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# Interface modification of $MoS_2$ counter electrode/electrolyte in dye-sensitized solar cells by incorporating $TiO_2$ nanoparticles

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ABSTRACT

To achieve the high efficiency in dye-sensitized solar cells (DSSCs), the interface modification of $MoS_2$ counter electrode (CE)/electrolyte should be carried out. Making the modified $MoS_2$ CE by incorporating $TiO_2$ nanoparticles provides possibilities to enhance electrocatalytic activity. The DSSCs with the $MoS_2$/$TiO_2$ CE show enhanced performance compared with DSSCs with the $MoS_2$ CE. The experimental results revealed that the $MoS_2$/$TiO_2$ nanocomposite influences on the power conversion efficiency by enhancing electrocatalytic activity and increasing the active surface area that serve to increase the short circuit current. This understanding can provide guidance for the development of highly efficient DSSCs with platinum-free CEs.



## 1. Introduction

Dye-sensitized solar cells (DSSCs) are widely regarded as one of the most promising candidate technologies for low-cost and simple-process photovoltaic power production with the high energy conversion efficiency ($\eta$) [1–3]. Typically, DSSCs are composed of a transparent conducting oxide (TCO), a dyed coated $TiO_2$ anode, an electrolyte, and a counter electrode (CE). The function of CE is to catalyze the $I_3^-/I^-$ redox couple and complete the electric circuit in DSSCs. CE possessing both high electrical conductivity and excellent electrocatalytic activity is indispensable to maintain a low overvoltage and to speed up the regeneration of $I^-$ from $I_3^-$. To date, platinum (Pt) is still the most widely-used CE for DSSCs [2,3]. While exploring commercial CE catalysts is a promising way to replace the expensive Pt CE catalyst. This can lead to the reduction of the cost of DSSCs. Hence, there is a need for further search for Pt-free CEs with fast transfer kinetics for $I_3^-/I^-$ redox reaction. A catalytic $MoS_2$ film has been used for the fabrication of DSSC CEs, establishing their particular potential properties [3–6]. $MoS_2$ is an indirect band gap semiconductor with an energy gap of ~1.2 eV in the bulk form and has also attracted interest as photovoltaic and photocatalytic materials [2,7–9]. To achieve the highly efficiency in DSSCs, the interface modification of $MoS_2$ CE/electrolyte should be carried out. Making the modified $MoS_2$ CE by incorporating $TiO_2$ nanoparticles provides possibilities to control the overpotential loss at the CE/electrolyte interfaces. To the best of our knowledge, using a $MoS_2$/$TiO_2$ nanocomposite as the CE in DSSCs has not yet been reported. In this study, we found that the incorporation of $TiO_2$ nanoparticles into the $MoS_2$ CE leads to the reduced overpotential loss and the increased active surface area, thus enhancing $\eta$. Knowledge of electrocatalytic activity of CEs is helpful for device performance improvement.

## 2. Experimental details

### 2.1. Preparation and characterization of CEs

First, the fluorine-doped tin oxide (FTO) transparent glass substrates (Hartford Glass, 7 Ω/sq) were ultrasonically cleaned sequentially in acetone, methanol and de-ionized water for 10 min, respectively. The $MoS_2$ (ACROS) and $TiO_2$ (Aeroxide P25, Degussa) nanoparticles were mixed in the weight ratio of 5:1 (referred to as $MoS_2$/$TiO_2$ nanocomposite). Typically, the CEs were prepared by a slurry coating procedure. These slurry consists of 80 wt% active material ($MoS_2$ nanoparticles or $MoS_2$/$TiO_2$ nanocomposite), 10 wt % acetylene black (Alfa Aesar) and 10 wt% polyvinylidene fluoride (Alfa Aesar) grinded together and then dispersed in N-methyl-2-pyrrolidinone (TEDIA), and followed by ultrasonication for 3 h to

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improve the dispersion of $MoS_2$ powder. Subsequently, the as-prepared slurry was coated on the FTO substrate by spin coating. Spin casting was performed at 500 rpm for 5 s per cast layer. After depositing by spin coating, the films were baked at 100 °C for 10 min on a hotplate. The procedures from coating to drying were repeated 2 times. The $MoS_2$ and $MoS_2/TiO_2$ CEs were annealed at 400 °C for 2 h in vacuum. The carrier mobility, carrier concentration and resistivity of CEs were measured by using the Van der Pauw method at four point contact configuration (Ecopia HMS-3000). The electrodes were fabricated by depositing Au metal on the $MoS_2$ ($MoS_2/TiO_2$) layer through a shadow mask.

### 2.2. Fabrication of DSSCs

$TiO_2$ nanoparticles are applied as a $TiO_2$ photoanode. The $TiO_2$ solution was prepared by adding $TiO_2$ (2 g) to ethanol (10 g) solution, followed by ultrasonication for 1 h. The solution was dropped onto FTO substrates, which were rotated at 500 rpm for 5 s, and rotated again at 2000 rpm for another 60 s. After depositing by spin coating, the films were baked at 100 °C for 30 min on a hotplate. The procedures from coating to drying were repeated 5 times. The samples were then inserted into a furnace and annealed at 400 °C for 1 h. A dye was loaded by immersing the $TiO_2$ anode in a 0.23 mM dye N719 ethanol solution for 24 h at 50 °C. The dye-sensitized $TiO_2$ photoanode was further assembled with a $MoS_2$ ($MoS_2/TiO_2$) CE into a sandwich-type cell, and then sealed with a thermoplastic hot-melt Surlyn resin. An electrolyte was injected, and final sealing completed the fabrication of the cell. The electrolyte was composed of lithium iodide (1.34 g), iodine (0.1269 g), and 4-tertbutylpyridine (1.79 g) in acetonitrile (20 mL) solution. For comparison, the DSSC with a Pt CE was fabricated.

### 2.3. Characterization of solar cells

In this work, we characterized the DSSCs using dc current–voltage (I–V) measurements and ac impedance spectroscopy (IS) analysis. Electrochemical IS (EIS) has primarily been used to study the charge carrier transport mechanism in organic semiconductor devices and solar cells [1,3,4], and measured impedance spectra can be electrically interpreted with a proper equivalent circuit model. EIS data were recorded by a HIOKI 3533, and ZView software was used for the data analysis. The dc I–V curves were measured using a Keithley Model-4200-SCS semiconductor characterization system. The cell performance was measured under AM 1.5G condition with an illumination intensity of 100 mW/cm$^2$ using a solar simulator. To rectify the measurement divergence, the light intensity was calibrated using a reference silicon solar cell certificated by the National Renewable Energy Laboratory. To elucidate the electrochemical properties, the samples with the $MoS_2$ and $MoS_2/TiO_2$ CEs were investigated by a cyclic voltammetry (CV) test. CV curves were conducted using a computer-controlled electrochemical analyzer (Jiehan ECW-5000). CV was used in investigating the catalytic activity of a catalyst in previous research [10].

## 3. Results and discussion

Fig. 1 shows the influence of the incorporation of $TiO_2$ nanoparticles into the $MoS_2$ CE on the current density-voltage (J-V) characteristics of DSSCs at 1 sun light intensity. The important figures for the solar cell are the open circuit voltage ($V_{oc}$), the short circuit current density ($J_{sc}$), $\eta$ and the so called fill factor (F), which is a measure of how rectangular the J-V curve is. Based on the experimental data (Fig. 1), the parameters ($J_{sc}$, $V_{oc}$, F and $\eta$) have been extracted and compared, as demonstrated in Table 1. There were no observable changes in $V_{oc}$ (F) of DSSCs. The incorporation

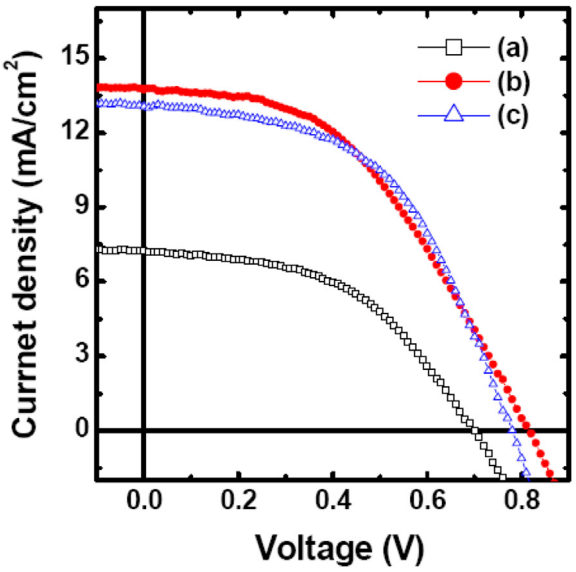


**Fig. 1.** J–V curves of DSSCs with the (a) $MoS_2$, (b) $MoS_2/TiO_2$ or (c) Pt CEs in the light (AM 1.5G, 100 mW/cm$^2$).

of $TiO_2$ nanoparticles into the $MoS_2$ CE led to the significant increase of $J_{sc}$, thus enhancing $\eta$. An explanation for this is given further on. In addition, Fig. 1 shows the photovoltaic performance of the DSSC assembled with a Pt CE. It is found that $\eta$ of the DSSC using a $MoS_2$ CE is lower than that of the DSSC using a Pt CE. However, the photovoltaic performance of the DSSC using a $MoS_2/TiO_2$ CE is comparable to that of the DSSC using a Pt CE.

Table 2 shows the carrier concentration, mobility and resistivity of the $MoS_2$ and $MoS_2/TiO_2$ CEs, respectively. All samples show p-type behavior. We found that the carrier mobility of the $MoS_2/TiO_2$ sample is lower than that of the $MoS_2$ sample and the hole concentration of the $MoS_2/TiO_2$ sample is larger than that of the $MoS_2$ sample, indicating that ionized defect scattering dominates in the high hole-density $MoS_2$ film and affects the carrier mobility. In addition, the electrical conductivity of the $MoS_2/TiO_2$ sample is lower than that of the $MoS_2$ sample. Although the $MoS_2/TiO_2$ CE generated a high $\eta$ value, the low conductivity was a negative factor in achieving an excellent catalytic activity. CE possessing both high electrical conductivity and excellent electrocatalytic activity is indispensable for highly efficient DSSCs. This finding confirms that $\eta$ can be affected by electrocatalytic activity, rather than the CE conductivity.

The obtained Nyquist plots (plots of Z′ vs Z″ are the real part and the imaginary part of the impedance, respectively) for frequency range from 0.1 Hz to 10 kHz under 1 sun illumination are shown in Fig. 2. A sinusoidal ac voltage signal varying by 10 mV was employed in all cases. The radius of the semicircles is related to the total impedance of the device. The nearly semi-circular shape of the impedance spectra indicates that the heterojunction can be expressed using an equivalent circuit model which is composed of a combination of resistance and capacitance (RC) networks.

**Table 1**
The open circuit voltage, the short circuit current density, the fill factor and the power conversion efficiency of DSSCs with the (a) $MoS_2$, (b) $MoS_2/TiO_2$ or (c) Pt CEs.

| | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | F | $\eta$ (%) |
|---|---|---|---|---|
| (a) | 0.70 | 7.24 | 0.49 | 2.54 |
| (b) | 0.82 | 13.76 | 0.45 | 5.08 |
| (c) | 0.78 | 13.06 | 0.52 | 5.27 |