

Communication

Enhanced Efficiency of Dye-Sensitized Solar Counter Electrodes Consisting of Two-Dimensional Nanostructural Molybdenum Disulfide Nanosheets Supported Pt Nanoparticles

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Abstract: This paper reports architecturally designed nanocomposites synthesized by hybridizing the two-dimensional (2D) nanostructure of molybdenum disulfide (MoS₂) nanosheet (NS)-supported Pt nanoparticles (PtNPs) as counter electrodes (CEs) for dye-sensitized solar cells (DSSCs). MoS₂ NSs were prepared using the hydrothermal method; PtNPs were subsequently reduced on the MoS₂ NSs via the water–ethylene method to form PtNPs/MoS₂ NSs hybrids. The nanostructures and chemical states of the PtNPs/MoS₂ NSs hybrids were characterized by high-resolution transmission electron microscopy and X-ray photoelectron spectroscopy. Detailed electrochemical characterizations by electrochemical impedance spectroscopy, cyclic voltammetry, and Tafel-polarization measurement demonstrated that the PtNPs/MoS₂ NSs exhibited excellent electrocatalytic activities, afforded a higher charge transfer rate, a decreased charge transfer resistance, and an improved exchange current density. The PtNPs/MoS₂ NSs hybrids not only provided the exposed layers of 2D MoS₂ NSs with a great deal of catalytically active sites, but also offered PtNPs anchored on the MoS₂ NSs enhanced I₃[−] reduction. Accordingly, the DSSCs that incorporated PtNPs/MoS₂ NSs CE exhibited an outstanding photovoltaic conversion efficiency (PCE) of 7.52%, which was 8.7% higher than that of a device with conventional thermally-deposited platinum CE (PCE = 6.92%).

Keywords: MoS₂ nanosheets; Pt nanoparticles; counter electrode; dye-sensitized solar cells

1. Introduction

A typical dye-sensitized solar cell (DSSC) is usually fabricated by dye-loaded TiO₂ nanoparticles coated on transparent conductive glass to act as the working electrode (WE), a Pt film deposited on the transparent conductive glass as the counter electrode (CE), and an electrolyte containing an iodide/triiodide (I[−]/I₃[−]) redox couple between the WE and CE [1]. Recently, considerable efforts have focused on improving the energy conversion efficiency and long-term stability of the dye, electrolyte, and working electrode [2–7]. However, a high catalytic material for CE is extremely important for promoting the charge transfer rate for I₃[−] reduction. Therefore, a CE with high electrochemical activity and low internal resistance is crucial to yielding high photovoltaic conversion efficiency (PCE).

Recently, inspired by the discovery of graphene—which opened up the new research field of two-dimensional (2D) nanomaterials [8,9]—studies on 2D nanomaterials have attracted great attention. As a typical transition metal dichalcogenide, 2D layered nanostructural molybdenum disulfide (MoS_2) is similar to the graphene structure, and is composed of three stacked atomic layers (a Mo layer sandwiched between two S layers, S-Mo-S) [10]. Layered nanostructural 2D MoS_2 has been extensively investigated as a promising catalyst in electrochemical applications in recent years such as H_2 evolution [11], Li-ion batteries [12], and DSSCs [13]. For instance, Jaramillo et al. reported electrochemical H_2 production with MoS_2 nanocatalysts based on their catalytically active sites for H_2 evolution [11]. Very recently, Mohammad et al. reported that the ultrathin MoS_2 nanostructured films possessed the outstanding catalytic performance of the CE for DSSCs, with rich catalytic active sites provided by the MoS_2 nanosheet crystal structure [13]. Furthermore, due to the high specific surface area of 2D nanomaterials, zero-dimensional (0D) catalytic nanoparticles anchored on the 2D nanomaterials to form 0D/2D functional hybrids bring novel properties that are different from those of their individual intrinsic properties. For example, graphene-supported Pt nanoparticles (PtNPs) such as PtNPs/graphene hybrids, have been investigated as advanced electrocatalysts for achieving superior activities of CEs in producing high-performing DSSCs [14–17]. Yanyan et al. reported that graphene acted as an ideal support for uniformly disperse PtNPs, which was intrinsically important for an effective CE in DSSCs [14]. Min-Hsin et al. reported that PtNPs/graphene CE displayed larger realistic electroactive surface areas and a constant higher intrinsic heterogeneous rate to improve the electrocatalytic abilities for the reduction of I_3^- , and therefore improved the PCE of DSSCs [15].

In terms of the above considerations, in this study, we report on our investigation of the performance of DSSCs that used the PtNPs/ MoS_2 NSs hybrid nanoarchitecture as the CE. This hybrid CE, constituted by 2D layered MoS_2 NS-supported 0D PtNPs, showed a number of advantages. The MoS_2 NSs not only provided exposed-layer active sites for I_3^- reduction, but also provided large surface areas for PtNP anchoring on the MoS_2 NSs to enhance electrochemical activities. The DSSCs fabricated with the PtNPs/ MoS_2 NSs CE had an increased exchange current density and reduced charge-transfer resistance, resulting in a superior PCE of 7.52%, 8.7% higher than that of a conventional thermally-deposited Pt CE (6.92%).

2. Materials and Methods

2.1. Preparation of MoS_2 NSs and PtNPs/ MoS_2 NSs

Two steps were used to synthesize PtNPs/ MoS_2 NSs CE. In Step 1, the hydrothermal method was applied to synthesize the MoS_2 NSs. Ammonium tetrathiomolybdate ($(\text{NH}_4)_2\text{MoS}_4$) powder (99.99% purity, ProChem Inc., Rockford, IL, USA) weighing 0.5 g was added to an aqueous solution with 5 mL of HCl in 100 mL deionized water. Subsequently, the aforementioned solution was transferred into a Teflon-lined autoclave and heated to 250 °C for 12 h. The suspension was then washed and centrifuged with deionized water and ethanol several times, respectively. The resulting powder was finally dried in vacuum at 60 °C to obtain MoS_2 NSs. In Step 2, PtNPs/ MoS_2 NSs hybrids were prepared using a water–ethylene method [17]. MoS_2 NSs (50 mg) were ultrasonically dispersed in a mixture containing 30 mL of deionized water, 100 mL of ethylene glycol (EG), and 1.5 mL of 0.05 M H_2PtCl_6 aqueous solution. This mixture was then heated at 120 °C with stirring for 6 h. Subsequently, the composite was washed and centrifuged with deionized water and ethanol, respectively, for a total of six times. Finally, the resulting powder was dried in vacuum at 60 °C to obtain the PtNPs/ MoS_2 NSs hybrids.

2.2. Fabrication of Various CEs and Assembly of DSSCs

Fluorine-doped tin oxide (FTO) transparent glasses (TEC-7, 2.2 mm, Hartford glass, Hartford, IN, USA) were used as the substrates for CEs and WEs. Prior to the fabrications of CEs and WEs, FTO glasses were ultrasonically cleaned sequentially in detergent, acetone (overnight), distilled water

(DI water, 1 h), and ethanol (1 h). The CEs with MoS₂ NSs and PtNPs/MoS₂ NSs hybrids were fabricated as follows: 5 mg MoS₂ NSs powder and PtNPs/MoS₂ NSs powder were added to 5 mL *N,N*-dimethylformamide (DMF) for dispersion and then sonicated for 1 h, respectively. Subsequently, the dispersed solutions were coated on FTO glasses by spin coating technology to control the flatness and thickness of the films. Finally, the prepared samples were dried in vacuum at 60 °C for 1 h to obtain the MoS₂ NSs CE and the PtNPs/MoS₂ NSs CE. In addition, a thermal deposition Pt (TD-Pt) CE was also prepared as a reference electrode by dropping a H₂PtCl₆ isopropanol solution on a FTO glass annealed at 450 °C for 20 min [18].

A screen-printing method was carried out to prepare the WEs: 10 µm TiO₂ nanoparticle films were coated onto the FTO glasses, and were then placed in the furnace for calcination at 550 °C in ambient air for 30 min. After slowly cooled to room temperature (RT), the TiO₂ WEs were removed from the furnace and immersed in a N719 (Solaronix) solution (3×10^{-3} M in a 1:1 volumetric mixture of acetonitrile and *tert*-butylalcohol) at RT for 24 h.

The DSSCs were assembled as follows. After the dye adsorption process, the dye-adsorbed TiO₂ WE was assembled with various CEs as the sandwich-type cell, and sealed with a 60 µm hot-melt surlyn (SX1170-60, Solaronix, Aubonne, Switzerland) between WE and CE. Then, the commercial iodide-based electrolyte (TDP-LE-M, Jintex Corporation Ltd., Taipei, Taiwan) was injected into the space between the two electrodes after the assembling process. A Class A quality solar simulator with a light intensity of 100 mW·cm⁻² (AM 1.5) was used as the light source to illuminate the DSSCs devices to measure the photocurrent-voltage characteristics.

2.3. Characterizations

Transmission electron microscopy (TEM, JEM-2100F, JOEL, Tokyo, Japan) was used to examine the nanostructures of the prepared PtNPs/MoS₂ NSs hybrids. The sample for TEM was prepared by dropping the sample solution on a copper grid coated with a carbon film. X-ray photoelectron spectroscopy (XPS) was carried out using a PHI Quantera SXM/AES 650 (ULVAC-PHI Inc., Kanagawa, Japan) system with a hemispherical electron analyzer and a scanning monochromated Al K α ($h\nu = 1486.6$ eV) X-ray source to investigate the chemical states of Mo, S, and Pt. To study the chemical states of the PtNPs/MoS₂ NSs hybrids, XPSPEAK 4.1 was used for fitting the obtained curves, peak de-convolution and assignment of binding energies, and referenced to the adventitious C 1s peak at 284.6 eV. For spectrum analysis, the background signal was subtracted by Shirley's method, and curve fitting was performed by using a Gaussian-Lorentzian peak after Shirley background correction.

The catalytic abilities of the CEs were examined by cyclic voltammetry (CV) measurements, equipped with a three-electrode configuration using potentiostat/galvanostat (PGSTAT 302N, Metrohm Autolab, Eco Chemie, Utrecht, The Netherlands) in an acetonitrile-based solution consisting of 10 mM LiI, 1.0 mM I₂, and 0.1 M LiClO₄. The Pt wire and an Ag/AgNO₃ electrode were employed as the counter and reference electrodes, respectively. Electrochemical impedance spectroscopy (EIS) was carried out to study the electrochemical properties of the CEs. The aforementioned potentiostat/galvanostat—equipped with a frequency response analysis (FRA) module—was used for the EIS analyses in a frequency range between 10⁶ Hz and 10⁻² Hz. Tafel polarization curves were also measured using the potentiostat/galvanostat equipped with a linear polarization module to further investigate the catalytic activities at the electrolyte-electrode interface of various CEs. Both EIS and Tafel-polarization measurements were obtained using symmetrical devices in the dark. The photocurrent-voltage characteristics of DSSC devices were measured under simulated solar illumination (AM 1.5, 100 mW·cm⁻², Oriel 91160, Newport Corporation, Irvine, CA, USA), equipped with an AM 1.5 G filter (Oriel 81088A, Newport Corporation, Irvine, CA, USA) and a 300 W xenon lamp (Oriel 6258, Newport Corporation, Irvine, CA, USA). The simulated incident light intensity was calibrated using a reference Si cell (calibrated at NREL, PVM-81).

3. Results

3.1. Nanostructural Features and Composition

The morphologies and nanostructures were studied using TEM and HRTEM (JEM-2100F, JOEL, Tokyo, Japan). Figure 1a shows a typical TEM image of the PtNPs/MoS₂ NSs. As we can see from Figure 1a, the PtNPs were uniformly dispersed on the MoS₂ NSs without aggregation. The HRTEM image in Figure 1b shows the plentifully exposed plans with an interlayer distance of the MoS₂ of about 0.64 nm, corresponding to the spacing between (002) planes of MoS₂, similar to previous studies in Reference [12]. In addition, the HRTEM image clearly shows PtNPs with a uniform size on the MoS₂ NSs, and particle sizes of the PtNPs in the range of 3–5 nm. The inset in Figure 1b shows a Pt nanoparticle with the lattice distance of 0.22 nm corresponding to the (111) plane of crystalline Pt.

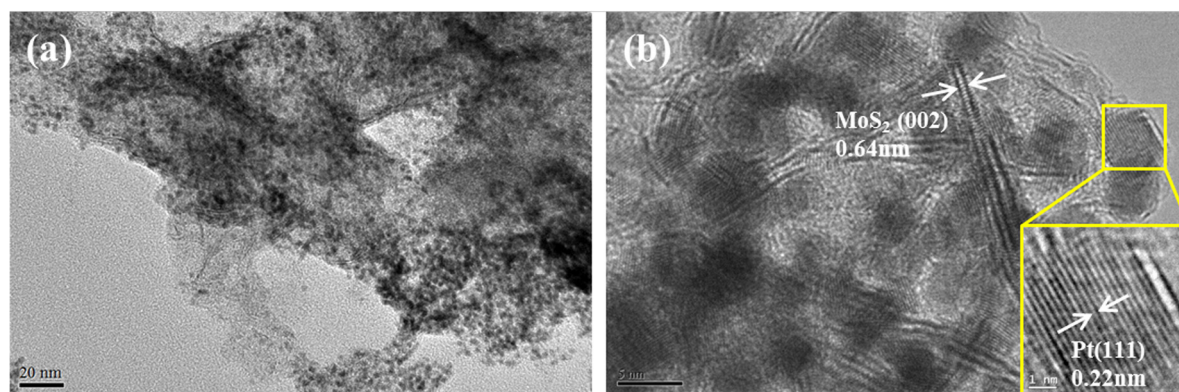


Figure 1. (a) TEM image of PtNPs distributed over MoS₂ NSs; (b) HRTEM of PtNPs/MoS₂ NSs, the inset showed the lattice distance of 0.22 nm corresponding to the (111) plane of Pt.

Figure 2 and Table 1 show the XPS fitting results of PtNPs/MoS₂ NSs. Figure 2a shows the XPS spectrum of the wide spectral region of the MoS₂ NSs and PtNPs/MoS₂ NSs, respectively. The relatively characteristic peaks of the elements are also illustrated in Figure 2a. As seen in Figure 2a, when compared with MoS₂ NSs, the Pt 4f peak of PtNPs/MoS₂ NSs can be clearly seen. Figure 2b–d show the chemical states of Pt 4f, Mo 3d, and the S 2p orbitals of the PtNPs/MoS₂ NSs, respectively. Figure 2b shows the high-resolution Pt 4f spectra, where the main peaks at 71.2 and 74.5 eV correspond to Pt⁰4f_{7/2} and Pt⁰4f_{5/2} of the metallic Pt. The smaller peaks at the higher binding energies of Pt²⁺4f_{7/2} at 72.0 eV, Pt²⁺4f_{5/2} at 75.3 eV, Pt⁴⁺4f_{7/2} at 73.6 eV, and Pt⁴⁺4f_{5/2} at 76.9 eV, correspond to PtO and PtO₂, respectively [19]. Figure 2c shows the high-resolution Mo 3d spectra, where the two main peaks of Mo 3d spectra are at 229.2 and 232.3 eV, which correspond to the Mo⁴⁺3d_{5/2} and Mo⁴⁺3d_{3/2} orbitals, and the revealed Mo⁴⁺ states indicated that the major formation was MoS₂ [20]. The other peaks of Mo⁵⁺3d_{5/2} at 230.3 eV, Mo⁵⁺3d_{3/2} at 233.4 eV, Mo⁶⁺3d_{5/2} at 231.4 eV, Mo⁶⁺3d_{3/2} at 234.5 eV, Mo⁶⁺3d_{5/2} at 232.5 eV, and Mo⁶⁺3d_{3/2} at 235.6 eV, corresponded to the minority products of Mo₂S₅, MoS₃, and MoO₃, respectively [20,21]. The relatively weak peaks of MoO₃ may come from the oxidation of Mo atoms at the edges, or defects on the crystal planes of the MoS₂ NSs during the chemical reaction [22]. Figure 2d shows the high-resolution S 2p spectra, the S^{2−}2p_{3/2} and S^{2−}2p_{1/2} peaks at 161.9 and 163.1 eV, which corresponds to MoS₂. The S₂^{2−}2p_{3/2} and S₂^{2−}2p_{1/2} of binding energy at 163.2 eV and 164.4 eV might represent the intermediate products of Mo₂S₅ and the MoS₃ with a formula of [Mo⁴⁺(S₂)^{2−}S^{2−}] [23,24].

Pt is predominantly present as metallic Pt along with surface oxides and hydroxide, as is normally observed in the case of Pt NPs [19]. Therefore, as above-mentioned, the oxidation groups on the crystal planes of the MoS₂ NSs probably act as nucleation sites to reduce the precursor Pt⁴⁺ to Pt²⁺ and Pt⁰ in the mixture solution (H₂PtCl₆-EG-water) for the subsequent formation of PtNPs by EG reduction.

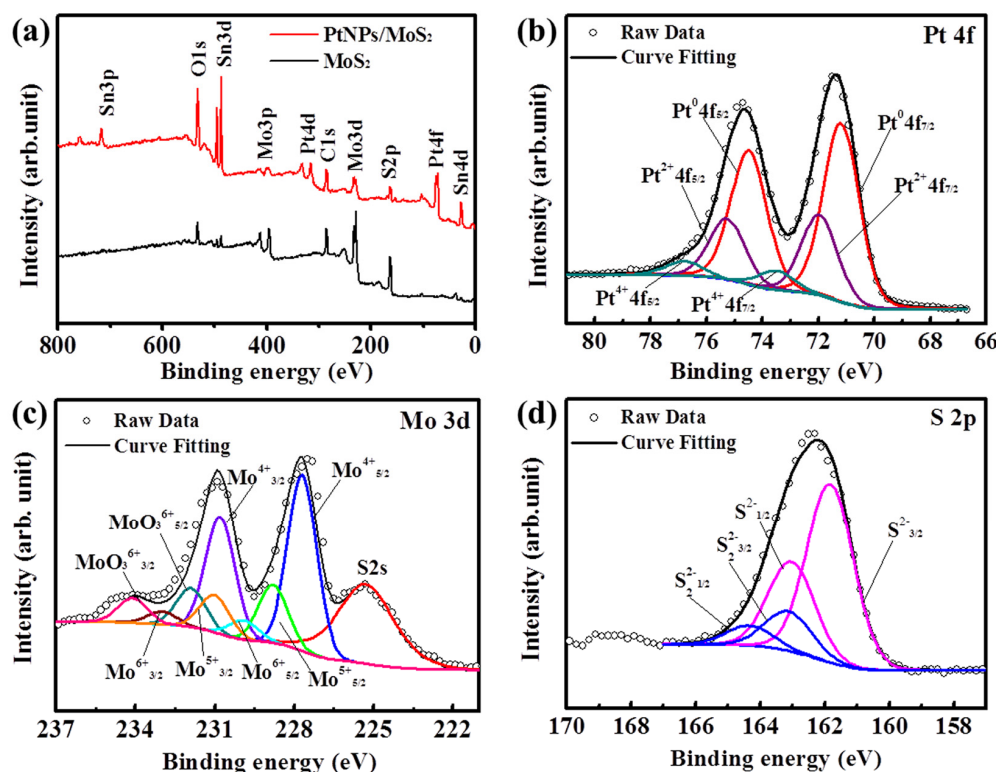


Figure 2. (a) XPS survey spectra; and high-resolution XPS analysis of (b) Pt 4f, (c) Mo 3d, and (d) S 2p of PtNPs/MoS₂ NSs hybrids.

Table 1. Mo 3d, S 2p, and Pt 4f peaks in the XPS spectra of PtNPs/MoS₂ NSs.

Peak	Fitting of the Peak Binding Energy (eV) and Product							
Pt 4f	Pt ⁰ 4f _{7/2}		Pt ⁰ 4f _{5/2}		Pt ²⁺ 4f _{7/2}		Pt ²⁺ 4f _{5/2}	
	71.2 (Pt)		74.5 (Pt)		72.0 (PtO)		73.6 (PtO ₂)	
Mo 3d	Mo ⁴⁺ 3d _{5/2}		Mo ⁴⁺ 3d _{3/2}		Mo ⁵⁺ 3d _{5/2}		Mo ⁵⁺ 3d _{3/2}	
	229.2 (MoS ₂)		232.3 (MoS ₂)		230.3 (Mo ₂ S ₅)		233.4 (Mo ₂ S ₅)	
S 2p	S ²⁻ 2p _{3/2}		S ²⁻ 2p _{1/2}		S ²⁻ 2p _{3/2}		S ²⁻ 2p _{1/2}	
	161.9 (MoS ₂)		163.1 (MoS ₂)		163.2 (Mo ₂ S ₅ , MoS ₃)		164.4 (Mo ₂ S ₅ , MoS ₃)	

3.2. Electrochemical Properties

EIS measurement was performed in a symmetrical cell comprised of two identical CEs to analyze the correlation between the electrocatalytic activities of the various CEs. Nyquist plots in Figure 3a display the impedance characteristics based on the PtNPs/MoS₂ NSs, MoS₂ NSs and TD-Pt CEs, and the corresponding electrochemical parameters obtained from the Nyquist plot were fitted with the Autolab FRA software (v4.9, EcoChemie B.V.) and are summarized in Table 2. Based on the equivalent circuit (the inset of Figure 3a), the R_s value was estimated from the intercept on the real axis in the left region, where R_s corresponded to the series resistance of the electrolyte and electrodes. The left semicircle in the high-frequency region corresponded to the charge-transfer resistance (R_{ct}) and the phase angle element (CPE) at the electrolyte-electrode interface, and the right semicircle in the low-frequency region corresponded to the Nernst diffusion impedance (Z_N) in the electrolyte. It is well known that a smaller R_s represents a higher conductivity and a smaller R_{ct} brings a faster charge-transfer rate from the CE to the electrolyte to enhance the electrocatalytic activities. The R_s value corresponds to the series resistance and includes the sheet resistance of the FTO substrate and the resistance of the contacts. The R_s of PtNPs/MoS₂ NSs, MoS₂ NSs and TD-Pt CEs were 27.8 $\Omega \cdot \text{cm}^2$, 27.9 $\Omega \cdot \text{cm}^2$, and 27.8 $\Omega \cdot \text{cm}^2$, respectively. Based on the R_s results, all CEs had similar conductivities.

The R_{ct} of PtNPs/MoS₂ NSs, MoS₂ NSs and TD-Pt CEs were 0.75 $\Omega \cdot \text{cm}^2$, 12.15 $\Omega \cdot \text{cm}^2$ and 3.81 $\Omega \cdot \text{cm}^2$, respectively. The results demonstrated that PtNPs/MoS₂ NSs CE had outstanding charge transfer ability, that the R_{ct} value of PtNPs/MoS₂ NSs CE was 16 times better than that of MoS₂ NSs CE, and five times better than that of TD-Pt CE.

In addition, Figure 3b shows the Bode plots used to investigate the charge-transfer kinetics of the various CEs where the high-frequency peak (f_{ct}) and the low-frequency peak (f_N) corresponded to the charge-transfer behavior of the catalytic material and the Nernst-diffusion behavior of the electrolyte, respectively. A higher charge-transfer frequency indicated a lower electron lifetime and led to a lower R_{ct} value for the charge transfer rate [25]. The charge-transfer frequency of PtNPs/MoS₂ NSs CE was 4.5 kHz, which was higher than that of MoS₂ NSs (0.8 kHz) and TD-Pt (4.3 kHz). The highest frequency of the PtNPs/MoS₂ NSs CE obtained from the Bode plot coincided with the lowest R_{ct} value obtained from the Nyquist plot (Figure 3a).

Figure 3c shows the cyclic voltammetry (CV) curves of various CEs, which was measured using a three-electrode system with the Pt sheet as the CE, Ag/AgNO₃ as the reference electrode, and various CEs as the working electrode. The relative peaks in Figure 3c corresponded to the redox reactions of I_3^-/I^- couples (reduction peak current density (I_{red}): $\text{I}_3^- + 2\text{e}^- \rightarrow 3\text{I}^-$, oxidation peak current density (I_{ox}): $3\text{I}^- \rightarrow \text{I}_3^- + 2\text{e}^-$). The electrocatalytic activity and the redox barrier of I_3^-/I^- couples was evaluated in terms of its reduction peak current density (I_{red}) and the voltage separation (E_{pp}) of the I_{red} peak to the I_{ox} peak, respectively. The magnitude of I_{red} corresponded to the catalytic activity of a CE for an I_3^- reduction in a DSSC [26], and the value of E_{pp} was negatively correlated with the standard electrochemical rate constant of a redox reaction [27]. As we can see from Figure 3c and Table 2, the I_{red} value of the PtNPs/MoS₂ NSs ($-2.17 \text{ mA} \cdot \text{cm}^{-2}$) was higher than those of the MoS₂ NSs ($-1.66 \text{ mA} \cdot \text{cm}^{-2}$) and TD-Pt ($-1.87 \text{ mA} \cdot \text{cm}^{-2}$). The E_{pp} of the PtNPs/MoS₂ NSs CE showed a relatively lower value of 0.23 V when compared to that of MoS₂ NSs (0.27 V) and TD-Pt (0.24 V) CEs. Therefore, the higher I_{red} and lower E_{pp} values meant better electrocatalytic activity of PtNPs/MoS₂ NSs CE in DSSC. The results obtained from CV indicated that PtNPs/MoS₂ NSs CE had a better charge transport rate when compared with MoS₂ NSs and TD-Pt CEs, which was consistent with the EIS results and Bode plots (Figure 3a,b).

Tafel-polarization curves were used to further investigate the catalytic activities of the exchange current densities (J_0) and the limiting current densities (J_{lim}) at the electrolyte-catalyst interface of various CEs. As shown in Figure 3d, the J_0 was approximately calculated by the Tafel linear extrapolation method, which was closely associated with the R_{ct} value (J_0 is inversely proportional to R_{ct}) and the J_{lim} is dependent on the intersection of the cathodic branch and the vertical axis (Equations (1) and (2)) [13].

$$J_0 = \frac{RT}{nFR_{CT}} \quad (1)$$

$$D = \frac{l}{2nFC} J_{lim} \quad (2)$$

where R is the gas constant; T is the temperature; F is the Faraday constant; l is the spacer thickness; C is the concentration of I_3^- species; and n represents the number of electrons transferred in the reduction reaction.

As shown in Figure 3d and Table 2, the PtNPs/MoS₂ NSs CE showed the highest values for J_0 ($5.2 \text{ mA} \cdot \text{cm}^{-2}$) and J_{lim} ($12.1 \text{ mA} \cdot \text{cm}^{-2}$), which were higher than those of MoS₂ NSs CE ($J_0 = 2.7 \text{ mA} \cdot \text{cm}^{-2}$, $J_{lim} = 10.2 \text{ mA} \cdot \text{cm}^{-2}$) and TD-Pt CE ($J_0 = 4.4 \text{ mA} \cdot \text{cm}^{-2}$, $J_{lim} = 11.9 \text{ mA} \cdot \text{cm}^{-2}$).

According to the results obtained from the Tafel-polarization curves, the highest J_0 and J_{lim} values of the PtNPs/MoS₂ NSs CE indicated the lowest R_{ct} value at the electrolyte-electrode interface, which was consistent with the EIS measurements. Furthermore, the highest J_0 and J_{lim} values of the PtNPs/MoS₂ NSs CE also coincided with the highest i_{pc} and lowest E_{pp} values obtained from the CV curves, which strongly agreed with the promotion of the I_3^- reduction rate, thus enhancing the catalytic activity.

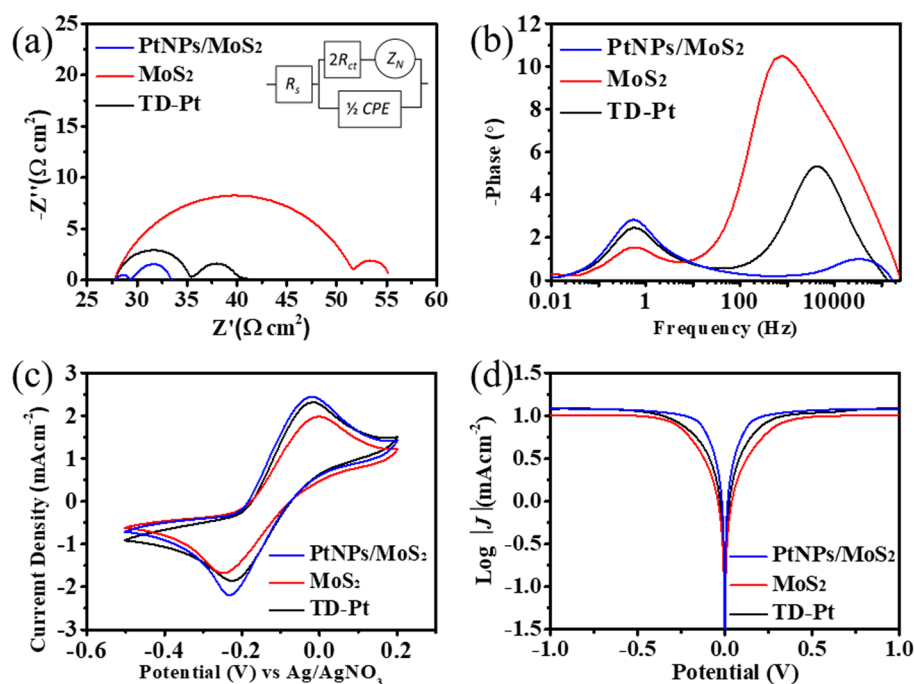


Figure 3. Electrochemical properties of various CEs. (a) Nyquist plots; (b) Bode plots; (c) CV curves; and (d) Tafel curves.

Table 2. Electrochemical properties obtained from Figure 3.

CE	R_s ($\Omega \cdot \text{cm}^2$)	R_{ct} ($\Omega \cdot \text{cm}^2$)	Z_N ($\Omega \cdot \text{cm}^2$)	f_{ct} (kHz)	f_N (Hz)	I_{ox} ($\text{mA} \cdot \text{cm}^{-2}$)	I_{red} ($\text{mA} \cdot \text{cm}^{-2}$)	E_{pp} (V)	J_0 ($\text{mA} \cdot \text{cm}^{-2}$)	J_{lim} ($\text{mA} \cdot \text{cm}^{-2}$)
PtNPs/MoS ₂ NSs	27.8	0.75	4.03	4.5	0.57	2.44	−2.17	0.23	5.2	12.1
MoS ₂ NSs	27.9	12.15	4.24	0.8	0.55	1.98	−1.66	0.27	2.7	10.2
TD-Pt	27.8	3.81	3.93	4.3	0.57	2.31	−1.87	0.24	4.4	11.9

3.3. Photovoltaic Performance of DSSCs

Figure 4 shows the photocurrent-voltage curves of DSSCs assembled with PtNPs/MoS₂ NSs, MoS₂ NSs, and TD-Pt CEs. The short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and PCE (η) used to characterize the photovoltaic performances of the DSSCs are summarized in Table 3. The highest J_{sc} , V_{oc} , and FF values of the DSSC for the PtNPs/MoS₂ NSs CE were 17.23 $\text{mA} \cdot \text{cm}^{-2}$, 0.71 V, and 0.61, respectively, yielding the highest η value of 7.52% out of all the CEs in this work. The J_{sc} , V_{oc} , and FF of the DSSC with the reference TD-Pt CE were 17.13 $\text{mA} \cdot \text{cm}^{-2}$, 0.7 V, and 0.57, respectively, yielding an η of 6.92%. The DSSC with the MoS₂ NSs CE exhibited an η of 6.76%, and the corresponding J_{sc} , V_{oc} , and FF were 16.12 $\text{mA} \cdot \text{cm}^{-2}$, 0.7 V, and 0.59, respectively. It is worth noting that the DSSC based on the MoS₂ NSs CE displayed a comparable performance with that obtained using the conventional TD-Pt CE, which can be considered indicative of a surface exposed nanosheet possessing rich catalytic active sites [13].

Table 3. Photovoltaic parameters obtained from Figure 4.

CE	J_{sc} ($\text{mA} \cdot \text{cm}^{-2}$)	V_{oc} (V)	FF	η (%)
PtNPs/MoS ₂ NSs	17.23	0.71	0.61	7.52
MoS ₂ NSs	16.12	0.7	0.59	6.76
TD-Pt	17.13	0.7	0.57	6.92

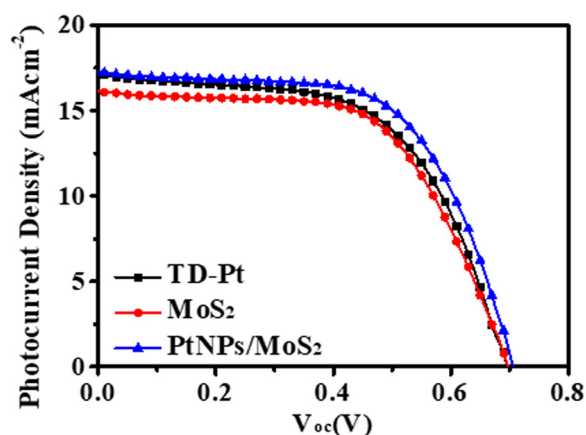


Figure 4. Photocurrent-voltage curves of DSSCs consisted with various CEs.

4. Conclusions

In summary, the PtNPs/MoS₂ NSs hybrids exhibited excellent catalytic activities, acting as an outstanding CE for the DSSCs. The two-dimensional nanostructural MoS₂ NSs played an important role in this work, as MoS₂ NSs not only provided the rich catalytic active sites for the redox reactions, but also displayed a high specific surface area for supporting plentiful Pt NPs. The combination of the two outstanding catalysts showed superior catalytic behavior and led to the superb redox reaction rate for the I₃[−]/I[−] couples. The EIS, Bode plots, CV, and Tafel results all explained the good photovoltaic performance of the DSSCs based on the PtNPs/MoS₂ NSs CE, where the lowest R_{ct} value reduced loss during charge transportation, and the highest redox frequency enhanced the charge transfer efficiency, thereby displaying the highest i_{pc} , J_0 , and J_{lim} for promoting the charge collection. The superior catalytic properties described above yielded an excellent PCE of 7.52% under AM 1.5 illumination of 100 mW·cm^{−2}, which was 8.7% higher than that of the conventional TD-Pt CE (6.92%).

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Conflicts of Interest: The authors declare no conflict of interest.

References

- Oregan, B.; Gratzel, M. A low-cost, high-efficiency solar-cell based on dye-sensitized colloidal TiO₂ films. *Nature* **1991**, *353*, 737–740. [[CrossRef](#)]
- Galliano, S.; Bella, F.; Gerbaldi, C.; Falco, M.; Viscardi, G.; Gratzel, M.; Barolo, C. Photoanode/electrolyte interface stability in aqueous dye-sensitized solar cells. *Energy Technol.* **2017**, *5*, 300–311. [[CrossRef](#)]
- Dissanayake, M.A.K.L.; Kumari, J.M.K.W.; Senadeera, G.K.R.; Thotawatthage, C.A.; Mellander, B.E.; Albinsson, I. A novel multilayered photoelectrode with nitrogen doped TiO₂ for efficiency enhancement in dye sensitized solar cells. *J. Photochem. Photobiol. A Chem.* **2017**, *349*, 63–72. [[CrossRef](#)]
- Bella, F.; Pugliese, D.; Zolin, L.; Gerbaldi, C. Paper-based quasi-solid dye-sensitized solar cells. *Electrochim. Acta* **2017**, *237*, 87–93. [[CrossRef](#)]
- Bella, F.; Galliano, S.; Falco, M.; Viscardi, G.; Barolo, C.; Gratzel, M.; Gerbaldi, C. Approaching truly sustainable solar cells by the use of water and cellulose derivatives. *Green Chem.* **2017**, *19*, 1043–1051. [[CrossRef](#)]

6. Shanti, R.; Bella, F.; Salim, Y.S.; Chee, S.Y.; Ramesh, S.; Ramesh, K. Poly(methyl methacrylate-co-butyl acrylate-co-acrylic acid): Physico-chemical characterization and targeted dye sensitized solar cell application. *Mater. Des.* **2016**, *108*, 560–569. [[CrossRef](#)]
7. Bella, F.; Galliano, S.; Gerbaldi, C.; Viscardi, G. Cobalt-based electrolytes for dye-sensitized solar cells: Recent advances towards stable devices. *Energies* **2016**, *9*, 384. [[CrossRef](#)]
8. Chang, L.H.; Hsieh, C.K.; Hsiao, M.C.; Chiang, J.C.; Liu, P.I.; Ho, K.K.; Ma, C.C.M.; Yen, M.Y.; Tsai, M.C.; Tsai, C.H. A graphene-multi-walled carbon nanotube hybrid supported on oxide as a counter electrode of dye-sensitized solar cells. *J. Power Sources* **2013**, *222*, 518–525. [[CrossRef](#)]
9. Hu, L.H.; Wu, F.Y.; Lin, C.T.; Khlobystov, A.N.; Li, L.J. Graphene-modified LiFePO₄ cathode for lithium ion battery beyond theoretical capacity. *Nat. Commun.* **2013**, *4*. [[CrossRef](#)]
10. Radisavljevic, B.; Radenovic, A.; Brivio, J.; Giacometti, V.; Kis, A. Single-layer MoS₂ transistors. *Nat. Nanotechnol.* **2011**, *6*, 147–150. [[CrossRef](#)] [[PubMed](#)]
11. Jaramillo, T.F.; Jorgensen, K.P.; Bonde, J.; Nielsen, J.H.; Horch, S.; Chorkendorff, I. Identification of active edge sites for electrochemical H₂ evolution from MoS₂ nanocatalysts. *Science* **2007**, *317*, 100–102. [[CrossRef](#)] [[PubMed](#)]
12. Sun, P.L.; Zhang, W.X.; Hu, X.L.; Yuan, L.X.; Huang, Y.H. Synthesis of hierarchical MoS₂ and its electrochemical performance as an anode material for lithium-ion batteries. *J. Mater. Chem. A* **2014**, *2*, 3498–3504. [[CrossRef](#)]
13. Al-Mamun, M.; Zhang, H.M.; Liu, P.R.; Wang, Y.; Cao, J.; Zhao, H.J. Directly hydrothermal growth of ultrathin MoS₂ nanostructured films as high performance counter electrodes for dye-sensitized solar cells. *RSC Adv.* **2014**, *4*, 21277–21283. [[CrossRef](#)]
14. Zhu, Y.Y.; Cui, H.J.; Jia, S.P.; Zheng, J.F.; Wang, Z.J.; Zhu, Z.P. Dynamics investigation of graphene frameworks-supported Pt nanoparticles as effective counter electrodes for dye-sensitized solar cells. *Electrochim. Acta* **2015**, *178*, 658–664. [[CrossRef](#)]
15. Yeh, M.H.; Lin, L.Y.; Su, J.S.; Leu, Y.A.; Vittal, R.; Sun, C.L.; Ho, K.C. Nanocomposite graphene/Pt electrocatalyst as economical counter electrode for dye-sensitized solar cells. *Chemelectrochem* **2014**, *1*, 416–425. [[CrossRef](#)]
16. Wan, T.H.; Chiu, Y.F.; Chen, C.W.; Hsu, C.C.; Cheng, I.C.; Chen, J.Z. Atmospheric-pressure plasma jet processed Pt-decorated reduced graphene oxides for counter-electrodes of dye-sensitized solar cells. *Coatings* **2016**, *6*, 44. [[CrossRef](#)]
17. Yen, M.Y.; Teng, C.C.; Hsiao, M.C.; Liu, P.I.; Chuang, W.P.; Ma, C.C.M.; Hsieh, C.K.; Tsai, M.C.; Tsai, C.H. Platinum nanoparticles/graphene composite catalyst as a novel composite counter electrode for high performance dye-sensitized solar cells. *J. Mater. Chem.* **2011**, *21*, 12880–12888. [[CrossRef](#)]
18. Lim, J.; Kim, H.A.; Kim, B.H.; Han, C.H.; Jun, Y. Reversely fabricated dye-sensitized solar cells. *RSC Adv.* **2014**, *4*, 243–247. [[CrossRef](#)]
19. Anumol, E.A.; Kundu, P.; Deshpande, P.A.; Madras, G.; Ravishankar, N. New insights into selective heterogeneous nucleation of metal nanoparticles on oxides by microwave-assisted reduction: Rapid synthesis of high-activity supported catalysts. *ACS Nano* **2011**, *5*, 8049–8061. [[CrossRef](#)] [[PubMed](#)]
20. Kibsgaard, J.; Chen, Z.B.; Reinecke, B.N.; Jaramillo, T.F. Engineering the surface structure of MoS₂ to preferentially expose active edge sites for electrocatalysis. *Nat. Mater.* **2012**, *11*, 963–969. [[CrossRef](#)] [[PubMed](#)]
21. 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. [[CrossRef](#)]
22. Yuwen, L.H.; Xu, F.; Xue, B.; Luo, Z.M.; Zhang, Q.; Bao, B.Q.; Su, S.; Weng, L.X.; Huang, W.; Wang, L.H. General synthesis of noble metal (Au, Ag, Pd, Pt) nanocrystal modified MoS₂ nanosheets and the enhanced catalytic activity of Pd-MoS₂ for methanol oxidation. *Nanoscale* **2014**, *6*, 5762–5769. [[CrossRef](#)] [[PubMed](#)]
23. Wang, H.W.; Skeldon, P.; Thompson, G.E.; Wood, G.C. Synthesis and characterization of molybdenum disulphide formed from ammonium tetrathiomolybdate. *J. Mater. Sci.* **1997**, *32*, 497–502. [[CrossRef](#)]
24. Weber, T.; Muijsers, J.C.; Niemantsverdriet, J.W. Structure of amorphous MoS₃. *J. Phys. Chem.* **1995**, *99*, 9194–9200. [[CrossRef](#)]
25. Choi, H.; Kim, H.; Hwang, S.; Han, Y.; Jeon, M. Graphene counter electrodes for dye-sensitized solar cells prepared by electrophoretic deposition. *J. Mater. Chem.* **2011**, *21*, 7548–7551. [[CrossRef](#)]

26. Hsieh, C.K.; Tsai, M.C.; Su, C.Y.; Wei, S.Y.; Yen, M.Y.; Ma, C.C.M.; Chen, F.R.; Tsai, C.H. A hybrid nanostructure of platinum-nanoparticles/graphitic-nanofibers as a three-dimensional counter electrode in dye-sensitized solar cells. *Chem. Commun.* **2011**, *47*, 11528–11530. [[CrossRef](#)] [[PubMed](#)]
27. Roy-Mayhew, J.D.; Bozym, D.J.; Punckt, C.; Aksay, I.A. Functionalized graphene as a catalytic counter electrode in dye-sensitized solar cells. *ACS Nano* **2010**, *4*, 6203–6211. [[CrossRef](#)] [[PubMed](#)]



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