

Ultrafast Electrochemical Preparation of Graphene/CoS Nanosheets Counter Electrodes for Efficient Dye-Sensitized Solar Cells

Chongyang Zhu,^{‡a} Huihua Min,^{‡a} Feng Xu,^{*ab} Jing Chen,^c Hui Dong,^a Ling Tong,^d Yimei Zhu,^b and Litao Sun^{*a}

^a*SEU-FEI Nano-Pico Center, Key Laboratory of MEMS of Ministry of Education, Southeast University, Nanjing 210096, China.*

E-mail: fxu@seu.edu.cn; Fax: +86-25-83792939; Tel: +86-25-83792632

^b*Condensed Matter Physics & Materials Science Department, Brookhaven National Laboratory, Upton, NY 11973, USA*

^c*School of Electronic Science & Engineering, Southeast University, Nanjing 210096, China.*

^d*Jiangnan Graphene Research Institute, Changzhou 213149, China*

[‡]These authors contributed equally to this work.

Utilizing inexpensive, high-efficiency counter electrodes (CEs) to replace the traditional platinum counterparts in dye-sensitized solar cells (DSSCs) is significantly beneficial. In this paper, we detail how we synchronously prepared composite CEs of CoS nanosheet arrays and reduced graphene oxide (rGO) layers for the first time via a low temperature, ultrafast one-step electrochemical strategy. With this approach, the whole fabrication process of the composite CEs was only a fraction of the averaged time (~15 hours) using other methods. The DSSC assembled with the rGO-CoS composite CE

achieved an enhanced power conversion efficiency (PCE) of 8.34%, which is dramatically higher than 6.27% of pure CoS CE-based DSSC and even exceeds 7.50% of Pt CE-based DSSC. The outstanding PCE breakthrough is indubitably attributed to the enhancement in electrocatalytic ability of the rGO-CoS composite CE due to the incorporation of highly conducting rGO layers and the GO layers-induced growth of CoS nanosheet arrays with higher density and larger surface area. Therefore, lower charge-transfer resistance and higher exchange current density can be achieved as corroborated by the electrochemical impedance spectra (EIS) and Tafel polarization curves (TPCs). Further experiments also proved that the electrochemical strategy exhibited its universality of fabricating other graphene-enhanced functional composite of chalcogenide films.

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted great attention due to their low cost, easy fabrication, and relatively high power conversion efficiency (PCE)¹⁻³. As one of the most important components, a platinum-loaded conducting substrate is commonly employed as the counter electrode (CE) due to its superior electrocatalytic activity toward I⁻/I₃⁻ redox couple⁴⁻⁷. However, platinum is rare on earth, and hence, very expensive. Considerable effort has been devoted to developing alternatives to Pt, including functional carbon nanomaterials⁸⁻⁹, conducting polymers¹⁰⁻¹¹, and transition-metal compounds¹²⁻¹⁴. Among these, cobalt sulfide (CoS) is regarded as one promising candidate with outstanding electrocatalytic activity toward the I⁻/I₃⁻ redox couple. To date, CoS nanostructures, including those with honeycomb-like morphology, acicular nanorod arrays, nanosheet arrays, and nanotube arrays have been applied successfully as the CEs that exhibit different electrocatalytic activities¹⁵⁻¹⁸. Obviously, the electrocatalytic activities of the CoS CEs greatly depended on their structures and/or morphologies that are susceptible to the strategies used in their preparation. Moreover, although CoS is an active electrocatalytic species, its charge conductivity and mobility are not up to the mark. Hence, much attention has been paid to incorporating materials with high electronic conductivity into CoS CEs along with optimizing their structure and morphology.

Recently, graphene has triggered much interest due to its excellent electronic conductivity, high transparency, and large specific surface area¹⁹. These properties make it very promising for applications in the CEs²⁰⁻²². In particular, graphene as highly conductive scaffold has been incorporated into the CoS CEs by numerous methods. For instance, Das *et al.*²³ and Bi *et al.*²⁴ prepared graphene films via a CVD system that were used as the substrate to fabricate CoS nanoparticle/graphene CEs. However, the CVD method required the utilization of high temperature up to 1000 °C to prepare graphene film, which restricted

its widespread application. Duan *et al.*²⁵ fabricated graphene-CoS₂ composite CEs through a hydrothermal synthesis and achieved a PCE of 6.55%. Further, Hu *et al.*²⁶ and Miao *et al.*²⁷ used electrophoretic deposition to fabricate graphene-CoS composite CEs, but the whole process took up about thirty hours. All these methods suffered from the restrictions of requiring high temperatures, toxic chemical agents, and tedious procedures that are time or labor consuming. Thus, the challenge remains of seeking an efficient, facile, and low temperature route to fabricate graphene-CoS CE.

In this study, we demonstrate how we synchronously prepared composite CEs of CoS nanosheet arrays and reduced graphene oxide (rGO) layers for the first time via a low temperature, ultrafast one-step electrochemical strategy. With this approach, the whole fabrication process of the composite CEs was only a small percentage of the average time (~15 hours) using other methods. In this strategy, the pre-prepared GO layers on ITO substrates provided a large number of active sites for the nucleation and crystal growth of CoS nanosheets. Thus, denser CoS nanosheet arrays with smaller size were formed compared with the products without incorporation of GO layers. This structure would allow more electrons to transport from external circuit to I-/I₃⁻ redox couple due to the relatively large surface area, resulting in improved catalytic activity. More importantly, the oxygen-containing groups on original GO layers also were effectively removed under applied negative potential, and the electronically conductive rGO layers were formed. It's demonstrated that the DSSCs assembled with rGO-CoS composite CEs fabricated by the electrochemical strategy exhibited considerably high PCEs compared with the reported ones with rGO-CoS composite CEs.

2. Results and discussion

[Fig. 1](#) is a schematic showing the electrochemical strategy for preparing the CoS nanosheets/graphene composite CEs. First,

pristine GO layers were pre-prepared on the ITO substrate by spray-coating method. Then, the CoS nanosheet arrays were directly grown on the GO/ITO substrate by electrochemical deposition; meanwhile, the GO layers also were synchronously electrochemically reduced by removing oxygen-containing groups on the surface of GO layers, forming reduced GO (rGO) layers with highly electronic conductivity. The whole process is facile and fast. The as-prepared rGO-CoS nanosheet composite CEs are able to be directly assembled into DSSCs without needing additional post-treatments. The electrochemical strategy has come true, as corroborated by the results in [Fig. 2](#) and [Fig. 3](#).

The morphology of the rGO-CoS nanosheet composite CEs is shown in [Fig. 2b](#) and exhibits 2D nanosheet arrays vertically grown on the rGO/ITO substrates, which is similar to the product directly electrodeposited on bare ITO substrate ([Fig. 2a](#)). However, after incorporating the GO layers, the former grew more densely, with smaller interspaces each other and show a distinct decrease in diameter from 0.6–0.8 μm to 0.3–0.4 μm . Generally, the binding effect existed between the negatively charged oxygen-containing groups on GO surface and the positively charged cations in solution. Therefore, a large number of active sites were provided by the GO layer for the crystal nucleation and growth of CoS nanosheets during the electrodeposition. As a result, smaller-sized, denser CoS nanosheet arrays were formed compared with the products without the incorporation of GO layers. The binding effect also was frequently applied to control the morphology and structure of the products hydrothermally grown on GO layers^{28–29}. TEM image ([Fig. 2c](#)) of rGO-CoS composite film scraped from the substrate displays an individual 2D CoS nanosheet with the same morphology as SEM observation. Ring-like ED patterns (inset of [Fig. 2c](#)) of the nanosheet reveal its polycrystalline character. Further high-resolution TEM image of the nanosheets ([Fig. 2d](#)) shows that the zone I, II, and III correspond to the (102), (101), and (100) crystallographic planes of CoS, respectively, in good agreement with the polycrystalline conjecture.

Crystal phase of CoS nanosheets and rGO-CoS nanosheets also was confirmed by XRD measurements (Fig. 3a). Both the two CEs have the nearly same diffraction peaks located at 30°, 34°, and 35°, which can be readily indexed to the (100), (002), and (101) planes of the hexagonal phase CoS (JCPDS, PDF no. 75-0605). However, the diffraction peak of graphene at 26° is covered by the broad peak at around 23° for SiO₂ in the substrate due to the much smaller quantity of rGO layers compared to the substrate³⁰. Therefore, raman spectroscopy was used to further corroborate the presence of rGO in the rGO-CoS composite CE, as shown in Fig. 3b. Two main characteristic peaks at 1356 cm⁻¹ and 1580 cm⁻¹ were observed in all samples, corresponding to the D-band and G-band of polycrystalline graphite³¹, respectively. The G-band usually is assigned to the E_{2g} phonons of C sp² atoms, while the D-band is attributed to the effect of particle size. From Fig. 3b, the D/G intensity ratios of GO and rGO are 0.786 and 0.84 respectively. This change is considered as the formation of more graphitic domains with smaller size upon electrochemical reduction³²⁻³³. Notably, the D/G ratio for the rGO-CoS composite CE is increased further to 1.03, which can be explained by the partial insertion of CoS nanosheets into the GO layers at the beginning of electrochemical process, thus resulting in more disordered carbon structure²⁸. In addition, the small 2D peak at around 2750 cm⁻¹ was observed for both the rGO and rGO-CoS samples, further demonstrating the existence of rGO³⁴⁻³⁵. Fig. 3c presents the FTIR spectroscopy of the GO, rGO, and rGO-CoS composite CEs. Before reduction, the three bands of GO, evident at 1050 cm⁻¹, 1720 cm⁻¹, and 3430 cm⁻¹, are due, respectively, to the C–O (ν(epoxy or alkoxy)), the C=O in the carboxylic acid and carbonyl moieties (ν(carbonyl)), and the O–H stretching mode of intercalated water³². This result clearly reveals that exfoliated graphite has turned into graphene oxide via Hummer's method. However, in the case of pure rGO and rGO-CoS after electrochemical treatment, the peak at 3430 cm⁻¹ disappears, while other oxygen-containing stretches, such as C=O and C–O, also weaken. This result implies that high-purity rGO can be obtained using the electrochemical approach.

The electrocatalytic ability and conductivity of pure CoS, rGO-CoS, and Pt CEs were investigated by cyclic voltammetry (CV), electrochemical impedance spectrum (EIS), and the Tafel polarization curve (TPC). From the CV results in Fig. 4a, two pairs of typical oxidation and reduction peaks clearly are observed for each CV curve. The left pair corresponds to the reaction of equation (1), and the right pair is attributed to the process of equation (2)³⁶. Note that the left pair of peaks (Ox-1 and Red-1) is the main concerns of our analysis because the function of a DSSC CE is to catalyze the reduction of I₃⁻ ions. Generally, the peak current density and the peak-to-peak separation (E_{pp}), which is associated with the reversibility of the redox reaction, are two important parameters for evaluating catalytic activities³⁷. From Fig. 4a, the rGO-CoS composite CE has the highest peak current density, implying that the electrocatalytic ability of rGO-CoS CE toward I-/I₃⁻ is superior to that of pure CoS and even better than that of Pt. In addition, its E_{pp} of 570 mV is lower than 680 mV of CoS. Thus, we confirmed that the rGO-CoS composite CE prepared by the one-step electrochemical method is a remarkable electrochemical catalyst.



EIS represents the intrinsic interfacial charge transfer and charge transport kinetics at the electrode/electrolyte interface³⁸. It has been tested using symmetric cells fabricated with two identical electrodes. Fig. 4b demonstrates the Nyquist plots of pure CoS, rGO-CoS, and Pt CEs, respectively. The inset shows the equivalent circuit model used for DSSCs. As displayed in Fig. 4b, the high-frequency intercept on the real axis determines the serial resistance (R_s), while two semicircles observed for each curve in the high-frequency (left) and low-frequency (right) regions are assigned, respectively, to the charge-transfer resistance (R_{ct}) at the electrode/electrolyte interface, and the ionic diffusion impedance (Z_N) of the I-/I₃⁻ redox couple in the electrolyte³⁹.

Table 1 lists the fit data for R_s and R_{ct} . Obviously, the R_s value decreases for the rGO-CoS composite CE compared with pure

CoS CE, revealing that the incorporation of rGO layers is beneficial for improving the conductivity of rGO-CoS. Moreover, the rGO-CoS CE has the smallest R_{ct} of $2.1 \Omega \text{ cm}^2$. The value is slightly lower than that of Pt CE, and only one third of $7.1 \Omega \text{ cm}^2$ of pure CoS CE. This result suggests that the incorporation of rGO layers can markedly decrease the internal resistance and thus accelerate the reduction process of I_3^- to I^- at the electrode/electrolyte interface. TPC also was conducted on the same symmetric cells used for EIS measurements to further elucidate the catalytic activity for the I_3^- reduction of Pt, CoS, and rGO-CoS CEs. From Fig. 4c, the rGO-CoS composite CE shows the largest slope of the anodic or cathodic branches around the Tafel zone compared with the Pt and pure CoS CEs, suggesting a higher exchange current density (J_0) on the electrode surfaces⁴⁰. Since J_0 also is related to the charge-transfer resistance (R_{ct}), it also can be calculated by equation (3) ,

$$J_0 = \frac{RT}{nFR_{ct}} \quad (3)$$

where R is the gas constant, F is Faraday's constant, T is the absolute temperature, and n is the number of electrons involved with the reduction of I_3^- . Accordingly, the calculated J_0 follows the order of rGO-CoS > Pt > CoS, in good agreement with the tendency of the peak current density observed in the CV curves and EIS results.

Photocurrent density-voltage (J - V) curves of the DSSCs with pure CoS, rGO-CoS, and commercial Pt CEs were obtained under a light intensity of 100 mW/cm^2 . A typical schematic configuration of the DSSC, based on the rGO-CoS composite CE, is illustrated in Fig. 5a and the J - V curves obtained are shown in Fig. 5b. The inset compares the optical photographs of the rGO-CoS composite CE and pure CoS CE. The photovoltaic parameters are summarized in Table 1. The DSSC with pure CoS CE yielded a PCE of 6.26%, comparable to that obtained in previous research¹⁶. Its photocurrent density (J_{sc}) is only 13.82 mA/cm^2 , which is the lowest among the three DSSCs; on the contrary, the J_{sc} of the DSSC with rGO-CoS composite CE is the highest (17.03 mA/cm^2), around 23% increase compared with that of pure CoS-based DSSC. Therefore, the DSSC with the

rGO-CoS composite CE achieved an enhanced PCE of 8.34% that is greatly increased by 33% compared with 6.26% of the CoS CE-based DSSC. Noticeably, the enhanced PCE is even superior to 7.5% of Pt CE-based DSSC. This demonstrated the feasibility of using the rGO-CoS CE to supersede the costly traditional Pt CE.

Since introducing rGO layers can greatly improve the properties of CEs and thus enhance the PCE of DSSCs, the GO loading content on substrates should be a paramount issue in deciding cell performance. Fig. 6a demonstrates the compared current-voltage (J - V) characteristics and EIS parameters based on rGO-CoS CEs fabricated by spray-coating GO solutions with different concentrations. All the DSSCs with rGO-CoS composite CEs show higher PCEs compared with the DSSC with pure CoS CE in Fig. 5b. The PCE increased from 7.35% to 8.34% with increasing GO concentration from 0.06 mg/mL to 0.09 mg/mL, and then declines to 7.28% corresponding to concentration of 0.12 mg/mL. The changes in PCE can be explained by the EIS measurements in Fig. 6b and c, which reveal that the R_s and R_{ct} of rGO-CoS CEs follow the order of 0.12 mg/mL > 0.06 mg/mL > 0.09 mg/mL, *i.e.*, totally consistent with the change tendency of PCE. Further AFM investigation (Fig. 6 d-f) shows that GO concentration of 0.09 mg/mL exhibit a relatively flat morphology, whereas the high-concentration GO solution resulted in wrinkles and stacking, which would increase the serial resistance, as reflected by the EIS results. In turn, the wrinkles and stacking of GO layers also greatly affects the morphology of CoS nanosheet arrays, including their density and size (Fig. 6 g-i). Obviously, the CoS nanosheet arrays grown on GO layers with a concentration of 0.09 mg/mL exhibits a higher density and smaller size, which would provide a larger surface area for yielding a higher exchange current. The extensive investigation proves that GO layers exert a correlative effect on the resultant DSSC performance.

Our electrochemical strategy for preparing the rGO-CoS CEs exhibits attractive superiorities compared with other

approaches including conventional hydrothermal or CVD methods, as summarized in [Table 2](#). The strategy allows the deposition of CoS nanosheets and the reduction of GO at low temperature, and requires relatively inexpensive equipments. The whole process of fabricating the CEs is facile without additional post-treatments including the doctor-blade or spray-coating procedures^{25,40-41}. Importantly, it provides a ultrafast route to prepare the rGO-CoS CE only in half an hour, which is several tens of times shorter than the average time (~15 h) using other approaches ([Table 2](#)). Due to the superior electrocatalytic activity, the composite films directly prepared on substrates produced a high PCE of 8.34%, indicating the unparalleled advantages of our electrochemical strategy in preparing the composite CEs. Furthermore, the electrochemical strategy also exhibits its universality in fabricating graphene-enhanced chalcogenide functional composite films. Here, we, for the first time, used the strategy to prepare rGO-MoS₂ and rGO-NiS composite CEs⁴²⁻⁴³ that also exhibited enhanced performances in DSSCs compared with the previous works^{24,44-45}, as shown in [Fig. 7](#) and [Table 3](#). Similarly, the fabrication process of both the two composite CEs also was ultrafast. Based on the above results, we believe that electrochemical strategy could be a universal method for fabrication of graphene-enhanced chalcogenide functional composite films.

3. Conclusion

In conclusion, we presented a facile, low temperature, and ultrafast electrochemical strategy to fabricate the rGO-CoS composite CEs that are low-cost and high-efficiency and can supersede costly traditional Pt CE in DSSCs. In this strategy, electroreduction of original GO layers and electrodeposition of CoS nanosheet arrays was synchronous. It's demonstrated that the incorporation of rGO layers could greatly decrease the charge-transfer resistance and improve the electrocatalytic ability. Furthermore, the GO layers-induced growth of CoS nanosheet arrays with higher density and larger surface area can provide

larger surface area for yielding higher exchange current. Thus, the DSSC based on the optimized rGO-CoS composite CEs showed marked enhancement in PCE compared with the previously reported works involved with other fabrication approaches. Further experiments also proved that our electrochemical strategy has potential for further exploiting other graphene-enhanced chalcogenide functional composite films with applications in electronic and optoelectronic devices.

4. Experimental

4.1 Preparation of rGO-CoS composite CE

Graphene oxide (GO) was prepared by chemically exfoliating graphite via the modified Hummer's method⁴⁶⁻⁴⁷. Then, solutions of GO ethanol of different concentrations (0.06–0.12 mg/mL) were spray-coated on the pre-cleaned ITO substrates heated at 50 °C, so forming GO layers. Afterwards, the GO layers on ITO substrates acted as working electrodes to electrodeposit CoS nanosheets via a three-electrode electrochemical system with a platinum sheet as a counter electrode (We note that the counter electrode is entirely different from the definition of CEs in DSSCs) along with a saturated calomel electrode (SCE) as a reference electrode. Meanwhile, the GO layers with oxygen-containing groups also were effectively reduced under the applied negative potential and thus, the rGO-CoS nanosheets as composite CEs were realized synchronously^{17,30}. The whole electrochemical process was carried out in a 40 mL aqueous solution electrolyte containing 5 mM $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 150 mM $\text{CH}_4\text{N}_2\text{S}$ at 40 °C. The deposition potential was -0.83V versus SCE, and the deposition time was 0.5 h. For comparison, pure CoS nanosheet arrays as the CE were also directly electrodeposited on ITO substrate without GO layers by a similar electrochemical procedure. The standard Pt CE was purchased from Dalian HepatChroma SolarTech Co. Ltd.

4.2 DSSC fabrication and testing

A layer of TiO₂ nanocrystal anode film with a thickness of 12 μm and active area of 0.30 cm² was prepared by the screen-printing technique and subsequently calcined at 450 °C for 30 min. The resultant TiO₂ photoanodes were sensitized in a 0.3 mM ethanol solution of ruthenium dye N719 at 60°C for 3h. Then, they were assembled with Pt, CoS, and rGO-CoS CEs into DSSCs, respectively. The DSSC electrolyte with 0.1 M LiI, 0.05 M I₂, 0.3 M 1,2-dimethyl-3-propylimidazolium iodine, and 0.5 M tert-butylpyridine in 3-methoxypropionitrile was injected into the gap between the photoanode and CE by capillarity action. The current–voltage characteristics of DSSCs were assessed with a Newport solar simulator (300W Xe lamp source), and a Keithley 2400 source meter under 1 sun illumination (AM 1.5G, 100 mW/cm²).

4.3 Characterization

The phase identification and surface morphology of the products were characterized by a powder X-ray diffractometer (XRD, ARL XTRA, Thermo Electron Co., USA) with Cu K_α radiation and a scanning electron microscope (SEM, JSM-7600F, JEOL, Japan) equipped with an energy dispersive X-ray spectrometer (EDS). Further structural analyses were carried out by a transmission electron microscope (TEM, ARM200, JEOL, Japan) and the electron diffraction (ED) pattern. Raman spectroscopy was recorded on Renishaw laser Raman spectrometer, using a 488 nm laser source. Fourier-transform infrared (FT-IR) spectra were collected with an FTIR-650 spectrophotometer by the KBr pellet method. Atomic force microscope (AFM) images were acquired using Bruker MultiMode 8 in a “tapping” mode. Cyclic voltammetry (CV) was carried out in a three-electrode system with an anhydrous acetonitrile solution of 0.1 M LiClO₄, 10 mM LiI, and 1 mM I₂ at a scan rate of 50 mV/s, using a platinum sheet as the counter electrode, a SCE as the reference electrode, and the as-prepared CEs as the

working electrode. Electrochemical impedance spectra (EIS) and Tafel polarization curves (TPCs) of various CEs were measured on a CHI-660D electrochemical workstation (CH Instruments, Inc., USA). The EIS were carried out at zero bias using symmetrical cells by applying an AC voltage with 10 mV amplitude in a frequency range from 0.05 Hz to 100 kHz. The resultant impedance spectra were fitted with ZsimpWin software. The Tafel Polarization Curves of the CEs were obtained using symmetrical cells at a scan rate of 10 mV/s. The electrolytes used in both EIS and TCP measurements were the same as those used in the DSSCs.

Acknowledgement. This work was supported by the National Basic Research Program of China (973 Program, Grant No. 2015CB352106), the National Natural Science Foundation of China (NSFC, Grant Nos. 51372039, 51202028), and the Jiangsu Province Science and Technology Support Program (Grant No. BK20141118). The work at Brookhaven National Lab is supported by U.S. DOE-BES under Contract number DE-AC02-98CH10886.

References and Notes

- 1 Wu, W. Q.; Feng, H. L.; Rao, H. S.; Xu, Y. F.; Kuang, D. B.; Su, C. Y. Maximizing Omnidirectional Light Harvesting in Metal Oxide Hyperbranched Array Architectures. *Nat. Commun.* **2014**, *5*, 3968.
- 2 Yun, S. N.; Hagfeldt, A.; Ma, T. L. Pt-Free Counter Electrode for Dye-Sensitized Solar Cells with High Efficiency. *Adv. Mater.* **2014**, *26*, 6210–6237.

- 3 Xu, F.; Chen, J.; Wu, X.; Zhang, Y.; Wang, Y. X.; Sun, J.; Bi, H. C.; Lei, W.; Ni, Y. R.; Sun, L. T. Graphene Scaffolds Enhanced Photogenerated Electron Transport in ZnO Photoanodes for High-Efficiency Dye-Sensitized Solar Cells. *J. Phys. Chem. C* **2013**, 117, 8619–8627.
- 4 Calogero, G.; Calandra, P.; Irrera, A.; Sinopoli, A.; Citro, I.; Marco, G. D. A New Type of Transparent and Low Cost Counter-Electrode Based on Platinum Nanoparticles for Dye-Sensitized Solar Cells. *Energy Environ. Sci.* **2011**, 4, 1838–1844.
- 5 Dao, V. D.; Kim, S. H.; Choi, H. S.; Kim, J. H.; Park, H. O.; Lee, J. K. Efficiency Enhancement of Dye-Sensitized Solar Cell Using Pt Hollow Sphere Counter Electrode. *J. Phys. Chem. C* **2011**, 115, 25529–25534.
- 6 Wan, J. W.; Fang, G. J.; Yin, H. J.; Liu, X. F.; Liu, D.; Zhao, M. T.; Ke, W. J.; Tao, H.; Tang, Z. Y. Pt–Ni Alloy Nanoparticles as Superior Counter Electrodes for Dye-Sensitized Solar Cells: Experimental and Theoretical Understanding. *Adv. Mater.* **2014**, 26, 8101–8106.
- 7 Tang, Z. Y.; Wu, J. H.; Zheng, M.; Tang, Q. W.; Liu, Q.; Lin, J. M.; Wang, J. L. High Efficient PANI/Pt Nanofiber Counter Electrode Used in Dye-Sensitized Solar Cell. *RSC Adv.* **2012**, 2, 4062–4064.
- 8 Wu, M. X.; Lin, X.; Wang, T. H.; Qiu, J. S.; Ma, T. L. Low-Cost Dye-Sensitized Solar Cell Based on Nine Kinds of Carbon Counter Electrodes. *Energy Environ. Sci.* **2011**, 4, 2308–2315.
- 9 Xue, Y. H.; Liu, J.; Chen, H.; Wang, R. G.; Li, D. Q.; Qu, J.; Dai, L. M. Nitrogen-Doped Graphene Foams as Metal-Free Counter Electrodes in High-Performance Dye-Sensitized Solar Cells. *Angew. Chem. Int. Ed.* **2012**, 51, 12124–12127.

- 10 Wu, J. H.; Li, Q. H.; Fan, L. Q.; Lan, Z.; Li, P. J.; Lin, J. M.; Hao, S. C. High-Performance Polypyrrole Nanoparticles Counter Electrode for Dye-Sensitized Solar Cells. *J. Power Sources* **2008**, 181, 172–176.
- 11 Kwon, J.; Ganapathy, V.; Kim, Y. H.; Song, K. D.; Park, H. G.; Jun, Y.; Yoo, P. J.; Park, J. H. Nanopatterned Conductive Polymer Films as a Pt, TCO-Free Counter Electrode for Low-Cost Dye-Sensitized Solar Cells. *Nanoscale* **2013**, 5, 7838–7843.
- 12 Sun, H. C.; Qin, D.; Huang, S. Q.; Guo, X. Z.; Li, D. M.; Luo, Y. H.; Meng, Q. B. Dye-Sensitized Solar Cells with NiS Counter Electrodes Electrodeposited by a Potential Reversal Technique. *Energy Environ. Sci.* **2011**, 4, 2630–2637.
- 13 Zhang, Z. Y.; Pang, S. P.; Xu, H. X.; Yang, Z. Z.; Zhang, X. Y.; Liu, Z. H.; Wang, X. G.; Zhou, X. H.; Dong, S. M.; Chen, X.; Gu, L.; Cui, G. L. Electrodeposition of Nanostructured Cobalt Selenide Films Towards High Performance Counter Electrodes in Dye-Sensitized Solar Cells. *RSC Adv.* **2013**, 3, 16528–16533.
- 14 Li, G.; Chen, X. S.; Gao, G. D. Bi₂S₃ Microspheres Grown on Graphene Sheets as Low-Cost Counter-Electrode Materials for Dye-Sensitized Solar Cells. *Nanoscale* **2014**, 6, 3283–3288.
- 15 Lin, J. Y.; Liao, J. H.; Chou, S. W. Cathodic Electrodeposition of Highly Porous Cobalt Sulfide Counter Electrodes for Dye-Sensitized Solar Cells. *Electrochim. Acta* **2011**, 56, 8818–8826.
- 16 Kung, C. W.; Chen, H. W.; Lin, C. Y.; Huang, K. C.; Vittal, R.; Ho, K. C. CoS Acicular Nanorod Arrays for the Counter Electrode of an Efficient Dye-Sensitized Solar Cell. *ACS Nano* **2012**, 6, 7016–7025.

- 17 Wang, M. K.; Anghel, A. M.; Marsan, B.; Ha, N. L. C.; Pootrakulchote, N.; Zakeeruddin, S. M.; Gratzel, M. CoS Supersedes Pt as Efficient Electrocatalyst for Triiodide Reduction in Dye-Sensitized Solar Cells. *J. Am. Chem. Soc.* **2009**, *131*, 15976–15977.
- 18 Guo, W. X.; Chen, C.; Ye, M. D.; Lv, M. Q.; Lin, C. J. Carbon Fiber/Co₉S₈ Nanotube Arrays Hybrid Structures for Flexible Quantum Dot-Sensitized Solar Cells. *Nanoscale* **2014**, *6*, 3656–3663.
- 19 Katsnelson, M. I. Graphene: Carbon in Two Dimensions. *Mater. Today* **2007**, *10*, 20–27.
- 20 Chang, Q. H.; Wang, Z. P.; Wang, J. Z.; Yan, Y.; Ma, Z. J.; Zhu, J. X.; Shi, W. Z.; Chen, Q.; Yu, Q. J.; Huang, L. Graphene Nanosheets Inserted by Silver Nanoparticles as Zero-Dimensional Nanospacers for Dye Sensitized Solar cells. *Nanoscale* **2014**, *6*, 5410–5415.
- 21 Peng, Y.; Zhong, J.; Wang, K.; Xue, B. F.; Cheng, Y. B. A Printable Graphene Enhanced Composite Counter Electrode for Flexible Dye-Sensitized Solar Cells. *Nano Energy* **2013**, *2*, 235–240.
- 22 Wang, H.; Hu, Y. H. Graphene as a Counter Electrode Material for Dye-Sensitized Solar Cells. *Energy Environ. Sci.* **2012**, *5*, 8182–8188.
- 23 Das, S.; Sudhagar, P.; Nagarajan, S.; Ito, E.; Lee, S. Y.; Kang, Y. S.; Choiet, W. B. Synthesis of Graphene-CoS Electro-Catalytic Electrodes for Dye Sensitized Solar Cells. *Carbon* **2012**, *50*, 4815–4821.
- 24 Bi, H.; Zhao, W.; Sun, S. R.; Cui, H. L.; Lin, T. Q.; Huang, F. Q.; Xie, X. M.; Jiang, M. H. Graphene Films Decorated with Metal Sulfide Nanoparticles for Use as Counter Electrodes of Dye-Sensitized Solar Cells. *Carbon* **2013**, *61*, 116–123.

- 25 Duan, X. L.; Gao, Z. Y.; Chang, J. L.; Wu, D. P.; Ma, P. F.; He, J. J.; Xu, F.; Gao, S. Y.; Jiang, K. CoS₂-Graphene Composite as Efficient Catalytic Counter Electrode for Dye-Sensitized Solar Cell. *Electrochim. Acta* **2013**, 114, 173–179.
- 26 Hu, H. W.; Ding, J. N.; Qian, J. F.; Li, Y.; Bai, L.; Yuan, N. Y. Layered CoS/Graphene Nanocomposite as High Catalytic Counter Electrodes for Quantum Dot-Sensitized Solar Cells. *Mater. Lett.* **2014**, 114, 7–10.
- 27 Miao, X. H.; Pan, K.; Wang, G. F.; Liao, Y. P.; Wang, L.; Zhou, W.; Jiang, B. J.; Pan, Q. J.; Tian, G. H. Well-Dispersed CoS Nanoparticles on a Functionalized Graphene Nanosheet Surface: A Counter Electrode of Dye-Sensitized Solar Cells. *Chem. Eur. J.* **2014**, 20, 474–482.
- 28 Gu, Y.; Xu, Y.; Wang, Y. Graphene-Wrapped CoS Nanoparticles for High-Capacity Lithium-Ion Storage. *ACS Appl. Mater. Interf.* **2013**, 5, 801–806.
- 29 Zou, Y. Q.; Wang, Y. NiO Nanosheets Grown on Graphene Nanosheets as Superior Anode Materials for Li-ion Batteries. *Nanoscale* **2011**, 3, 2615–2620.
- 30 Zhou, Y.; Chen, J.; Wang, F.; Sheng, Z.; Xia, X. A Facile Approach to the Synthesis of Highly Electroactive Pt Nanoparticles on Graphene as an Anode Catalyst for Direct Methanol Fuel Cells. *Chem. Commun.* **2010**, 46, 5951–5953.
- 31 Tuinstra, F.; Koenig, J. L. Raman Spectrum of Graphite. *J. Chem. Phys.* **1970**, 53, 1126–1130.
- 32 Guo, H. L.; Wang, X. F.; Qian, Q. Y.; Wang, F. B.; Xia, X. H. A Green Approach to the Synthesis of Graphene Nanosheets. *ACS Nano* **2009**, 3, 2653–2659.

- 33 Stankovich, S.; Dikin, D. A.; Piner, R. D.; Kohlhaas, K. A.; Kleinhammes, A.; Jia, Y. Y.; Wu, Y.; Nguyen S. T.; Ruoff, R. Synthesis of Graphene-based Nanosheets via Chemical Reduction of Exfoliated Graphite Oxide. *Carbon* **2007**, 4, 1558–1565.
- 34 Ferrari, A. C. Raman Spectroscopy of Graphene and Graphite: Disorder, Electron–Phonon Coupling, Doping and Nonadiabatic Effects. *Solid State Commun.* **2007**, 143, 47–57.
- 35 Ferrari, C.; Meyer, J. C.; Scardaci, V.; Casiraghi, C.; Lazzeri, M.; Mauri, F.; Piscanec, S.; Jiang, D.; Novoselov, K. S.; Roth, S.; Geim, A. K. Raman Spectrum of Graphene and Graphene Layers. *Phys. Rev. Lett.* **2006**, 97, 187401.
- 36 Gong, F.; Wang, H.; Xu, X.; Zhou G.; Wang, Z. S. In Situ Growth of $\text{Co}_{0.85}\text{Se}$ and $\text{Ni}_{0.85}\text{Se}$ on Conductive Substrates as High-Performance Counter Electrodes for Dye-Sensitized Solar Cells. *J. Am. Chem. Soc.* **2012**, 134, 10953–10958.
- 37 Roy-Mayhew, J. D.; Bozym, D. J.; Punckt, Christian.; Aksay, I. A. Functionalized Graphene as a Catalytic Counter Electrode in Dye-Sensitized Solar Cells. *ACS Nano* **2010**, 4, 6203–6211.
- 38 Zheng, X. J.; Deng, J.; Wang, N.; Deng, D. H.; Zhang, W. H.; Bao, X. H.; Li, C. Podlike N-Doped Carbon Nanotubes Encapsulating FeNi Alloy Nanoparticles: High-Performance Counter Electrode Materials for Dye-Sensitized Solar Cells. *Angew. Chem. Int. Ed.* **2014**, 53, 7023–7027.
- 39 Guo, J. H.; Shi, Y. T.; Chua, Y. T.; Ma, T. L. Highly Efficient Telluride Electrocatalysts for Use as Pt-free Counter Electrodes in Dye-Sensitized Solar Cells. *Chem. Commun.* **2013**, 49, 10157–10159.

- 40 Bi, E. B.; Chen, Han.; Yang, X. D.; Peng, W. Q.; Gratzel, M.; Han, L. Y. A Quasi Core–Shell Nitrogen-Doped Graphene/Cobalt Sulfide Conductive Catalyst for Highly Efficient Dye-Sensitized Solar Cells. *Energy Environ. Sci.* **2014**, *7*, 2637–2641.
- 41 Wang, G. Q.; Zhang, J.; Kuang, S.; Liu, S. M.; Zhuo, S. P. The Production of Cobalt Sulfide/Graphene Composite for Use as a Low-Cost Counter-Electrode Material in Dye-Sensitized Solar Cells. *J. Power Sources* **2014**, *269*, 473–478.
- 42 Chen, S.; Duan, J. J.; Tang, Y. H.; Jin, B.; Qiao, S. Z. Molybdenum Sulfide Clusters-Nitrogen-Doped Graphene Hybrid Hydrogel Film as an Efficient Three-Dimensional Hydrogen Evolution Electrocatalyst. *Nano Energy* **2015**, *11*, 11–18.
- 43 Sun, H. C.; Qin, D.; Huang, S. Q.; Guo, X. Z.; Li, D. M.; Luo, Y. H.; Meng, Q. B. Dye-sensitized Solar Cells with NiS Counter Electrodes Electrodeposited by a Potential Reversal Technique. *Energy Environ. Sci.* **2011**, *4*, 2630–2637.
- 44 Lin, J. Y.; Chan, C. Y.; Chou, S. W. Electrophoretic Deposition of Transparent MoS₂-Graphene Nanosheet Composite Films as Counter Electrodes in Dye-Sensitized Solar Cells. *Chem. Commun.* **2013**, *49*, 1440–1442.
- 45 Liu, C. J.; Tai, S. Y.; Chou, S. W.; Yu, Y. C.; Chang, K. D. Wang, S.; Chien, F. S. S.; Lin, J. Y.; Lin, T. W. Facile Synthesis of MoS₂/Graphene Nanocomposite with High Catalytic Activity Toward Triiodide Reduction in Dye-sensitized Solar Cells. *J. Mater. Chem.* **2012**, *22*, 21057–21064.
- 46 Bi, H. C.; Yin, K. B.; Xie, X.; Zhou, Y. L.; Wan, N.; Xu, F.; Banhart, F.; Sun, L. T.; Ruoff, R. S. Low Temperature Casting of Graphene with High Compressive Strength. *Adv. Mater.* **2012**, *24*, 5124–5129.
- 47 Hummers, W. S.; Offeman, R. E. Preparation of Graphitic Oxide. *J. Am. Chem. Soc.* **1958**, *80*, 1339.