Supplementary Information

Dye-sensitized solar cells with NiS counter electrodes electrodeposited by a potential reversal technique

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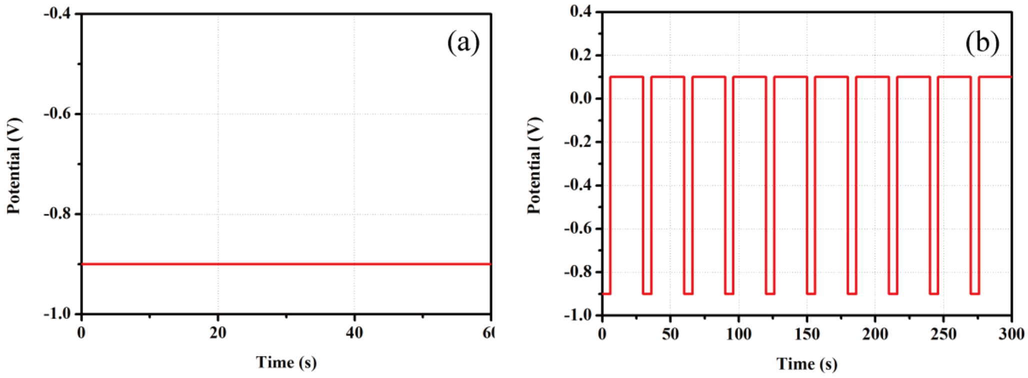

Figure S1. The applied potential at the FTO glass *vs.* time in (a) potentiostatic (PS) and (b) periodic potential reversal (PR) techniques.

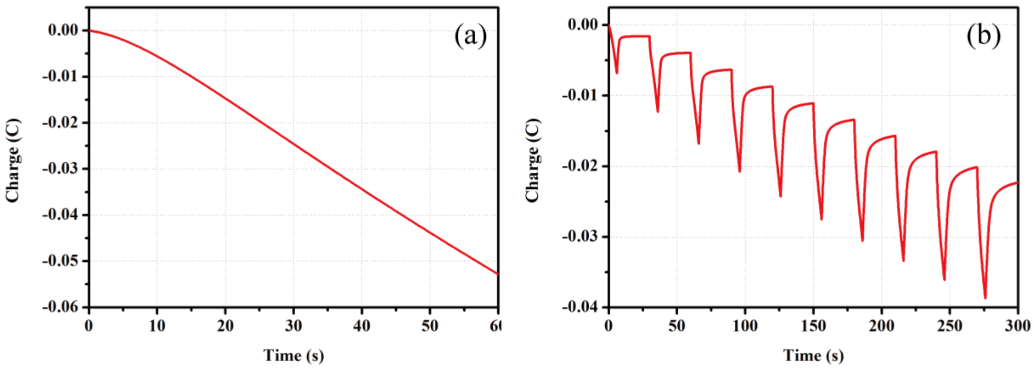

Figure S2. The accumulated charge at the FTO glass *vs.* deposition time during electrodeposition using (a) PS and (b) PR techniques. The cathodic deposition bias is -0.9 V for both techniques and the anodic bias for PR is 0.1 V.

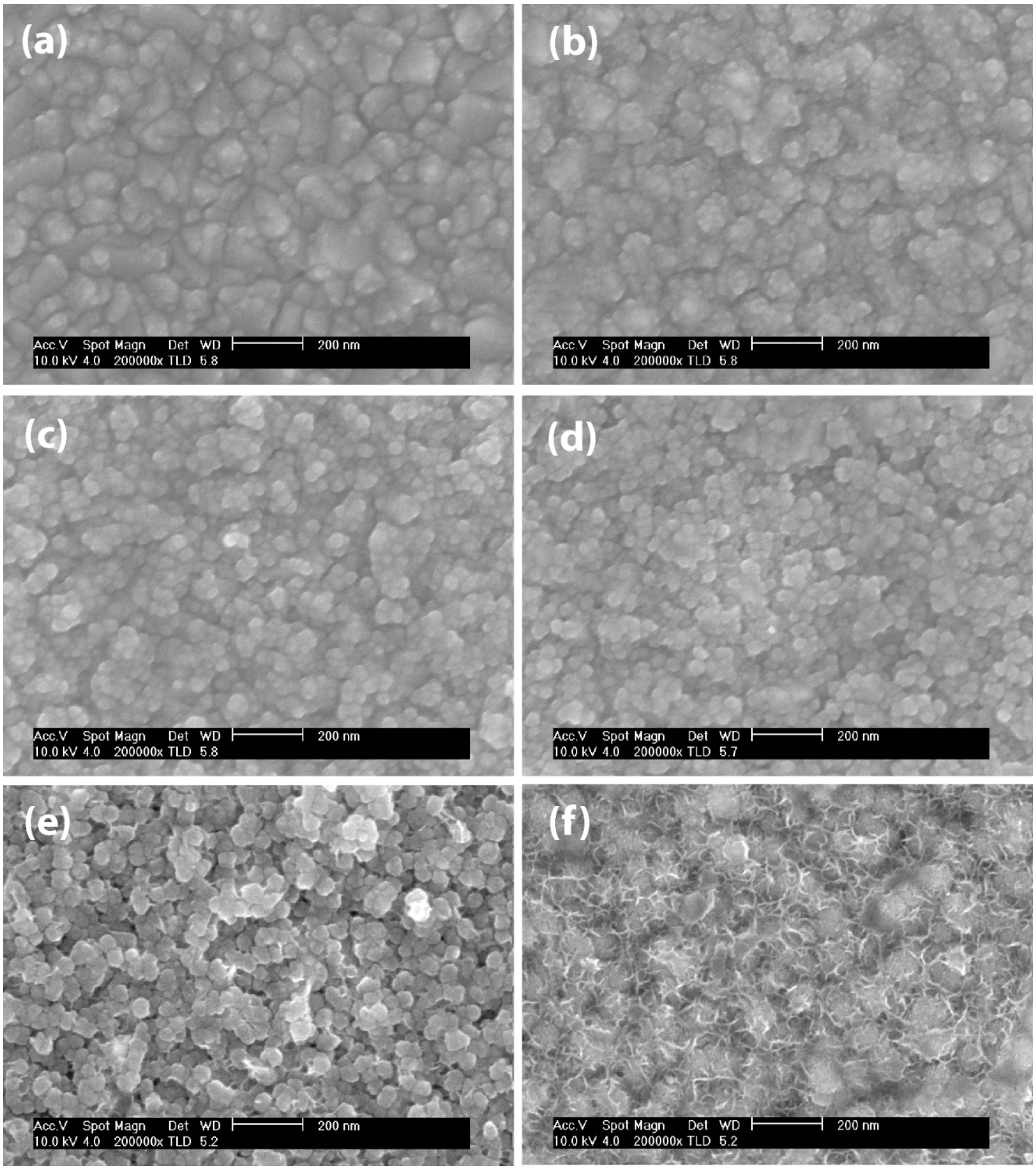

Figure S3. SEM images of NiS_{PR} films prepared under (a) 2 cycles, (b) 5 cycles, (c) 10 cycles, (d) 15 cycles, (e) 20 cycles, and (f) NiS_{PS} film.

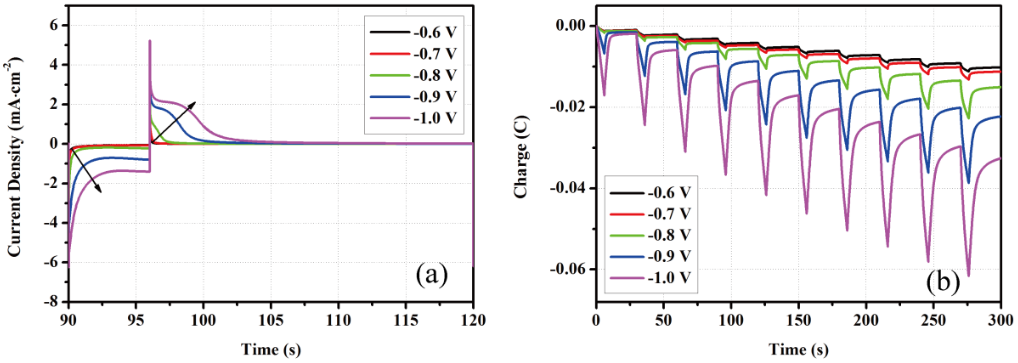

Figure S4. (a) The i-t curves of the 4th period and (b) the calculated Q-t curves during PR deposition with various cathodic bias.

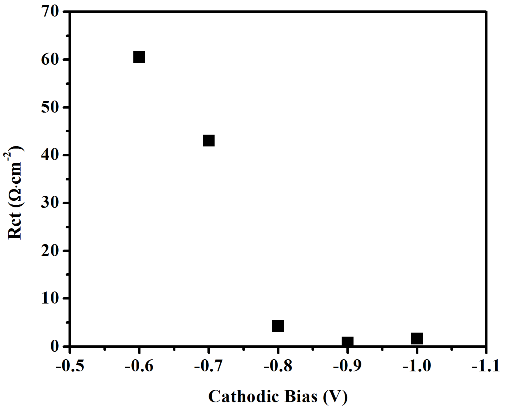

Figure S5. Rct of the $\mathrm{NiS_{PR}}$ electrodes prepared under various cathodic bias.

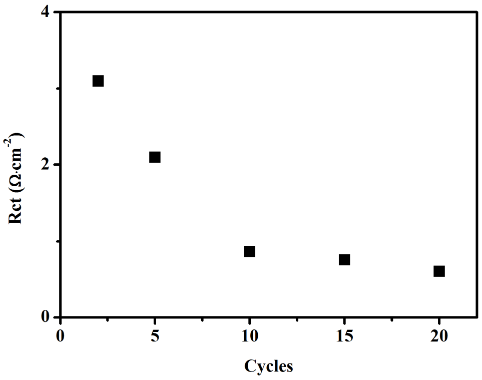

Figure S6. Rct of the NiS_{PR} electrodes prepared with various cycles of periods.

Optimization of PR technique

Since we have obtained the efficient electrocatalytic active NiS through PR technique, further study should be done to optimize the fabrication. The amount of electroactive materials is a crucial factor that can influence their catalytic activity, especially for the porous materials[1]. It depends on the current density and fabrication time in the case of electrodeposition. In the PR technique, the current density is mainly controlled by the applied overpotential, while the fabrication time can be expressed as the number of the periods. Previous study has shown great impact of the charge-transfer resistance (*Rct*) of CEs on the photovoltaic parameters of the assembled dye-sensitized solar cells (DSCs), especially on the fill factor (*FF*)[2]. Thus, the *Rct* is a good index of the performance of counter electrodes (CEs), provided that the sheet resistances (*Rs*) of the CEs are identical. Since the CEs with fluorine doped tin oxide (FTO) substrate exhibits almost the same *Rs*, the *Rct* has been used to study the influence of the cathodic bias and the deposition cycles on the NiS_{PR}.

A direct method to control the deposition current is to adjust the applied cathodic bias. The performance of the NiS electrodes prepared under cathodic bias from -0.60 to -1.0 V is studied by EIS measurements. Increase in the cathodic bias results in faster cathodic deposition, and the anodic dissolving becomes more significant since more Ni has been deposited (Fig S4a). The current has greatly increased under the applied bias below -0.8 V, which is in good accordance with the LSV. The Q-t curve calculated from the i-t curve confirms that more NiS has been deposited under higher cathodic bias (Fig S4b). Trace amount of NiS is supposed to be deposited onto the electrode under a cathodic bias of -0.60 V, for its *Rct* is rather low (60.5 $\Omega\cdot cm^2$) compared with the *Rct* of bare FTO glass

(Fig S5). The *Rct* of NiS drops under 2 $\Omega\cdot cm^2$ after the applied cathodic bias is below -0.9 V. Further increase the overpotential is not necessary for the well improved CE performance. If a fast cathodic deposition rate is really needed, either the cathodic time should be shortened or the anodic time should be longed to ensure the complete removal of excess Ni.

Another way to change the amount of NiS is to vary the deposition time. A cycle is defined as one cathodic and the next anodic polarization. The NiS is deposited during each cycle, since the charges accumulates for each cycle. Thus, increase the cycles of the periods will result in more NiS on the CE. Fig S6 shows the *Rct* of CEs prepared under various cycles. To our surprise, the Rct of the NiS electrode prepared under 2 cycles already drops to 3.1 $\Omega\cdot cm^2$, showing a quite good electroactivity. Unlike the carbonaceous materials, whose catalytic activity comes from their high specific area, the electroactivity of NiS for I_3^- reduction is more like ‘intrinsic’. After 10 cycles, the *Rct* of the electrode drops below 1 $\Omega\cdot cm^2$ and the NiS CE reaches its best performance.

Notes and References

1 Y. Saito, W. Kubo, T. Kitamura, Y. Wada and S. Yanagida, *J. Photochem. Photobiol. A:Chem*, 2004, **164**, 153.

2 L. Y. Han, N. Koide, Y. Chiba, A. Islam, R. Komiya, N. Fuke, A. Fukui and R. Yamanaka, *Appl. Phys. Lett.*, 2005, **86**, 213501.