

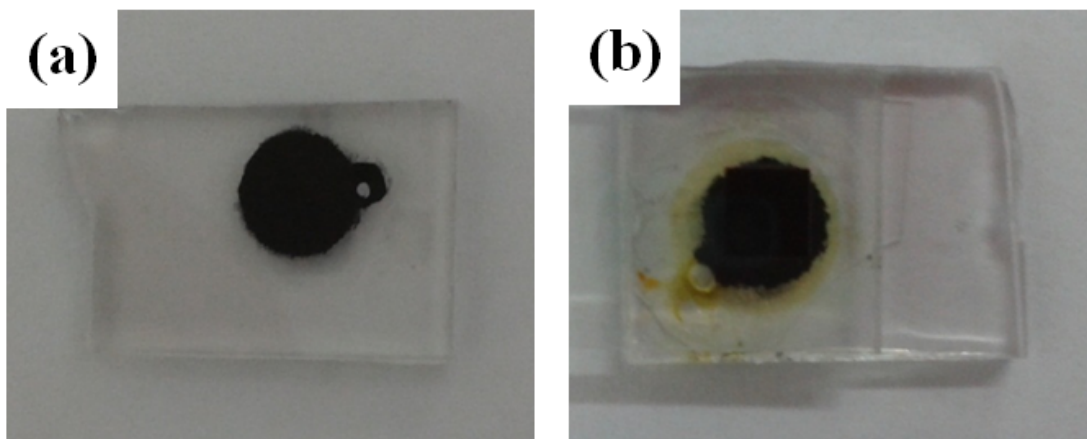
*Electronic Supplementary Information for*

**Organic molecule controlled synthesis of three-dimensional  
rhododendra-like cobalt sulfide hierarchitectures as counter  
electrodes for dye-sensitized solar cells**

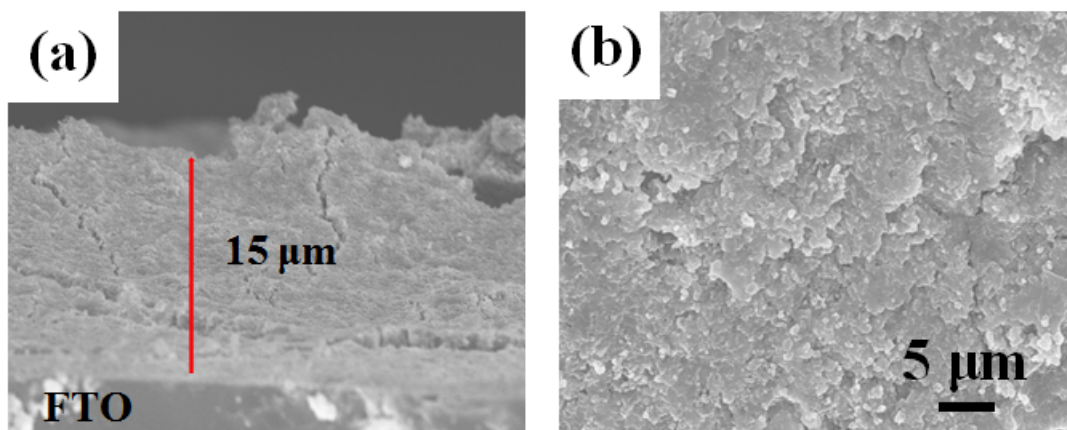
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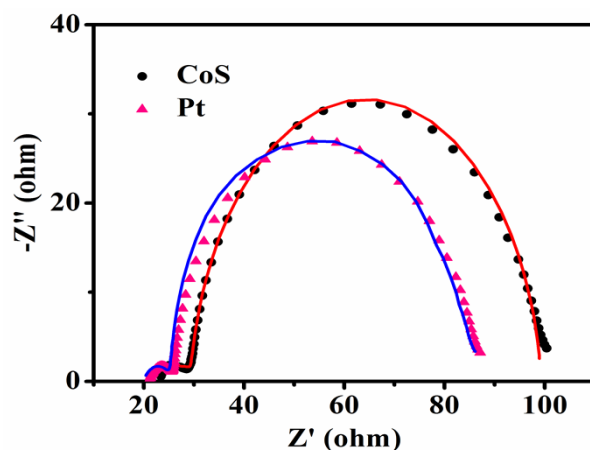
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**Figure S1** (a) The photo of the CoS counter electrode. (b) The photo of the DSSC based on the CoS counter electrode.



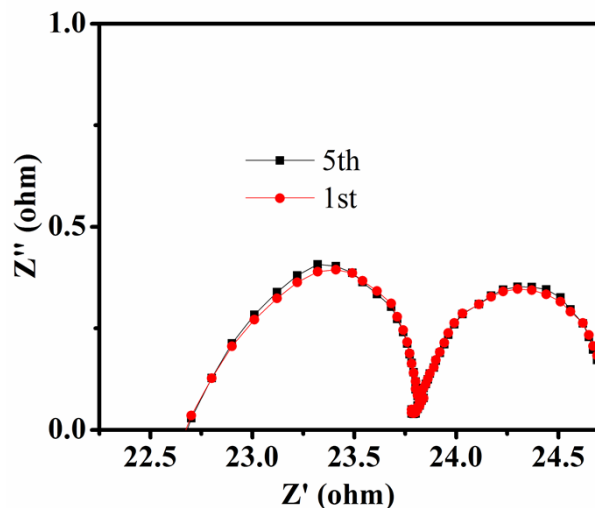
**Figure S2** (a) The cross section SEM image of the CoS counter electrode. (b) The magnified image of the cross section.



**Figure S3** Electrochemical impedance spectra of the DSSC with CoS and Pt counter electrode, the lines are the related simulated data.

In order to understand the electron transport and recombination properties in various DSSCs, we further measured the EIS in the frequency range of 0.05 Hz–100 kHz, at open circuit voltage in dark. The Nyquist plots are shown in Figure S3. Generally, the semicircle at high frequency (in the kHz range) is attributed to the charge transfer resistance ( $R_{ct1}$ ) at the counter electrode/electrolyte interface while the response in the intermediate-frequency region ( $R_{ct2}$ ) is associated with the electron transport in the anode film and the recombination of electron at the anode/electrolyte interface. The low-frequency region reflects the diffusion resistance in the electrolyte ( $Z_w$ ).<sup>1,2</sup> As shown in Figure S3, similar semicircles in the high frequency region are observed, indicating that the CoS and Pt electrodes have similar catalytic activity.<sup>3</sup> However, in the intermediate-frequency region, CoS electrode exhibits a larger  $R_{ct2}$  value than Pt. This result suggests that in the CoS based DSSC, the back reaction was inhibited. According to the previous report,<sup>1</sup> in the dark,  $I_3^-$  is generated at counter electrode and diffuse to the  $TiO_2$  mesoporous films, the back reaction occurred subsequently. Therefore, the larger  $R_{ct2}$  value can be ascribed to the thicker film of active materials is not beneficial to the diffusion of  $I_3^-$ .

Additionally, the series resistance ( $R_s$ ) was investigated. As shown in Figure S3, the CoS electrode with a  $R_s$  (22.87  $\Omega$ ), is larger than that of the Pt electrode (19.80  $\Omega$ ), this result can be attributed to the low conductivity of the active materials. According to the literatures,<sup>4-6</sup> the  $R_s$  is closely related to  $FF$ , a larger  $R_s$  value will lead to a lower  $FF$ , thus a slightly lower  $FF$  was obtained for CoS based device.



**Figure S4** Electrochemical impedance spectra of the symmetrical cell with identical CoS electrodes, after one and five-time cyclic voltammetry scans.

The EIS measurement was carried out as follows:  $2 \times$  cyclic voltammetry scans (from  $0 \text{ V} \rightarrow 1 \text{ V} \rightarrow -1 \text{ V} \rightarrow 0 \text{ V}$ , scan rate  $10 \text{ mV s}^{-1}$ ) followed by 20 s relaxation at  $0 \text{ V}$  followed by EIS measurement at  $0 \text{ V}$  from  $100 \text{ kHz}$  to  $0.1 \text{ Hz}$ .<sup>7</sup> As shown in Figure S4, after five-time cyclic voltammetry scans, the impedance configuration is nearly irrelevant to the cycle history, this is ascribed to the electrochemical stability of CoS electrode.

## References

- 1 Q. Wang, J-E. Moser, and M. Grätzel, *J. Phys. Chem. B.*, 2005, **109**, 14945–14953.
- 2 F. Shao, J. Sun, L. Gao, J. Z. Chen, S. W. Yang, *RSC Adv.*, 2014, **4**, 7805–7810.
- 3 S. Das, P. Sudhaga, S. Nagarajan, E. Ito, S. Y. Lee, Y. S. Kang, W. Choi, *Carbon*, 2012, **50**, 4815–4821.
- 4 M. K. Wang, C. Grätzel, S. M. Zakeeruddin, M. Grätzel, *Energy Environ. Sci.*, 2012, **5**, 9394–9405.
- 5 S. Yun, L. Wang, W. Guo, T. Ma, *Electrochem. Commun.*, 2012, **24**, 69–73.
- 6 L. Han, N. Koide, Y. Chiba, A. Islam, R. Komiya, N. Fuke, A. Fukui and R. Yamanaka, *Appl. Phys. Lett.*, 2005, **86**, 213501.
- 7 L. Kavan, J-H. Yum, and M. Grätzel, *Nano Lett.*, 2011, **11**, 5501–5506.