopy (EIS) measurements were carried out in a symmetrical dummy cell fabricated with two identical electrodes. Fig. S1 shows the typical Nyquist plots of the dummy cells.<sup>3</sup> As depicted in Table S1, the value of the charge transfer resistance ( $R_{ct}$ ) reaches the minimum when the deposition process is cycled six times, indicating that the corresponding CSG electrode features the highest catalytic activity. Since the internal resistance elements are related to the  $R_{ct}$  at the electrode, the  $Z_n$  in the electrolyte, and the  $R_s$ ,<sup>4</sup> the total series resistance also reaches the minimum ( $R_s=22.5 \Omega$ ,  $R_{ct}=4.8 \Omega$ ,  $Z_n=5.7 \Omega$ ) when the deposition is cycled six times. The as-prepared CSG electrode exhibits the highest catalytic activity and lowest internal resistance, thus the corresponding device is expected to achieve optimal photovoltaic performance.

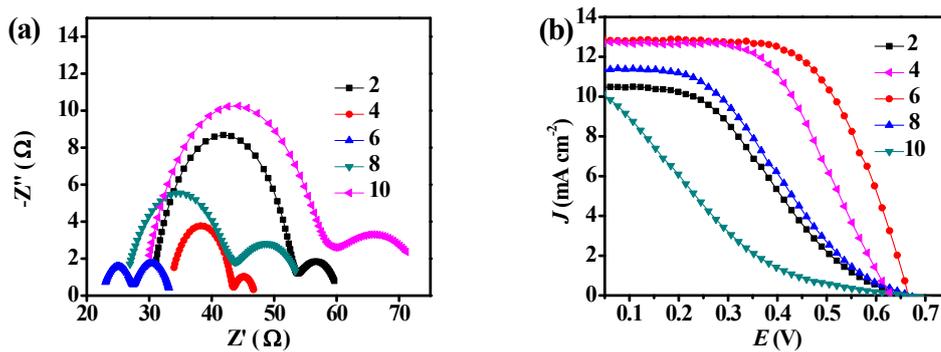
To evaluate the performance of the CEs with different deposition cycle times, we assembled the DSSCs with these CEs. Fig. S1(b) shows the current density–voltage ( $J$ – $V$ ) curves of these DSSCs. As depicted in Table S2, the device using CSG counter electrode with six deposition cycles yields the highest power conversion efficiency ( $PCE$ ) of 5.4%, which is higher than the corresponding efficiencies of the devices using other CEs.

## 6. Electrochemical stability measurement

In order to investigate the electrochemical stability of different electrodes, the dummy cells with CSG and Pt electrodes were subjected to repeated EIS measurements after a pretreatment of CV scanning. Fig. S2 shows the evolution of the impedance spectra for the fresh and aged dummy cells at room temperature. For both of the CSG and Pt samples, the  $R_s$  and  $R_{ct}$  remained unchanged upon aging. This implies that the cell aging has no significantly influence on the serial ohmic resistance and the electron transfer process at the electrode/electrolyte interface. These results confirm that the CSG electrode has similar electrochemical stability to its Pt counterpart.<sup>5</sup>

## References

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**Fig. S1** (a) Nyquist plots of symmetric cells with CSG electrodes with different deposition cycle of GO. (b) Current density–voltage ( $J$ – $V$ ) curves of DSSCs with CSG CE with different deposition cycle of GO.

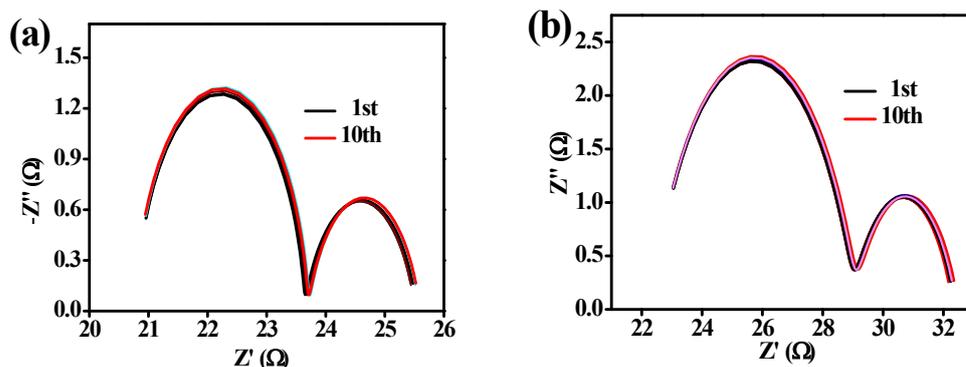
**Table S1.** Impedance parameters of the CSG electrodes with different deposition times ( $n$ ) of GO.

$n$	$R_s$ ( $\Omega$ )	$R_{ct}$ ( $\Omega$ )	$Z_n$ ( $\Omega$ )
2	30.4	22.8	7.1
4	33.2	10.1	3.5
6	22.5	4.8	5.7
8	25.9	17.2	11.7
10	28.9	18.2	28.0

**Table S2.** Photovoltaic parameters of the DSSCs with CSG CE with different deposition times ( $n$ ) of GO.

$n$	$J_{sc}$ ( $\text{mA cm}^{-2}$ )	$V_{oc}$ (V)	$FF$	$PCE$ (%)
2	10.51	0.66	0.37	2.6
4	12.63	0.63	0.52	4.1
6	12.87	0.67	0.63	5.4
8	11.45	0.67	0.38	2.9
10	10.67	0.66	0.2	1.4

$V_{oc}$ : open circuit voltage,  $J_{sc}$ : short circuit current,  $FF$ : fill factor,  $PCE$ : power conversion efficiency.



**Fig. S2** Nyquist plots of EIS for the symmetrical cells with Pt (a) and CSG (b) electrodes. The cells were first subjected to CV scanning from 0 to 0.6 V and then from -0.6 V to 0 V with a scan rate of 10 mV s<sup>-1</sup>, followed by 20 s relaxation at 0 V, and then EIS measurement at 0 V from 0.1 Hz to 100 kHz was performed. This sequential electrochemical test was repeated 10 times.

**Table S3.** Impedance parameters of the CSG and Pt electrodes.

CE	$R_s$ ( $\Omega$ )	$R_{ct}$ ( $\Omega$ )	$Z_n$ ( $\Omega$ )
CSG	22.5	4.8	5.7
Pt	20.7	3.4	1.9