



## Full Length Article

# A transparent nickel selenide counter electrode for high efficient dye-sensitized solar cells



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## ABSTRACT

Nickel selenide ( $\text{Ni}_{0.85}\text{Se}$ ) was synthesized by a facile one-step hydrothermal reaction and  $\text{Ni}_{0.85}\text{Se}$  film was prepared by spin-coating  $\text{Ni}_{0.85}\text{Se}$  ink on FTO and used as counter electrode (CE) in dye-sensitized solar cells (DSSC). The  $\text{Ni}_{0.85}\text{Se}$  CEs not only show high transmittance in visible range, but also possess remarkable electrocatalytic activity toward  $\text{I}^-/\text{I}_3^-$ . The electrocatalytic ability of  $\text{Ni}_{0.85}\text{Se}$  films was verified by cyclic voltammetry, electrochemical impedance spectroscopy and Tafel polarization curves. The DSSC using  $\text{Ni}_{0.85}\text{Se}$  CE exhibits a power conversion efficiency (PCE) of 8.96%, while the DSSC consisting of sputtered Pt CE only exhibits a PCE of 8.15%. When adding a mirror under  $\text{Ni}_{0.85}\text{Se}$  CE, the resultant DSSC exhibits a PCE of 10.76%, which exceeds that of a DSSC based on sputtered Pt CE (8.44%) by 27.49%.

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## 1. Introduction

Dye-sensitized solar cell (DSSC) is a great scientific invention to deal with the growing concern about energy crisis and has aroused wide attention since its appearance in 1991 [1]. So far, the best conversion efficiency of 14.7% has been obtained by co-photosensitized with an alkoxysilyl-anchor dye and a carboxy-anchor organic dye [2]. Generally speaking, a DSSC is composed of dye-adsorbed  $\text{TiO}_2$  film, electrolyte with the redox couple of iodide/triiodide ( $\text{I}^-/\text{I}_3^-$ ), and platinum (Pt) counter electrode (CE). However, the high cost of Pt make DSSC devices difficult to commercialize. Hence, many substitute materials have been proposed, such as alloy materials [3–6], carbon materials [7–10], conducting polymers [11–13] and transition metal compounds which include carbides [14,15], nitrides [14,16] and chalcogenide [17–24]. Among these substitutes, transition metal compounds have exhibited excellent electrocatalytic activity in particular. Besides, they are low-cost and abundant, indicating high potential of replacing Pt as CEs in DSSC.

In this work, nickel selenide ( $\text{Ni}_{0.85}\text{Se}$ ) was prepared by a facile one-step hydrothermal process,  $\text{Ni}_{0.85}\text{Se}$  film was prepared by spin-coating  $\text{Ni}_{0.85}\text{Se}$  ink on FTO and used as counter electrode in DSSC. It is noteworthy that  $\text{Ni}_{0.85}\text{Se}$  CE shows a high power conversion efficiency (PCE) of 8.96% under  $100 \text{ mW cm}^{-2}$ , which is higher than

that of a DSSC with sputtered Pt CE (8.15%). Due to its high transparency, when using a mirror under  $\text{Ni}_{0.85}\text{Se}$  CE, the PCE is up to 10.76%.

## 2. Experimental

### 2.1. Synthesis of $\text{Ni}_{0.85}\text{Se}$ CEs

In a typical experiment, 0.7896 g of Se powder (99.999%), 0.5675 g of  $\text{NaBH}_4$  (96%) and 25 ml distilled water were added into a beaker, reacted for 30 min to form a reddish brown solution A. Transparent solution B in 100 ml autoclave is made up of 1.1885 g of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , 0.75 g of PVP (polyvinylpyrrolidone, MW = 10000) and 50 ml distilled water. The solution A was slowly added to the solution B and stirred for another 10 min. The mixture was heated at  $180^\circ\text{C}$  for 12 h. When the process was completed, the black precipitate was collected by centrifugal separation at a rate of 8000 rpm for 6 min and washed several times by distilled water. Afterwards, the wet black products were dispersed in ethanol with different concentrations, and ultra-sonic for about 60 min. Then the  $\text{Ni}_{0.85}\text{Se}$  ink was obtained. The concentration of  $\text{Ni}_{0.85}\text{Se}$  ink in this experiment was 0.02, 0.04 and  $0.06 \text{ g ml}^{-1}$ .  $\text{Ni}_{0.85}\text{Se}$  CEs were fabricated by spin-coating  $\text{Ni}_{0.85}\text{Se}$  ink on FTO conducting glass substrate (Fluorine doped tin oxide over-layer, sheet resistance  $14 \Omega \text{ cm}^{-1}$ ) at a rate of 3000 rpm for 20 s. These CEs were simply marked as  $\text{Ni}_{0.85}\text{Se-x}$  ( $x$  = concentration of  $\text{Ni}_{0.85}\text{Se}$  ink,  $\text{g ml}^{-1}$ ) CEs.

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### 2.2. Fabrication of DSSCs

The dye-sensitized TiO<sub>2</sub> photoanodes were prepared according to our previous report [25] and the active areas were about 0.11 cm<sup>2</sup>. The I<sup>-</sup>/I<sub>3</sub><sup>-</sup> electrolyte was a acetonitrile solution containing 0.10 M tetramethyl ammonium iodide, 0.1 M tetraethyl ammonium iodide, 0.1 M tetrabutyl ammonium iodide, 0.1 M sodium iodide, 0.1 M potassium iodide, 0.1 M lithium iodide, 0.05 M iodine and 0.50 M 4-*tert*-butyl-pyridine. The sputtered Pt CE was bought from Wuhan Lattice Solar Energy Technology Co. Ltd.

### 2.3. Characterizations and measurements

The composition of Ni<sub>0.85</sub>Se powder was examined by X-ray diffraction (XRD, Cu Kα radiation, Smart Lab 3 kW, Rigaku, Japan). The morphologies of the as-prepared Ni<sub>0.85</sub>Se CEs were observed by a field emission scanning electron microscopy (FESEM, SU8010, HITACHI). A Lamda 950 UV/vis-NIR spectrophotometer was used to evaluate the optical transparencies of Ni<sub>0.85</sub>Se CEs. The photocurrent-voltage (J-V) curves were measured by an AM 1.5G simulated solar light coming from an AAA solar simulator (Newport-94043A) and the digital source meter is Keithley 2400. The cyclic voltammetry (CV) curves were recorded in a three-electrode system with CHI660E setup at a scan rate of 50 mV s<sup>-1</sup>. The three-electrode system use a Pt sheet as counter electrode, an Ag/AgCl electrode as reference electrode and various CEs as working electrode. The electrolyte in three-electrode system is acetonitrile solution with 10 mM LiI, 1 mM I<sub>2</sub> and 0.1 M LiClO<sub>4</sub> into it. Electrochemical impedance spectroscopy (EIS) measurements and Tafel polarization curves were tested by assembling symmetric cell with a Zennium electrochemical workstation (IM6). The EIS measurements were carried out at an amplitude of 5 mV in a frequency range from 100 mHz to 100 kHz and the results of EIS were analyzed with Zview software.

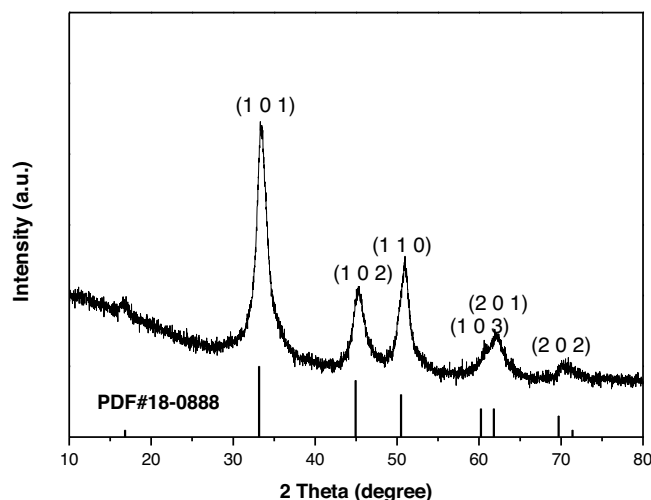


Fig. 1. XRD pattern for Ni<sub>0.85</sub>Se powder.

## 3. Results and discussion

### 3.1. Compositions

The chemical composition of Ni<sub>0.85</sub>Se powder was characterized by X-ray diffraction (XRD) and the XRD pattern is shown in Fig. 1. The XRD pattern in Fig. 1 reveals that the powder is mainly composed of Ni<sub>0.85</sub>Se (PDF#18-0888). Three strong diffraction peaks at 33.5°, 45.6° and 51.2° can be corresponded to the crystal planes of (101), (102) and (110), respectively.

### 3.2. Morphology observation

Fig. 2 shows the surface morphologies of FTO and different Ni<sub>0.85</sub>Se film on FTO. The FESEM images reveal that pristine FTO layer is scalelike and the surface become foggy when Ni<sub>0.85</sub>Se

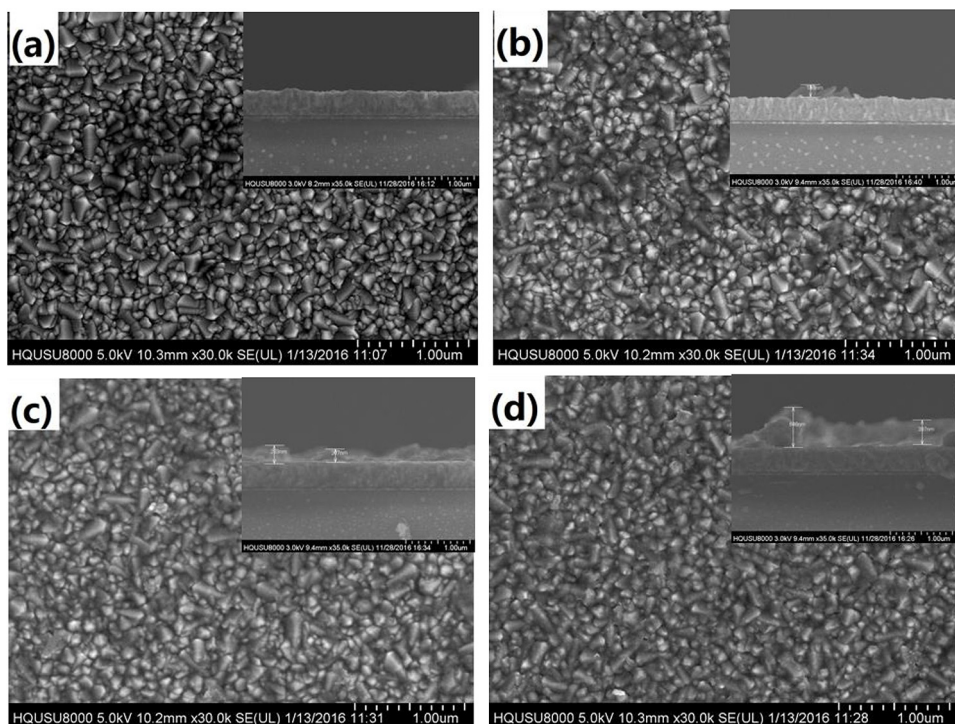


Fig. 2. FESEM images of (a) FTO, (b) Ni<sub>0.85</sub>Se-0.02, (c) Ni<sub>0.85</sub>Se-0.04 and (d) Ni<sub>0.85</sub>Se-0.06, the inset is sectional view of the corresponding films on FTO.

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