Supplementary Information for Journal of Material Chemistry A

High performance Pt-free counter electrode of nickel sulfide/multi-wall carbon nanotube/titanium used in dye-sensitized solar cells

Jihuai Wu,* Yaoming Xiao, Jeng-Yu Lin, Gentian Yue, Jianming Lin, Miaoliang Huang, Yunfang Huang, Zhang Lan and Leqing Fan

Figs S1-S5

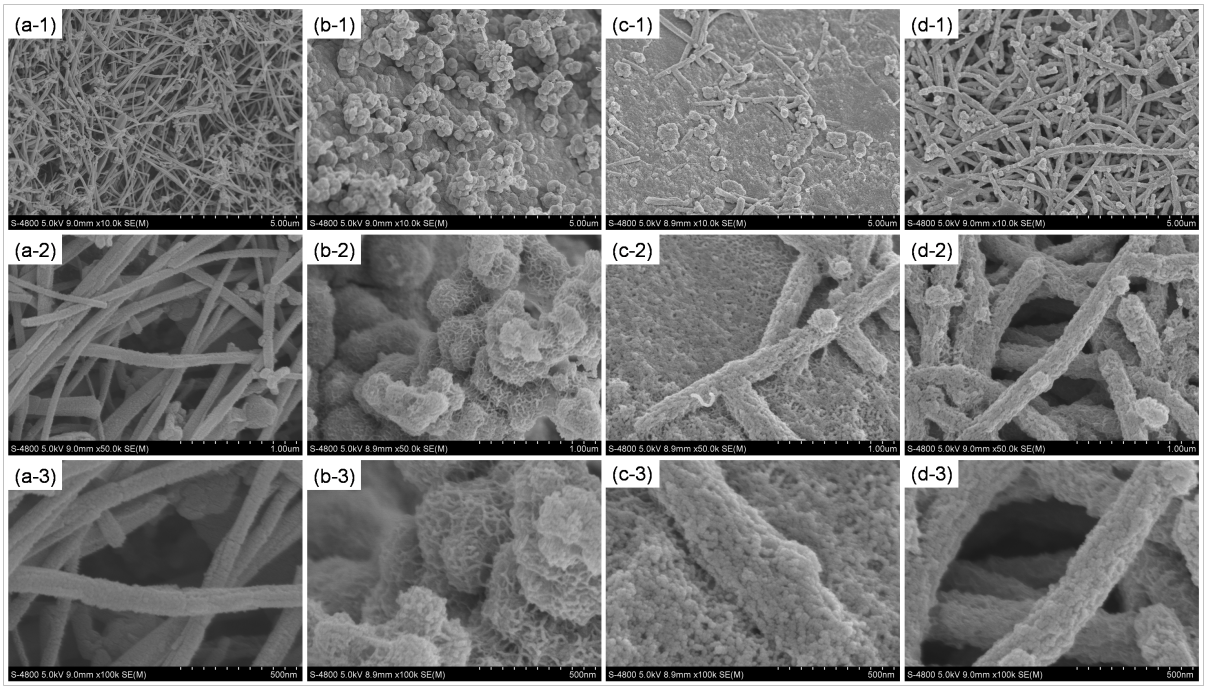

Fig. S1 SEM images of MWCNT/Ti (a-1, a-2, and a-3), NiS/Ti (b-1, b-2, and b-3), NiS/MWCNT/Ti with sparse MWCNT (c-1, c-2, and c-3), and NiS/MWCNT/Ti with enough MWCNT (d-1, d-2, and d-3) CEs, respectively.

Fig. S1 shows the SEM images of four samples with three magnifications of 10.0k, 50.0k, and 100k, respectively. Figs S1 a-1, a-2, and a-3 show the fiber-like morphology MWCNT on the Ti

foil substrate. It can be found that the MWCNT may be heaped up onto the Ti foil substrate with weak adhesion. Figs S1 b-1, b-2, and b-3 present that the nano-corallines structure NiS is fabricated on the Ti foil substrate using the pulse potentiostatic technique. To study the NiS growth on both of the MWCNT and Ti foil surfaces, two MWCNT/Ti foil substrates were prepared with sparse or enough MWCNT, respectively. Figs S1 c-1, c-2, and c-3 reveal that the NiS uniformly and continuously grows on the both surfaces of MWCNT and Ti foil, thus improving the adhesion of the MWCNT on the Ti foil substrates, meanwhile, enhancing the adhesion among the MWCNT. Compared to the Figs S1 b-1, b-2, and b-3, no nano-corallines NiS is gathered to bigger particles in Figs S1 d-1, d-2, and d-3, this reveals that NiS is preferably deposited on the MWCNT surface.

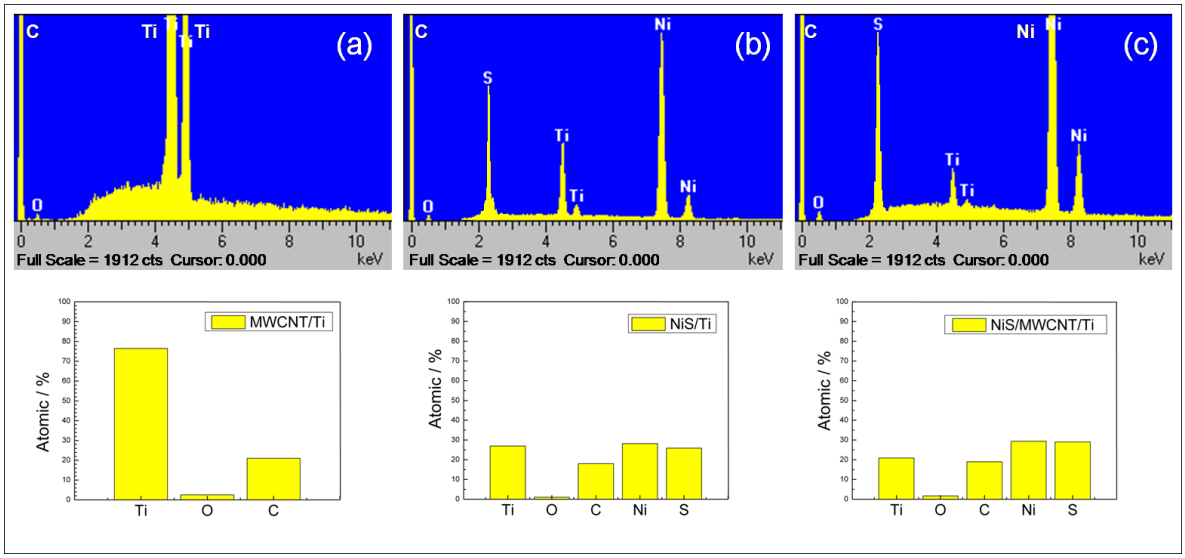

Fig. S2 EDS spectra of the MWCNT/Ti (a), NiS/Ti (b), and NiS/MWCNT/Ti (c) CEs, respectively.

EDS analyses were carried out to further indentify the compositions of the MWCNT/Ti, NiS/Ti, and NiS/MWCNT/Ti CEs, respectively. Fig. S2 shows that Ni and S are found in the NiS/Ti or NiS/MWCNT/Ti CEs. Moreover, the atomic percentage of Ni and S reveals that the Ni : S ratio is both nearly 1 : 1. This demonstrates that NiS is deposited on the Ti foil or MWCNT/Ti foil. Other elements, such as Ti, O, and C, are found in the three CEs. A large number of Ti is because of the

Ti foil substrate, a little O is due to the passive oxide film of TiO_2 on the Ti foil substrate, and C comes from a holey conductive carbon glue or MWCNT.

Fig. S3 shows the equivalent circuit used for fitting the EIS results of the symmetric cells.

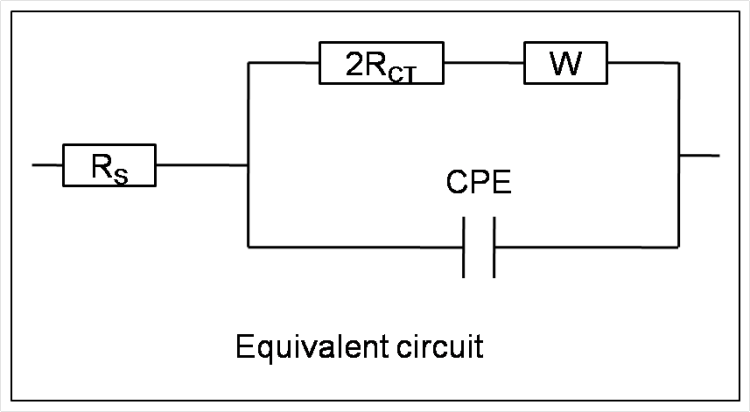

Fig. S3 Equivalent circuit used for fitting the EIS results of the symmetric cells.

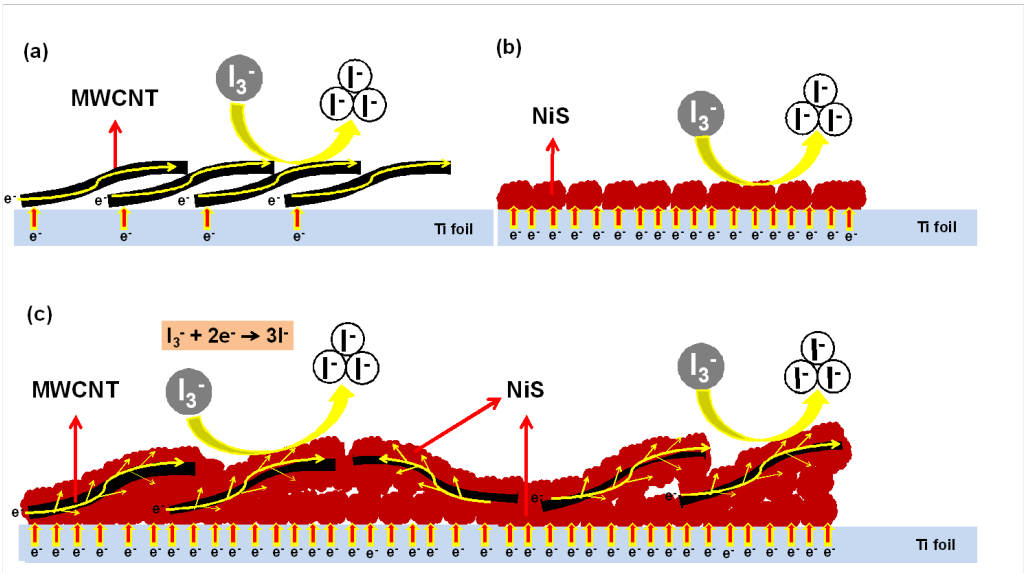

Fig. S4 Schematic of the catalytic mechanisms of MWCNT (a), NiS (b), and NiS/MWCNT (c) CEs, respectively.

Fig. S4 shows the possible catalytic mechanisms of MWCNT, NiS, and NiS/MWCNT CEs toward I_3^- reduction during the operation of the DSSC. In the case of the MWCNT/Ti CE, although the MWCNT has superior electrical conductivity, but there is a few of electron transport paths between the MWCNT and Ti foil, this is due to the MWCNTs were piled up onto the Ti foil with

weak adhesion. For the NiS/Ti CE, the NiS thin film displays lots of electron transport paths between the NiS and Ti foil. By taking advantage of the high electrical conductivity of the MWCNT and superior electrocatalytic activity of the NiS, the NiS/MWCNT/Ti CE was fabricated. In the NiS/MWCNT/Ti CE, the NiS thin film enhances the adhesion of the MWCNT on the Ti foil substrates, meanwhile, improves the connection among the NiS/MWCNT. This supplies large number of electron transport paths for the electrons can be transferred to the MWCNT and surface of NiS/MWCNT. Therefore, the NiS/MWCNT/Ti CE demonstrates the highest catalytic activity toward the reduction of I_3^- among the MWCNT/Ti and NiS/Ti CEs.

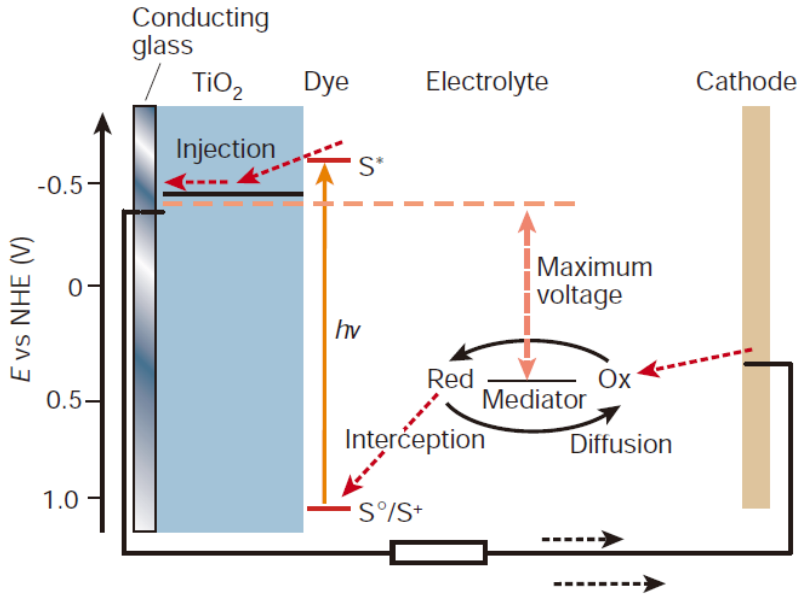

Fig. 5 Schematic of energy levels and operation of the DSSC. (cited from M. Gratzel, *Nature* **2001**, *414*, 338-344).