NiS$_2$ Nanosheet Films Supported on Ti Foils: Effective Counter Electrodes for Quantum Dot-Sensitized Solar Cells

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Ni(OH)$_2$ nanosheet films were fabricated on Ti foils by a simple hydrothermal method and subsequently converted into NiS$_2$ via a Vulcanized post-treatment at high temperature. The resultant NiS$_2$ nanosheet films were applied to quantum dot-sensitized solar cells (QDSSCs) as counter electrodes (CEs), showing great electrocatalytic activity with low charge-transfer resistance and high exchange current density in the redox couple of the polysulfide electrolyte. An optimized power conversion efficiency up to 2.25% was achieved for the optimum NiS$_2$-based QDSSC, suggesting an 51% enhancement in comparison with that of the CdS QDSSC featuring the Pt CE (1.49%).

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Quantum dot-sensitized solar cells (QDSSCs) have attracted great attention due to their low cost, easy fabrication, and high theoretical power conversion efficiency. Quantum dots (QDs) have attractive merits as the light absorber because of, for example, the size-dependence of the optical properties with strong light response, tunable band gaps, and the possibility to achieve high efficiency by generating multiple electron/hole pairs due to the impact-ionization effect in QDs. A typical QDSSC is assembled with a photoanode (e.g., Cu$_2$S, CuS, or PbS), an electrolyte containing a redox couple (e.g., S$^{2−}$/S$_2$$^{2−}$), and a counter electrode (e.g., Pt, CuS, and CoS). To improve the cell performance, significant effort has been devoted to optimizing all of the components in QDSSCs. So far, the highest power conversion efficiency (PCE) of QDSSCs is over 11%.

The counter electrode (CE) is one of the indispensable components in QDSSCs, in which the electron transfer occurs to regenerate the oxidized species in the electrolyte and keep the circuit running. Pt was widely used as the CE material in the early QDSSCs after Gratzel et al. found that it had excellent electric catalytic reduction properties in the I$_3$$^−$/$I^−$ redox couple. However, the catalytic reduction activity of Pt is poorly active in the S$^{2−}$/S$_2$$^{2−}$ redox couple in QDSSCs because sulfur atoms would be actively absorbed on Pt’s surface to reduce its conductivity, consequently generating a considerable overpotential for the electrolyte reduction, and thereby resulting in the performance decrease of QDSSCs. In addition, Pt is an expensive precious metal. To improve the PCE of QDSSCs and lower their cost, many researchers have searched for new alternatives to Pt.

To date, a variety of electrode materials have been developed to use in QDSSCs as CEs, such as carbon materials, chalcogenide, nanostructured composite materials, and organic polymer materials. Among these, chalcogenide electrode materials including CuS, Cu$_2$S, CuS, and PbS have been extensively applied in QDSSCs due to their relatively high electrocatalytic activity in the polysulfide redox system. Among the various metal sulfides, NiS$_2$, a typical p-type semiconductor, has also attracted much attention because of its novel electrical, optical, and magnetic properties for significant potential applications in many fields, for example, dye-sensitized solar cells. However, as compared to NiS, the application of NiS$_2$ films as CEs in QDSSCs is relatively rare. In addition, the direct growth of NiS$_2$ nanostructured films on metal foils has not been reported. The metal foil supported NiS$_2$ films may inherit some advantages from the metal substrates, such as the excellent conductivity and flexibility for potential application in bendable electrochemical devices.

In this regard, a vertical NiS$_2$ nanosheet film consisting of numerous small NiS$_2$ nanorods was grown in situ on Ti foils via a multi-step strategy: high-temperature annealing of Pt foils, subsequently hydrothermal formation of $β$-Ni(OH)$_2$ nanosheet films, and final sulfuration of $β$-Ni(OH)$_2$ into NiS$_2$ nanosheet films. Compared to Pt electrodes, such NiS$_2$ films showed superior electrocatalytic activity toward the reduction of polysulfide electrolyte, which reflected increased PCEs in the corresponding QDSSCs.

**Experimental**

*Preparation of NiS$_2$ counter electrodes.*—The process for preparing NiS$_2$ nanosheet films is shown in Fig. 1. Ti foils (0.1 mm thick, 99.6 wt%, 1 × 1.5 cm) were washed in turn with acetone, ethanol, and deionized water in ultrasonic bath and dried in air. The cleaned Ti foils were then put into the muffle furnace and annealed at 550°C for 30 min to oxidize their surface. An aqueous mixture of 0.36 M CO(NH$_2$)$_2$, 0.14 M NH$_4$F, and 0.07 M Ni(NO$_3$)$_2$ was prepared for future use. Subsequently, the oxidized Ti foils were placed in a Teflon-lined stainless steel autoclave (100 mL) with the above mixing solution and reacted at 150°C for 2 h. After the samples were washed with deionized water and dried naturally, the $β$-Ni(OH)$_2$ films grown on Ti foils were obtained.

These $β$-Ni(OH)$_2$ samples and a combustion boat which contained sulfur powder were put into the tube furnace, and the sulfuration process was performed in a nitrogen environment at a certain temperature for 30 min. Finally, the samples were cooled to room temperature, and the NiS$_2$ products were obtained.

*Preparation of TiO$_2$ nanorods/CdS/CdSe photoanodes.*—Etched TiO$_2$ nanorod arrays (TNARs) on seeded FTO substrates as photoanodes were synthesized as previously described. Briefly, FTO substrates were ultrasonically washed in turn with acetone, ethanol, and deionized water, followed by an immersion treatment in 0.18 M H$_2$SO$_4$ aqueous solution at 70°C for 30 min. Then, the pre-treated FTO substrates were washed, dried and annealed at 550°C for 60 min to obtain the TiO$_2$-seeded FTO substrates. Subsequently, the TNARs were grown on such TiO$_2$-seeded FTO substrates through a hydrothermal process in a solution containing 30 mL DIW, 30 mL concentrated hydrochloric acid (36.0–38.0 wt%) and 3 mL TiCl$_4$ at 150°C for 4.5 h. After cooling to room temperature, the TNAR samples were removed, rinsed with DIW, and then processed by another hydrothermal reaction in the solution of 25 mL DIW and 35 mL concentrated hydrochloric acid at 150°C for 4.5 h.
hydrochloric acid (36.0–38.0 wt%) at 150 °C for 7 h. After cooling and washing treatment, the etched TNARs underwent a calcination process at 450 °C for 2 h.

According to the literature,25,26 deposition of CdS and CdSe QDs onto the etched TiO2 photoanodes was conducted by chemical bath deposition methods in succession: (1) immersing the samples in an aqueous solution containing CdSO4 (20 mM), NH4Cl (60 mM), CN2H4S·H2O (260 mM) at 5 °C for 75 min for the CdS QD-sensitized TiO2 photoanodes; (2) subsequently immersing the CdS QD-sensitized TiO2 samples in a mixture of Na2SeSO3 solution from the reaction of 0.1 M Se, 0.18 M Na2SO3, and 0.16 M Na3NTA at 70 °C for 7 h and 0.08 M Cd(NO3)2solution (v/v = 1:1) at 5 °C for 30 h for the CdS/CdSe QD-sensitized TiO2 photoanodes.

Preparation of Pt CEs.—To fabricate the Pt counter electrodes as reference, 5 mM HPCl3 aqueous (0.01 mL) was drop casted onto the FTO substrates (1 cm × 1.5 cm) and annealed at 400 °C for 20 min after dried in air.

Cell fabrication.—The NiS2 CEs were combined with TNARs/CdS/CdSe photoanodes to organize the QDSSCs by using a 60 μm thick hot-melt sealed film as the spacer. The polysulfide electrolyte composed of 0.5 M Na2S, 0.2 M S, and 0.2 M KCl in a mixture of methanol and DIW (3:7 vol/vol) was injected into the sealed cells. For comparison, Pt and β-Ni(OH)2 CEs were also assembled into cells.

Characterization.—The morphologies of NiS2 nanosheet films were surveyed by field-emission scanning electron microscope (FE-SEM, HITACHI S-4800) and transmission electron microscopy (TEM, F20). The crystal phase was observed by X-ray diffraction (XRD, Panalytical X’pert PRO) at a scanning speed of 20°/min. The observed diffraction peaks of the sample without vulcanization (463.9 eV) peaks of the oxidized Ti foil was obtained, but with a slight redshift. As for oxygen, a distinct O 1s peak located at 529.8 eV of the oxidized Ti foil indicated the formation of TiO2 after the oxidized treatment. The observed diffraction peaks of (111), (200), and 59.2 °= 64.9) was slightly higher than that of the pristine Ti foil (Ra = 64.9), which would provide more crystallization sites for the further growth of Ni(OH)2 nanosheets and facilitate a well contact between the Ti foil and the Ni(OH)2 film.

Results and Discussion

As shown in Fig. 1, the products were prepared by hydrothermal treatment of the oxidized Ti foils in an aqueous solution with 0.36 M CO(NH2)2, 0.14 M NH4F, and 0.07 M Ni(NO3)2 with and without sulfuration at different temperatures. The Ti foils were oxidized via a high-temperature treatment. According to the XPS spectra (Fig. 2), a comparison of spin-energy separation of about 5.9 eV between Ti 2p(1/2) (457.6 eV) and Ti 2p(3/2) (463.5 eV) peaks indicated a normal chemical state of Ti4+ in the pristine Ti foil.27 Fortunately, almost the same energy difference between Ti 2p(1/2) (457.9 eV) and Ti 2p(3/2) (463.9 eV) peaks of the oxidized Ti foil was obtained, but with a slight redshift. As for oxygen, a distinct O 1s peak located at 529.8 eV of the oxidized Ti foil indicated the formation of TiO2 after the oxidized treatment. However, a broad peak of O in the pristine Ti foil sample was produced by the air passivation on the Ti foil surface. Figure 3 shows the 3D and flat images of the surface morphologies of the pristine and oxidized Ti foils. Based on the results, the roughness of the oxidized Ti foil (Ra = 65.9) was slightly higher than that of the pristine Ti foil (Ra = 64.9), which would provide more crystallization sites for the further growth of Ni(OH)2 nanosheets and facilitate a well contact between the Ti foil and the Ni(OH)2 film.

Figure 4a shows the corresponding XRD patterns of the products. The observed diffraction peaks of the sample without vulcanization at 2θ = 33.4° and 59.2° can be assigned to (100) and (110) planes of β-Ni(OH)2 (JCPDS Card No. 14-177).28 After sulfuration of β-Ni(OH)2 at different temperatures, the diffraction peaks of β-Ni(OH)2 disappeared, while the diffraction peaks at 2θ = 27.5°, 31.8°, 45.5°, 56.4°, 58.7°, and 61.3° were respectively attributed to (111), (200),
Figure 3. 3D images of the surface morphologies of the pristine (a) and (b) oxidized Ti foils, the insets are the optical images of the corresponding samples; and the flat images of the surface morphologies of the pristine (c) and (d) oxidized Ti foils.

Figure 4. (a) XRD patterns of $\beta$-Ni(OH)$_2$ and NiS$_2$ films prepared at different sulfurizing temperatures and XPS spectra of the NiS$_2$ in (b) nickel region and (c) sulfur region.
Figure 5. Top-view scanning electron microscope (SEM) images of the (a) $\beta$-Ni(OH)$_2$ and NiS$_2$ films sulfurated at (b) 400 $^\circ$C, (c) 475 $^\circ$C, (d) 550 $^\circ$C, (e) 625 $^\circ$C and (f) 700 $^\circ$C.

Figure 6. EDS measurement of (a) $\beta$-Ni(OH)$_2$, and NiS$_2$ films sulfurated at (b) 400 $^\circ$C, (c) 475 $^\circ$C, (d) 550 $^\circ$C.

High-resolution XPS spectra of the Ni and S elements in NiS$_2$ are shown in Figs. 4b and 4c, respectively. The binding energies obtained in the XPS analysis were corrected for specimen charging by referencing the C 1s to 284.5 eV. Two strong peaks at about 852.8 and 870.4 eV in Fig. 4b can be attributed to Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$, respectively. Two peaks at about 161.7 and 162.9 eV in Fig. 4c can be assigned to S 2p$_{3/2}$ and S 2p$_{1/2}$, respectively. These results are in well accordance with the XPS data of the NiS$_2$ single crystals.$^{29}$

Figure 5a shows the SEM images of the $\beta$-Ni(OH)$_2$ films. It was observed that the $\beta$-Ni(OH)$_2$ nanosheet film was synthesized by the hydrothermal method. The length of these nanosheets was about 1–2 $\mu$m with the thickness of about 10 nm. Figures 5b–5f show the SEM images of the NiS$_2$ nanosheet films prepared by sulfuration of $\beta$-Ni(OH)$_2$ at different temperatures. When the $\beta$-Ni(OH)$_2$ sample was sulfurated at 400 $^\circ$C (Fig. 5b), the obtained film was compact with interlaced NiS$_2$ nanosheets and similar feature to the $\beta$-Ni(OH)$_2$ nanosheets. To verify the transformation from $\beta$-Ni(OH)$_2$ to NiS$_2$, the EDS measurement was employed, the corresponding results were shown in Fig. 6. From Fig. 6a, it was observed that the oxygen content was closed to 34%, and the atomic ratio of Ni to O was about 1:2 in $\beta$-Ni(OH)$_2$. After the sulfuration process at 400 $^\circ$C (Fig. 6b), the oxygen content plummeted to zero while a Ni:S chemical stoichiometric ratio of 1:2 was achieved, indicating the formation of NiS$_2$ without any impurity. The same results were shown as the sulfuration temperature increased to 475 $^\circ$C (Fig. 6c) and 550 $^\circ$C (Fig. 6d). Further increasing the sulfuration temperature to 475 $^\circ$C (Fig. 5c), the nanosheets became thicker (20–30 nm) with several tiny nanoplates on the nanosheet surface. Such phenomenon was strengthened for the sample sulfurated at 550 $^\circ$C and more obvious when the sulfuration temperature increased to 625 and 700 $^\circ$C. As shown in Fig. 5d, the low-magnification SEM image exhibited similar morphology of the sample sulfurated at 550 $^\circ$C to that of 475 $^\circ$C. However, it could be observed clearly in the inset high-magnification image that the nanosheets consisted of numerous tiny nanoplates with a diameter of about 50 nm, which stacked and arrayed together to retain the nanosheets structure. Moreover, these nanoplates were aggregated into big pieces in the length of 1–2 $\mu$m and the thickness about 0.5 $\mu$m for the sample sulfurated at 625 $^\circ$C (Fig. 5e), which became bigger and thicker as the sulfuration temperature risen to 700 $^\circ$C (Fig. 5f). The nanosheet feature disappeared when the sulfuration temperature was up to 550 $^\circ$C. Therefore, 550 $^\circ$C is the
optimum temperature to keep the well-defined nanosheet structure with numerous tiny nanoplates for the NiS2 films, which would provide more active sites for the electrolyte diffusion and the reduction reaction of the polysulfide electrolyte.

It was supposed that this process was mainly caused by the crystal growth along with higher temperature. At sulfuration temperature of 400°C, the reaction rate was slow, bringing to the small crystal size. Similarly, the crystals grew larger at a higher temperature of 475°C, but retained the nanosheet structure. As the temperature risen to 550°C, the reaction rate increased more, thus leading to the complete transformation of the original nanosheets into small nanoplates with a diameter of about 50 nm, which randomly connected with their neighbors. Further raising the temperature to 625°C or even 700°C, crystalline grain chosen to aggregate into big pieces in Figs. 5e–5f.

The crystalline structure of the NiS2 nanosheets scraped from the NiS2 films obtained from β-Ni(OH)2 sulfurated at 550°C was characterized by transmission electron microscopy (TEM). As observed in Fig. 7a, the scraped pieces presented nanoplate feature with a diameter of about 50 nm, in good agreement with the related SEM image (Fig. 5d). Moreover, the corresponding high resolution TEM (HRTEM) image indicated good crystallization of the NiS2 nanoplates (Fig. 7b). The intact lattice fringe of 0.29 nm corresponded to the interplanar spacing of the (200) plane of NiS2.

To reduce accidental error, we tested three parallel samples for Pt, β-Ni(OH)2 and different NiS2 films as CEs, and assembled them with CdS/CdSe QD-sensitized TiO2 nanorod arrays photoanodes into QDSSCs under the same conditions for several times. The medium results were picked up to be plotted in the J-V curves which were shown in Fig. 8a and the related photovoltaic parameters were listed in Table I. The short-circuit current density ($J_{SC}$) of the cell with the β-Ni(OH)2 CE was 5.05 mA cm$^{-2}$, which was obviously increased after sulfuration from 10.01 to 12.81 mA cm$^{-2}$ as the sulfuration temperature increased from 400 to 550°C. Correspondingly, the PCE of QDSSCs was increased from 1.75% to 2.25%, which was highly enhanced as compared with 0.63% of the β-Ni(OH)2-based device. However, the $J_{SC}$ was decreased to 9.27 mA cm$^{-2}$ as the sulfuration temperature increased to 625°C, yielding a low PCE of 1.66%. Compared with the Pt CE, the PCE value of the optimized NiS2 CE-based QDSSC exhibited a 51% improvement from 1.49% to 2.25% with enhanced $J_{SC}$ and FF values (Table I). Thus, it was deduced that the NiS2 film

| Samples | $V_{OC}$ (V) | $J_{SC}$ (mA/cm$^2$) | FF (%) | PCE (%) | $R_s$ (Ω) | $R_{CT}$ (Ω) |
|---------|-------------|---------------------|-------|---------|----------|-----------|
| Pt      | 0.49        | 8.93                | 33.59 | 1.49    | 8.82     | 2222      |
| β-Ni(OH)2 | 0.38        | 5.05                | 32.43 | 0.63    | 10.39    | 277.1     |
| NiS2 (400°C) | 0.43        | 10.01               | 39.71 | 1.75    | 16.61    | 58.48     |
| NiS2 (475°C) | 0.43        | 11.49               | 40.21 | 1.88    | 12.68    | 55.42     |
| NiS2 (550°C) | 0.45        | 12.81               | 42.72 | 2.25    | 11.59    | 48.91     |
| NiS2 (625°C) | 0.41        | 9.27                | 38.91 | 1.66    | 15.84    | 69.26     |

Figure 7. Transmission electron microscopy (TEM) images of NiS2 films sulfurated at 550°C: (a) low magnification of top-view image, and (b) HRTEM image of the selected region in Figure 4a.

Figure 8. (a) J-V curves of the QDSSCs based on Pt, β-Ni(OH)2, and different NiS2 CEs and electrochemical characterization of the different CEs: (b) cyclic voltammogram plots performed in a mixture of methanol and DI water (3/7, v/v) containing 0.5 M Na2S, 0.2 M S, and 0.2 M KCl using a three-electrode system with SCE used as reference. (c) EIS plots and (d) Tafel curves of the symmetric cells based on Pt, β-Ni(OH)2 and different NiS2 CEs.
obtained at 550 °C had the best electrocatalytic activity, mainly due to its well-defined nanosheet feature stacked with tiny nanoplates providing more space for the diffusion and larger surface area for the reduction of the polysulfide electrolyte. While the poor performance of the NiS2 film obtained at 625 °C was mainly due to the large pieces formed from the aggregation of small nanoplates, leaving less active area for the electrochemical reaction. Moreover, the results of multiple tests were presented in the Fig. 9. The similar J-V curves of each set of three parallel samples indicated the common trend of the above conclusion. To investigate the electrochemical characteristics of different CEs in the polysulfide electrolyte, cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and Tafel polarization measurements were carried out, respectively.

CV analysis was performed to study the electrochemical catalytic activities and stability of different CEs. In the CV curves, the negative currents can be assigned to the reduction of S2− ions to S2− ions while the positive currents are ascribed to the oxidation of S2− ions in the polysulfide electrolyte. For CEs in QDSSCs, the reduction peak currents are most important, revealing the electrocatalytic ability of CEs for S2− reduction. In this regard, the current densities at the reduction peaks of the NiS2 CEs (Fig. 8b) were remarkably larger than the Pt and β-Ni(OH)2 electrodes, suggesting their superior efficient electrocatalytic ability for the S2− reduction. Among the different NiS2 CEs, the sample prepared at 550 °C had the highest reduction peak with the best electrocatalytic ability.

To study the electron transport behavior at the interface between the electrodes and the polysulfide electrolyte, the EIS measurements of different counter electrodes were carried out. All the corresponding Nyquist plots were fitted via the inset equivalent circuit and the results were listed in Table 1. The equivalent circuit has a series resistance (R0) at the high frequency intercepting on real axis, and one semicircle attributed to the interfacial charge transfer resistance (RCT) with a constant phase angle element (CPE). As shown in Fig. 8c and Table 1, the RCT values of the NiS2 electrodes were smaller than that of β-Ni(OH)2, implying that the electron mobility of samples was enhanced after sulfuration. With the sulfuration temperature increased from 400 to 550 °C, the RCT values of the NiS2 electrodes became smaller, which conversely became bigger again when the temperature reached 625 °C. This indicates that the electrode sulfurated at 550 °C had the smallest charge transfer resistance, which facilitated the transport of the electrons and contributed to a higher PCE value. As reference, the Pt electrode has the biggest RCT value, revealing its poor catalytic activity in the polysulfide electrolyte.

To further evaluate the electrocatalytic activity of different CEs, Tafel-polarization analysis was performed. The Tafel polarization curves exhibit the logarithmic current density (log J) as a function of the voltage (V). The exchange current density (J0) can be determined as the intercept of the extrapolated linear region of the anodic and cathodic branches. The higher J0 reflects the better catalytic ability. As showed in Fig. 8d, the NiS2 CE at 550 °C had the highest J0 value and thus the best electrocatalytic activity, in well agreement with the CV and EIS results.

Conclusions

In summary, NiS2 counter electrodes composed of nanosheet films in-situ grown on Ti foils were synthesized by a multi-step strategy including an annealing pre-oxidation of Ti foils, a simple hydrothermal formation of β-Ni(OH)2 films and a final sulfuration conversion of NiS2 nanosheet films. When used as CEs in CdS/CdSe QDSSCs, the NiS2 electrodes exhibited superior electrocatalytic performance as compared with the Pt electrode, showing a highest PCE enhancement of 51% (NiS2: 2.25% vs. Pt: 1.49%). We believe that the nanostructured NiS2 electrodes are capable to be a good choice as CEs in QDSSCs. Currently, we are focusing on preparing more effective quantum dot-sensitized photoanodes to integrate with the NiS2 CEs, aiming to achieve higher device efficiency for QDSSCs.

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