Journal Name

ChemComm

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

High catalytic activity and stability of the nickel sulfide and cobalt sulfide hierarchical nanospheres on the counter electrodes for dye-sensitized solar cells

Jie Yang [a,b], Chunxiong Bao [a,b], Kai Zhu [d], Tao Yu* [a,b], Faming Li [a,b], Jianguo Liu [a,c], Zhaosheng Li [a,c] and Zhigang Zou [a,b,d]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

In-situ grown nickel sulfide and cobalt sulfide hierarchical nanospheres on F-doped SnO_2 (FTO) substrates exhibited comparable catalytic activities to sputtering Pt on the counter electrodes for dye-sensitized solar cells (DSSCs). The fresh cells with the nickel sulfide and cobalt sulfide on the counter electrodes could reach power conversion efficiencies of 6.81% and 6.59% respectively, approaching to the efficiency of 6.85% based on the sputtering Pt counter electrode. Both nickel sulfide and cobalt sulfide counter electrodes could maintain the cell's relatively high performance in the long-term stability test in 504 hours.

Dye-sensitized solar cells (DSSCs) have been considered as the potential next-generation photovoltaic devices due to their acceptable efficiencies, low cost materials and simple fabrication procedures and so on.[1-3] One of the most important components in a DSSC is the counter electrode (CE) whose main role is to collect the electrons from the external circuit and catalyze the reduction of I_3^- to I^- at the CE/electrolyte interface. Therefore, a high electrical conductivity for the electrons collecting[4-5], a large specific surface area for the CE/electrolyte contact[6-9] and a high catalytic activity for the reaction of I_3^- to I^- are supposed to be preferred characteristics for the ideal CEs in DSSCs. In this respect, Pt sheets have been recognized as the suitable counter electrodes because of their high catalytic activity and stability. However, Pt is an expensive and scarce metal, which inevitably influences large-scale manufacturing of the DSSCs containing expensive Pt. Therefore, the Pt-free materials used as DSSCs' counter electrodes are important for the future industrial application of DSSCs.

The nickel sulfides and cobalt sulfides have high catalytic activities for the redox couples I^-/I_3^- in DSSCs. In 2009, CoS electrodeposited on the flexible ITO/PEN substrate showed a comparable catalytic activity to Pt as the counter electrodes in DSSCs, which opens up the way to exploring more transition metal sulfides.[10] In 2011, Sun et.al. found that electrodeposited NiS counter electrode by a potential reversal technique showed high catalytic activity for the reduction of I_3^- to I^-.[11]

It is well known that a high specific surface area is benefit for the increase of the active sites. In the past years, the hierarchical nanostructures have been applied in both of the working electrodes[12, 13] and the counter electrodes[14-16] in DSSCs due to a lot of advantages such as the large specific surface area providing large electrode/electrolyte interface contact, the accessible inner surface for electrolyte filling and so on. Hierarchical Pt aggregates have been deposited on a thin TiO_2 layer modified ITO substrate as a counter electrode for the flexible DSSC by Fu et al..[14] Wang et al. has reported that hierarchical cobalt sulfide spindles in the counter electrodes in DSSCs showed high catalytic activity.[15] However, the fabrication procedures of hierarchical structure were relatively complicated. In-situ growth has been supposed to be much simple method for fabrication of thin films on the substrates.[17] Our previous work employed in-situ growth procedures in the preparation of the vertically oriented $CuInS_2$ nanosheet thin films with high catalytic activity as counter electrodes in DSSCs.[18] However, indium is still an expensive and scarce metal. Herein, we present one-step solvothermal process to in-situ prepare highly stable hierarchical nickel sulfide and cobalt sulfide nanospheres without any scarce elements, which increase catalytic sites for the catalytic reaction of the couple redox I^-/I_3^-. Meanwhile, DSSCs assembled with the nickel sulfide and cobalt sulfide counter electrodes were further investigated by long term stability test and showed comparable stability to Pt in 504 hours, which are the potential materials for future manufacturing.

The nickel sulfide and cobalt sulfide thin films were in-situ grown on the FTO conductive glass by solvothermal method without any post-treatment. The experimental details were shown in the supplementary information. The SEM image in Fig. 1a shows that the nickel sulfide nanospheres are distributed uniformly on the FTO glass. The inset of Fig. 1a is the higher resolution SEM image of the nickel sulfide nanospheres which shows that the nickel sulfide nanospheres with sizes of about 200 nm are composed of smaller nanoparticles. Fig. 1c and its inset are TEM images of nickel sulfide nanospheres which demonstrate that the nanospheres are composed of crystalline grains with smaller size. Fig. 1b and Fig. 1d show that the morphologies of the cobalt sulfide nanospheres are almost the same with those of the nickel sulfide nanospheres. The SEM and TEM images indicate that both of the two materials present hierarchical nanospheres structures with high surface roughness. The BET tests were undertaken on the films in-situ grown on the FTO

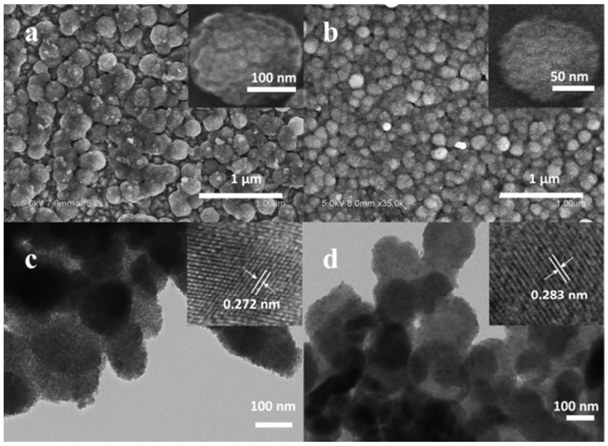

Fig. 1 The SEM image of hierarchical nickel sulfide (a) and cobalt sulfide (b) nanospheres with high resolution SEM inset. The TEM image of nickel sulfide (c) and cobalt sulfide (d) nanospheres with high solution TEM images inset.

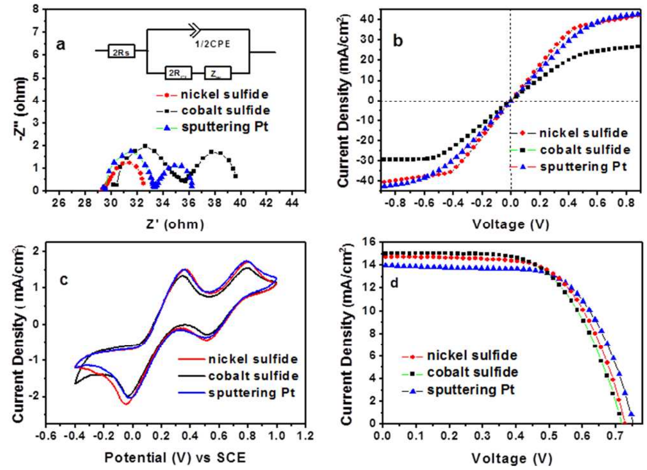

Fig. 2 The EIS Nyquist plots (a), polarization curves (b) and CV curves (c) of the nickel sulfide, cobalt sulfide and sputtering Pt counter electrodes. (d) The J-V curves of different DSSCs integrated with the same photoanode and the nickel sulfide, cobalt sulfide and sputtering Pt as counter electrodes.

substrates. Unfortunately, we could not get the data of surface areas because the films were too thin to meet the lowest requirement in BET test.

From the HRTEM image inset in Fig. 1c and Fig. 1d we can measure the lattice spacing of the nickel sulfide and cobalt sulfide crystalline grain is about 0.272 nm and 0.283 respectively, which corresponds to the (222) lattice plane spacing of Ni_3S_4 and the (211) lattice plane spacing of Co_3S_4. The result was in accordance with XRD data in Fig S1. However, the EDS and XPS results shown in Fig. S2 indicated the atomic ratio of sulfur to metal was not 4:3, which demonstrate that there are some other phases or amorphous nickel sulfide or cobalt sulfide in the nanospheres besides Ni_3S_4 and Co_3S_4.

Electrochemical impedance spectroscopy (EIS) is widely applied in the investigation of the electrochemical behaviour of the counter electrodes.[19-21] Fig. 2a is the Nyquist plots of the corresponding symmetrical cells with the equivalent circuit in the inset. The simulated data from the EIS spectra are summarized in Table 1. The nickel sulfide and cobalt sulfide counter electrodes show pretty small R_{ct} of 0.43 $\Omega \cdot cm^2$ and 0.75 $\Omega \cdot cm^2$ respectively, which are comparable to that (0.56 $\Omega \cdot cm^2$) of sputtering Pt, indicating the catalytic activities of the nickel sulfide, cobalt sulfide nanospheres are comparable to that of sputtering Pt. The similar serial resistances R_S listed in Table 1 indicate that the electrical conductivities of nickel sulfide and cobalt sufide film are comparable to sputtering Pt.

Polarization curves and cyclic voltammetry (CV) were used to further demonstrate the catalytic activity of the counter electrodes. From the polarization curves in Fig. 2b, the slope values at 0 V of nickel sulfide and cobalt sulfide counter electrodes are close to that of sputtering Pt, indicating that the catalytic activities of nickel sulfide and cobalt sulfide counter electrodes are comparable to sputtering Pt, which is corresponding to the EIS data. From the polarization curves, the values of the limiting diffusion current density of the symmetrical cells assembled with nickel sulfide, cobalt sulfide and the sputtering Pt electrodes respectively range from 30 mA/cm^2 to 40 mA/cm^2, which are much larger than short-circuit current of the DSSCs assembled with the three counter electrodes showed in Fig. 2d. From our previous research on the maximum performance of the counter electrodes, we can see the three counter electrodes plays no obvious negative effects on the assembled DSSCs.[22] CV curves in Fig. 2c all show two pairs of redox peaks. The two redox peaks at more negative potentials correspond to the reaction of

$$3I^- \leftrightarrow I_3^- + 2e^- \quad (1)$$

The catholic peak current densities (I_{pc}) indicate the catalytic activities of the CEs for I_3^- reduction in DSSCs. The nickel sulfide and cobalt sulfide thin films show comparable I_{pc} to that of the sputtering Pt, demonstrating that nickel sulfide and cobalt sulfide counter electrodes comparable catalytic activities to the sputtering Pt.

The J-V curves of integrated DSSCs based on nickel sulfide and cobalt sulfide counter electrodes were shown in Fig. 2d. The detailed photovoltaic parameters are summarized in Table 1. From Fig. 2d, the assembled DSSCs based on the nickel sulfide and cobalt sulfide thin film reach power conversion efficiencies of 6.81% and 6.59% on the first day, which are comparable to that (6.85%) of sputtering Pt. The high performances of nickel sulfide and cobalt sulfide counter electrodes benefit from their high catalytic activities and electrical conductivities as well as their rough surface and accessible inner surface for electrolyte filling.

Long-term stability is an important factor for device industrialization. The sensitizer, electrolyte and sealant have been considered as key factors for long service life of DSSCs.[23-25] Although some reports have claimed that the Pt counter electrodes are at the risk of corrosion in the triiodide-containing solutions to generate platinum iodides such as PtI_4, Pt counter electrodes are more stable than the mentioned factors above.[26] Long-term stability of the DSSCs assembled with nickel sulfide, cobalt sulfide and sputtering Pt in 504 hours were shown in Fig. 3. From the variation of Eff, J_{sc}, V_{oc} and FF of the DSSCs during 504 hours, we can see that the performances of the DSSCs stayed stable and showed no obvious degration. The CV curves of each counter electrode for 50 cycles were further obtained to investigate the stability of the CEs. The variations of the three counter electrodes are shown in Figure S3. The photovoltaic

Table 1 Photovoltaic performance, EIS parameters of the CEs with nickel sulfide、cobalt sulfide nanospheres and sputtering Pt.

CE	V_{OC} (V)	J_{SC} ($mA\cdot cm^{-2}$)	FF (%)	PCE (%)	R_{ct} ($\Omega \cdot cm^2$)	R_s ($\Omega \cdot cm^2$)	CPE ($\mu F \cdot cm^{-2}$)
nickel sulfide	0.73	14.70	63.50	6.81	0.43	4.18	10.9
cobalt sulfide	0.72	15.03	61.00	6.59	0.75	4.30	18.2
sputtering Pt	0.75	14.00	65.24	6.85	0.56	4.20	17.7

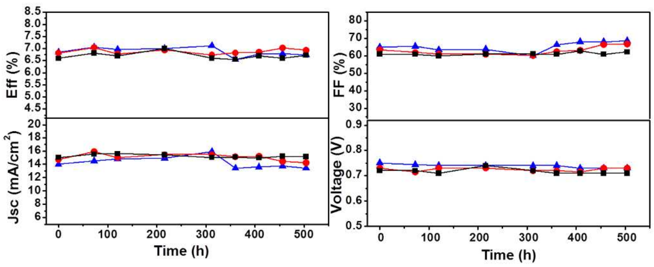

Fig. 3 Photovoltaic parameters variations of the DSSCs assembled with nickel sulfide (—●—), cobalt sulfide (—■—) and sputtering Pt (—▲—) as counter electrodes subjected to aging for 504 hours.

parameters and CV data demonstrated that nickel sulfide and cobalt sulfide counter electrodes had good stability compared to Pt. It is worth mentioning that, during the 504 hours, the highest power conversion efficiencies of nickel sulfide, cobalt sulfide and sputtering Pt cells were 7.02%, 7% and 7.12% respectively.

In summary, the nickel sulfide and cobalt sulfide hierarchical nanospheres counter electrodes were fabricated using a facile one-step in-situ solvothermal method. The introduction of the hierarchical structure to the counter electrodes lead to large interface contact between the electrolyte and the nickel sulfide, cobalt sulfide counter electrodes, accessible electrolyte filling in the counter electrode and good electrode conductivity, which is benefit for the catalytic reaction of the I^-/I_3^-. The as-synthesized nickel sulfide and cobalt sulfide thin films were characterized with various electrochemical methods and showed comparable catalytic activities as counter electrodes to sputtering Pt. The power conversion efficiencies of the DSSCs using nickel sulfide (6.85%) and cobalt sulfide (6.59%) thin films as the counter electrodes were comparable to that using sputtering Pt (6.81%). The DSSCs assembled with nickel sulfide and cobalt sulfide counter electrodes showed pretty high stability during 504 h of aging at room temperature without illumination indicating that nickel sulfide and cobalt sulfide counter electrodes showed good stability.

We thank the financial support from the National Natural Science Foundation of China (11174129, 61377051 and 51272102), the National Basic Research Program of China (2011CB933303 and 2013CB632404), the Jiangsu Provincial Science and Technology Research Program (BK2011056, BE2012089 and BK20130053). We thank Dr. Hao Gao and Dr. Zhiqiang Wang for their information discussions and experimental and technical assistance.

Notes and references

[a]*National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, P. R. China. E-mail: yutao@nju.edu.cn*
[b]*Eco-Materials and Renewable Energy Research Center (ERERC), Department of Physics, Nanjing University, Nanjing 210093, P. R. China.*
[c]*Department of Materials Science and Engineering, Nanjing University, Nanjing, 210093, P. R. China*
[d]*Kunshan Innovation Institute of Nanjing University, Kunshan 215347, P. R. China.*

1 B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737-740**.**
2 M. Grätzel, *Nature*, 2001, **414**, 338-344.
3 A. Yella, H. W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, M. d. Khaja Nazeeruddin, E. W. G. Diau, C. Y. Yeh, S. M. Zakeeruddin, M. Grätzel, *Science*, 2011, 629-34.
4 Y. Saito, T. Kitamura, Y. Wada, S. Y. Ã, *Chem. Lett*, 2002, 1060-1061.
5 Q. H. Li, J. H. Wu, Q.W. Tang, Z. Lan, P. J. Li, J. M. Lin, L. Q. Fan, *Electrochem. Commun.*, 2008, **10**, 1299-1302.
6 K. Imoto, K. Takahashi, T. Yamaguchi, T. Komura, J. Nakamura, K. Murata, *Sol. Energy Mater. Sol. Cells*, 2003, **79**, 459-469.
7 S. I. Cha, B. K. Koo, S. H. Seo, D. Y. Lee, *J. Mater. Chem*, 2010, **20**, 659-662.
8 J. D. Roy-mayhew, D. J. Bozym, C. Punckt, I. A. Aksay, *ACS nano*, 2010, **4**, 6203-6211.
9 S. Solar, C. Based, L. Kavan, J. H. Yum, M. Grätzel, *ACS nano*, 2011, **5**, 165-172.
10 M. K. Wang, A. M. Anghel, B. Marsan, N. C. Ha, N. Pootrakulchote, S. M. Zakeeruddin, and M. Grätzel, *J. Am. Chem. Soc.*, 2009, **131**, 15976–15977.
11 H. C. Sun, D. Qin, S. Q. Huang, X. Z. Guo, D. M. Li, Y. H. Luo and Q. B. Meng, *Energy Environ. Sci.*, 2011, **4**, 2630–2637.
12 D. Hwang, H. Lee, S. Y. Jang, S. M. Jo, D. H. Kim, Y. Seo, D. Y. Kim, *ACS Appl. Mater. Interfaces*, 2011, **3** (7), 2719–2725.
13 P. N. Zhu, M.V. Reddy, Y. Z. Wu, S. J. Peng, S. Y. Yang, A. S. Nair, K. P. Loh, B. V. R. Chowdari, and S. Ramakrishna, *Chem Commun.*, 2012 , **48**(88), 10865-10867.
14 N. Q. Fu, Y. Y. Fang, Y. D. Duan, X. W. Zhou, X. R. Xiao, and Y. Lin, *ACS Nano*, 2012, **6**, 9596-9605.
15 G. Q. Wang and S. P. Zhuo, *Phys. Chem. Chem. Phys.*, 2013, **15**, 13801-13804.
16 X. Y. Zhang, X. Chen, S. M. Dong, Z. H. Liu, X. H. Zhou, J. H. Yao, S. P. Pang, H. X. Xu, Z. Y. Zhang, L. F. Li and G. L. Cui, *J. Mater. Chem.*, 2012, **22**, 6067–6071.
17 F. Gong, H. Wang, X. Xu, G. Zhou, Z. -S. Wang, *J. Am. Chem. Soc.*, 2012, **134**, 10953-10958.
18 J. Yang, C. X. Bao, J. Y. Zhang, T. Yu, H. Huang, Y. L. Wei, H. Gao, G. Fu, J. G. Liu, Z. G. Zou, *Chem Commun.*, 2013, **49**, 2028-2030.
19 R. Kern, R. Sastrawan, J. Ferber, R. Stangl and J. Luther, Electrochimica Acta 2002, **47,** 4213-4225.
20 Q. Wang, J. Moser, and M. Grätzel, J. Phys. Chem. B, 2005, **109**, 14945-14953.
21 M. X. Wu, X. Lin, T. H. Wang, J. S. Qiu and T. L. Ma, Energy Environ. Sci., 2011, **4**, 2308-2315.
22 C.X. Bao, H. Huang, J. Yang, H. Gao, T. Yu., J. G. Liu, Y. Zhou, Z. S. Li and Z. G. Zou, *Nanoscale*, 2013, **5**, 4951-4957.
23 M. K. Kashif, M. Nippe, N.W. Duffy, C. M. Forsyth, C. J. Chang, J. R. Long**,** L. Spiccia and U. Bach, *Angew. Chem. Int. Ed.*, 2013, **52**, 5527 -5531.
24 G. G. Xue, Y. Guo, T. Yu, J. Guan, X. R. Yu, J. Y. Zhang, J. G. Liu, Z. G. Zou, *Int. J. Electrochem. Sci.*, 2012, **7**, 1496-1511.
25 M. Grätzel, *C. R. Chimie*, 2006, **9**, 578-583.
26 E. Olsen, G. Hagen, S. E. Lindquist, Sol. Energy Mater. Sol. Cell, 2000, **63**, 267-273.