Large area growth of MoTe$_2$ films as high performance counter electrodes for dye-sensitized solar cells

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A cost effective and efficient alternative counter electrode (CE) to replace commercially existing platinum (Pt)-based CEs for dye-sensitized solar cells (DSSCs) is necessary to make DSSCs competitive. Herein, we report the large-area growth of molybdenum telluride (MoTe$_2$) thin films by sputtering-chemical vapor deposition (CVD) on conductive glass substrates for Pt-free CEs of DSSCs. Cyclic voltammetry (CV), Tafel curve analysis, and electrochemical impedance spectroscopy (EIS) results showed that the as-synthesized MoTe$_2$ exhibited good electrocatalytic properties and a low charge transfer resistance at the electrolyte-electrode interface. The optimized MoTe$_2$ CE revealed a high power conversion efficiency of 7.25% under a simulated solar illumination of 100 mW cm$^{-2}$ (AM 1.5), which was comparable to the 8.15% observed for a DSSC with a Pt CE. The low cost and good electrocatalytic properties of MoTe$_2$ thin films make them as an alternative CE for DSSCs.

Dye-sensitized solar cells (DSSCs) are gaining considerable interest for next-generation photovoltaic devices due to their acceptable energy conversion efficiency, low cost, environmental friendliness, and easy fabrication processes$^{1,2}$. Typically, DSSCs have a sandwich structure with a photoanode (a semiconductor film on an FTO substrate sensitized by dye molecules), an electrolyte containing the iodide/triiodide ($I^-/I_3^-$) redox couple, and a counter electrode (CE) catalyzing the reduction of $I_3^-$ to $I^-$. Platinum (Pt) is an excellent catalyst for the reduction of $I_3^-$ to $I^-$ due to its superior conductivity, electrocatalytic activity, and stability$^{3,4}$. However, Pt is a noble metal and it is scarce and expensive. Therefore, new materials have been explored to develop cost-effective Pt-free CEs for DSSCs. To date, numerous attempts have been made to find alternative CEs, including transition metal dichalcogenides (TMDC), carbon materials, conducting polymers$^{5,6}$, nitrides$^{7,8}$, and carbides$^{9,10}$. In particular, interests in 2D materilas such as TMDC materials including selenides and sulphides are high because of their good electrocatalytic activity and stability$^{11-16}$. Previously, our group demonstrated that molybdenum disulfide (MoS$_2$) and tungsten disulfide (WS$_2$) are good CE materials for DSSCs. They exhibited photovoltaic conversion efficiencies (PCEs) of 6.0% and 6.3%, respectively$^{16,16}$. However, the efficiency is still not satisfactory, and efforts to improve the efficiency and discover a new TMDC materials are ongoing. Recently, tellurides such as WTe$_2$, and MoTe$_2$ in the family of TMDC materials are gaining interests in electronic and optoelectronic devices$^{17-19}$. Like other TMDC materials, the band gap of MoTe$_2$ also depends on the number of layers. MoTe$_2$ has an lowest indirect band gap of ~1.0 eV, and single-layer MoTe$_2$ is a direct gap material with an optical band gap of 1.1 eV$^{20}$, close to that of Si (1.1 eV)$^{21}$. MoTe$_2$ has a low band gap in the family of TMDC materials. MoTe$_2$ crystal is highly stable.

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in semiconducting (2 H) and metallic (1 T′) phase in nature22,23. The hydrogen evolution reaction catalytic activity of MoTe2 was reported24. In this work, we report the catalytic activities of MoTe2, as counter electrode in DSSCs.

Herein, we have grown MoTe2 thin films via sputtering combined with a post-deposition annealing process on conductive glass substrates with different thickness. This work is a continuation of our research focusing on TMDC material search and growth for DSSC applications. MoTe2 films used as CEs in DSSC showed good electrical conductivity and electrocatalytic activity, and a DSSC employing a MoTe2 CE synthesized under optimized conditions had a 7.25% PCE, which is comparable to the value of 8.15% obtained for the Pt CE under the same conditions. To the best of our knowledge, this is the highest PCE for (I−/I3−) redox couple-based DSSCs employing MoTe2 CE under a simulated solar illumination of 100 mW·cm−2 (AM 1.5).

Results and Discussion
In this study, we fabricated large-area and high-quality MoTe2 directly onto FTO substrate by sputtering-CVD growth, as depicted in Fig. 1. Our synthesis method consists of two steps. Initially, Mo films were deposited onto FTO substrates using magnetron sputtering, and the film was annealed at 500 °C in a tellurium environment in a CVD chamber. Three samples were sputtered at three different times (20, 30, and 40 min) and subsequently tellurized, and referred to S1 (~185 nm), S2 (~335 nm), and S3 (~688 nm), respectively.

Field emission scanning electron microscopy (FE-SEM) analysis was performed to reveal the surface morphology of the MoTe2/FTO structure. Figure 2(a–c) provide FE-SEM images of samples S1, S2, and S3, respectively. Samples exposed to the longest tellurization (40 min) exhibits the biggest grains in Fig. 2(c). Cross-sectional SEM images show that the thicknesses of the S1, S2 and S3 are ~185, ~355 and ~688 nm, respectively (Fig. 2d–f). The low magnification FE-SEM image with EDS spectrum for the sample S2 is provided in supporting information (Figure S1a,b). The cross-sectional view with their EDS profile is provided to confirm the presence of Mo and Te in the MoTe2 film (Figure S1c,d).

The structures of the MoTe2 films were characterized by Raman spectroscopy using a 514 nm excitation laser. Figure 3(a) shows prominent peaks at ~161, and ~267 cm−1, which correspond to the A1g mode. A shoulder peak was observed at ~189 cm−1, and this was ascribed to the B2g mode, for MoTe2 in the 1 T’ phase. The spectrum agrees well with the previously reported results22,23. XRD measurements were performed to further evaluate the identity and structure of the film, as shown in Fig. 3b. The XRD patterns show that the synthesized MoTe2 films were polycrystalline in nature with a monoclinic structure. The diffraction peaks were at 38.0°, 42.7°, 51.7°, 54.7°, 61.7°, 64.7°, 65.9°, 71.2°, and 78.8°, which correspond to (210), (006), (022), (221), (411), (125), (219), and (504) lattice planes of MoTe2, respectively (JCPDS No. 71–2157). No impurities or other reflections from deleterious crystalline phases were observed, which suggests that well oriented MoTe2 films were deposited.

X-ray photoemission spectroscopy (XPS) was used to verify the surface chemical compositions and valence states of 1 T′-MoTe2. The survey spectrum indicates the coexistence of Mo and Te elements in the MoTe2 films (Figure S2). High-resolution spectra of each element are also given in Fig. 4a,b. As shown in Fig. 4a, the Mo 3d spectrum exhibits two main peaks at 229.2 and 232.2 eV, corresponding to the doublet of Mo 3d5/2 and Mo 3d3/2, respectively18. The stoichiometry of Mo and Te elements in our synthesized MoTe2 film is confirmed by EDS spectrum (Fig. S1b). Hall measurements were performed on MoTe2/glass at room temperature (RT) with an active area of (1 × 1) cm2 (Figure S3). MoTe2 CE revealed p-type behavior similar to that reported in the literature25. The conductivity = 3.3 × 10−1 Ω−1 cm−1, and charge mobility = 95 cm2 V−1 s−1 were extracted from the device.

To investigate the application of the MoTe2 as a CE in DSSCs, cyclic voltammetry (CV) studies were performed to estimate the reaction kinetics and electrocatalytic performance. CV was conducted using a three-electrode system in an acetonitrile solution consisting of 10 mM LiI, 1 mM I2, and 0.1 mM LiClO4 at a scan rate of 20 mV s−1. The redox reaction of I3− + 2e− ↔ I− was used to evaluate the integral electrocatalytic ability of CEs to reduce triiodide ions to iodide ions. This reduction occurs in DSSCs, and the current density of this

![Figure 1. Schematic illustration of tellurization for the preparation of MoTe2 from Mo/FTO substrate using a two-zone chemical vapor deposition chamber.](image-url)
reaction is mainly determined by the number of reduction-active sites on the surface area of the electrocatalyst and the intrinsic electrocatalytic ability of each site. Ox₁ and Red₁ represent the same electrochemical reaction \( \text{I}_3^- + 2e^- \leftrightarrow 3\text{I}^- \), in which Ox₁ indicates the left direction and Red₁ indicates the right direction. CV curves show that, like Pt, S₁ and S₂ also are catalytically active for the reaction that regenerates the redox couple. The higher cathodic peak current density can be used to evaluate the catalytic activity of the CE, and comparable peak current densities imply good electrocatalytic activity. The ~335 nm-thick (S₂) CE showed higher current density than the ~185 nm CE (S₁), suggesting faster reduction of triiodide ions in the S₂ CE compared to the S₁ CE (Fig. 4a). The higher cathode current density could be attributed to its relatively higher surface roughness compared to the much smoother S₁. Furthermore, S₁ and S₂ samples displayed similar anodic and cathodic peaks to Pt CE, suggesting that they are active in catalyzing the reduction of \( \text{I}_3^- \) to \( \text{I}^- \). The peak current and peak to peak separation is important parameters for determining the catalytic activity of CE. The rate constant of a redox reaction is inversely proportional to its peak separation (Epp)27–29. Epp is calculated using the formula

\[
E_{pp} = E_{p(anodic)} - E_{p(cathodic)}
\]

In DSSCs, the CE has more influence on the negative peak. So, we used this peak for Epp calculations. The Epp for the Pt CE was 295 mV, while those for S₁, S₂ and S₃ were ~354, ~459 and ~308 mV, respectively.

To investigate the electrochemical stability of MoTe₂ S₂ sample and Pt CE, CVs were recorded for 50 consecutive cycles with a potential range from −0.2 to 1 V vs. Ag/AgCl, as presented in Figure S4a.

**Figure 2.** (a–c) Top down FE-SEM images of S₁, S₂ and S₃ (Inset shows the corresponding image of MoTe₂ sample) and (d–f) cross-sectional images of S₁, S₂ and S₃. The observed thickness were ~185 nm, ~335 nm and ~668 nm for S₁, S₂ and S₃, respectively.

**Figure 3.** (a,b) Raman spectra and XRD patterns of MoTe₂ samples.
scans, the CV shape of sample S2 almost overlapped, and the redox peak current (cathodic and anodic peak current density) for sample S2 was almost constant, which suggests that the MoTe2 CE possesses reversible redox activity, good electrochemical and chemical stability, and strong adhesion on the FTO glass substrate. The CVs of sample S1, S2 and S3 were measured using different scan rates from 10 to 100 mVs⁻¹ for the (I⁻/I₃⁻) redox reaction, as shown in Figure S4b–d, respectively. There are a linear increment in the current peak value with increasing scan rate, indicating that the inner sites of MoTe2 also become reactive and possess catalyst activity at higher scan rate²⁹,³⁰.

To further evaluate the charge transfer kinetics and internal resistance of DSSCs, EIS measurements were performed using symmetric cells fabricated with two identical electrodes (CE/electrolyte/CE). The equivalent circuit model used for fitting the resultant impedance data is illustrated in Fig. 5b. In each curve, there are two well-defined semicircles. The first semicircle at high frequency is related to impedance of charge transfer process occurring at CE/electrolyte and lower frequency range can be assigned to the Nernst diffusion impedance (Zₑ) within electrolyte. The extracted charge–transfer resistance (Rₑ) values of the Pt, S1, S2 and S3 CEs are 0.93, 27.01, 25.97, and 37.44 Ω cm², respectively. The sample S3 has the largest Rₑ and S2 has the lowest one among the MoTe2 samples. Rₛ values of S1, S2, S3 and Pt are 16.47, 13.79, 13.83, and 7.05 Ω cm², respectively. The sample S2 has the lowest Rₛ. The Rₛ value of S3 is largest probably due to the largest film thickness.

Tafel polarization analyses were also performed using symmetric cells at a scan rate of 50 mVs⁻¹ for Pt, S1, S2 and S3 samples (Fig. 5d). The Tafel curve is usually divided into three regions. The lower potential zone is called the polarization zone, and the middle region (with a sharp slope) is the Tafel zone, which determines the catalytic activity of the electrode. The last zone is the diffusion zone, which determines the diffusion of ions in the electrode. The tangent slope in the anodic or cathodic branch provides information about the exchange current density (J₀) on the electrode³¹. The comparison indicates that S2 (S₂ > S₁ > S₃) is more effective than S₁ and S₃ at catalyzing the reduction of I₃⁻. The exchange current density, J₀ is inversely proportional to Rₑ from the equation

$$J_0 = \frac{(RT/nF)q}{R_e}$$

where R is a gas constant, T is an absolute temperature, n is the number of electrons involved in the reaction, and F is Faraday’s constant²⁷,³². A higher J₀ for Pt and S2 CE implies a lower value of Rₑ in the impedance measurement.

The schematic of DSSCs with MoTe2 CE is illustrated in Fig. 6a. The photocurrent density versus photovoltage (J-V) curves of the DSSCs are shown in Fig. 6b. The photovoltaic parameters including the short circuit current density (Jₛ), open circuit voltage (Vₒ), fill factor (FF) and PCE (η) of DSSCs with Pt and MoTe2 (S1, S2 and S3) CEs under a simulated solar illumination of 100 mWcm⁻² (AM 1.5) are summarized in the Table 1. The sample S2 CE exhibits the best performance. The DSSC with S1 CE has lower FF than that with S2 CE, which is related to red-ox behaviour as discussed in earlier. The Jₛ and FF values are increased for the S2 CE, which leads to enhancing PCE from 6.38% to 7.25%. And, the low efficacy of S3 CE is mainly due to low Vₒ, and FF. This could be attributed to higher Rₑ value as confirmed by EIS analysis.
The \( J_{sc} \) values are decreased in the order of \( S_3 > S_2 > S_1 > Pt \), and PCE values are decreased in the order of \( Pt > S_2 > S_3 > S_1 \). It is believed that thick film (S3) could affect electrolyte penetration and result in weaker adhesion to the FTO substrate.

The observed PCE (7.25%) value of the S2 CE was much higher than those of earlier reports based on TMDCs, which include WS\(_2\) films prepared by a doctor-blading technique (4.56%)\(^\text{34}\), multi-walled carbon nanotubes-MWCNTs@MoS\(_2\) (6.45%)\(^\text{35}\), multi-wall carbon nanotubes decorated with tungsten sulfide-MWCNTs@WS\(_2\) (6.41%)\(^\text{36}\), composite films of molybdenum disulfide (MoS\(_2\))/graphene flakes (5.98%)\(^\text{29}\), and molybdenum disulfide and graphene-MoS\(_2\)/RGO (6.04%)\(^\text{37}\). The variations of \( V_{oc} \) and \( J_{sc} \) values for MoTe\(_2\) and Pt CEs can be attributed to the nanoporous nature of the MoTe\(_2\) CE in contrast to the planar Pt CE, and the high conductivity of Pt.

Figures S5 shows incident photon-to-current-conversion efficiency (IPCE) curves of DSSCs with the MoTe\(_2\) CE and Pt CE. These results indicate that catalytic activities depend on the MoTe\(_2\) thickness since active sites and morphology vary with the growth time, supporting that catalytic activities of thin MoTe\(_2\) could be modulated by their film thickness and morphology.

Conclusions

In summary, we presented the sputtering-CVD post annealing route for synthesizing MoTe\(_2\) as counter electrodes for DSSCs. Detailed electrochemical investigations were carried out using cyclic voltammetry, electrochemical impedance spectroscopy, and Tafel curve analysis to determine the suitability for CE for DSSCs. CV performance revealed that MoTe\(_2\) CEs possess good electrocatalytic activity and fast reaction kinetics for the reduction of triiodide to iodide. It was found that catalytic activities of thin MoTe\(_2\) could be modulated by their film thickness and morphology.

The optimum MoTe\(_2\) CE in a fabricated DSSC exhibited a 7.25% PCE, which is comparable to the 8.15% Pt CE under the same illumination conditions. The presented work suggests that MoTe\(_2\) would be a promising counter electrode material as a low-cost and highly efficient alternative to Pt in DSSCs.

Experimental Section and Device preparation.

FTO/glass substrates were cleaned with a standard piranha solution and deionized water and were then baked at 120°C for 5 min. After loading the FTO substrates in a sputter chamber, the chamber was evacuated by a rotary pump and a turbomolecular pump combination to a pressure of \( \sim 1 \times 10^{-7} \) torr. Next, Mo thin films were deposited onto FTO/glass substrates using a Mo target...
(99.99%) by magnetron sputtering. During the film deposition, the Ar gas flow ratio was maintained at 10 sccm, and the power was fixed at 100 W. Mo films were deposited at different sputtering times (such as 20, 30, and 40 min) at room temperature, and these are denoted as S1 (185 nm), S2 (335 nm), and S3 (668 nm) samples, respectively. After removing the samples from the sputter chamber, the as-sputtered films were placed downstream of the chemical vapor deposition (CVD) chamber and heated. The as-sputtered Mo films were annealed in tellurium vapor at 500 °C for 30 min to form MoTe2 films and to improve the crystalline quality of the films. A pure tellurium powder (99.99%) was placed upstream of the CVD chamber, and a heating filament for the tellurium boat was fixed at 350 °C. The tellurium powder was evaporated at 350 °C using a mixture of argon and hydrogen (60 sccm - Ar and 30 sccm - H2) carrier gases, and the pressure of the CVD chamber was kept at \(2 \times 10^{-2}\) Torr.

Fabrication of DSSCs. DSSCs were fabricated to evaluate the CE performance of the MoTe2 films using our method38–41. Briefly, thin blocking layer TiO2 was deposited onto a cleaned FTO glass substrate (15 × 15 mm2) by dipping it in 40 mM TiCl4 solution for 30 min at 70 °C and annealing it at 450 °C for 30 min. A homemade titanium dioxide (TiO2) powder paste of P25 was coated on the cleaned FTO glass as the main layer (~12 µm thickness) using a simple doctor blade coating technique. The TiO2-coated FTO was then sintered in five steps of 70, 325, 375, 450, and 500 °C for 30, 5, 5, 15, and 15 min, respectively, in a high temperature furnace (Lab House Co.). Additionally, a scattering layer (~6 µm) was coated over the main layer and sintered using the same sintering steps. The TiO2 film was then sensitized with 0.5 mM N719 prepared in an absolute ethanol: acetonitrile (1:1) solution for 24 h. The polymer electrolyte, which was composed of 0.5 M LiI, 0.6 M 1-propyl-2,3-dimethylimidazolium iodide, 0.05 M I2, 0.5 M 4-tert-butylypyridine, and 3% w/w polyethylene oxide (Mw 250,000) with acetonitrile as the solvent was then injected between the two electrodes. The Pt-coated CE was prepared by spreading a drop of 2 mM chloroplatinic acid hexahydrate (H2PtCl6) in isopropanol onto the FTO substrates using a simple brush method and heating it to 400 °C for 15 min in ambient air42,43. The dye-sensitized TiO2 photoanode with an active area of 0.25 cm2 and the as-fabricated CE were assembled using a 50-µm-thick spacer made of polyimide adhesive tape.

Figure 6. (a) Schematic diagram of the electrocatalytic mechanism in DSSC using MoTe2 CE. (b) Photocurrent–voltage curves of DSSCs with different CEs, measured at AM1.5 G illumination (100 mW cm−2).

Table 1. Photovoltaic and EIS parameters of Pt, S1, S2 and S3 based DSSC CEs.
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Author Contributions
S.H. and D.V. initiated the study, performed the extensive experiments related to the growth of the samples and wrote the paper with assistance from the co-authors. S.A.P. and N.M. carried out electrochemical and solar cell performances. H.L. helped us experimental work and data analyses. W.S. and K.A. performed XPS analyses. H.-S.K., S.H.J. and J. J. participation included planning, design experimental work and discussion. All authors read and approved the final manuscript.

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