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Rapid sintering of MoS_2 counter electrode using near-infrared pulsed laser for use in highly efficient dye-sensitized solar cells

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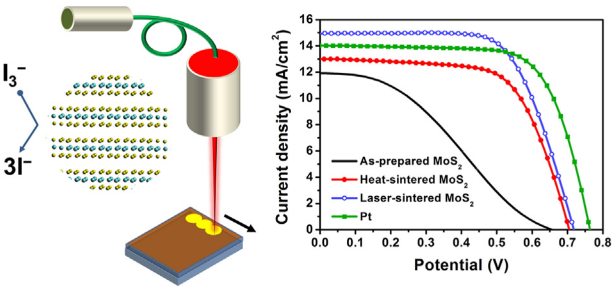
HIGHLIGHTS

- Highly efficient MoS_2 counter electrodes are prepared at a low temperature.
- A near-IR pulsed laser is proposed for post-sintering of MoS_2 films.
- Laser-sintered MoS_2 counter electrodes exhibit a comparable performance with Pt.

GRAPHICAL ABSTRACT



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ABSTRACT

Molybdenum disulfide (MoS_2) is a promising material for use as a low-cost electrocatalytic counter electrode (CE) in photoelectrochemical dye-sensitized solar cells (DSSCs). However, currently, the MoS_2 CEs are generally prepared with a high temperature sintering for the synthesis and crystallization of MoS_2. Here, we report a simple and rapid method for the preparation of highly efficient MoS_2 CEs. The MoS_2 films were synthesized at 70 °C, followed by sintering with a near-infrared (IR) pulsed laser for 1 min. Compared to the conventional heat-sintered MoS_2 CE, the laser-sintered CE showed enhanced crystallinity and improved interconnection between the MoS_2 particles, resulting in superior electrocatalytic activity towards the I^-/I_3^- redox couple. When used in a DSSC, the laser-sintered MoS_2 CE exhibited a higher conversion efficiency ($\eta = 7.19\%$) compared to that of the heat-sintered CE ($\eta = 5.96\%$). Furthermore, the laser-sintered CE had a comparable conversion efficiency compared to that of the conventional Pt CE ($\eta = 7.42\%$).

1. Introduction

Since the discovery of graphene and its success in a variety of applications [1], two-dimensional (2D) transition-metal dichalcogenides (TMDCs) have received considerable attention as

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promising materials for applications in electronics and catalysis [2–15]. Of the TMDCs, molybdenum disulfide (MoS_2) has been intensively investigated as a potential material for transistors [4,5], chemical sensors [6], batteries [7,8], electrocatalysts for the hydrogen evolution reaction (HER) [9,10], and photovoltaics [11–15]. This broad applicability is possible because of their unique properties including high mobilities, large specific surface areas, and excellent catalytic activities. In particular, it has been reported that MoS_2 is a promising electrocatalytic counter-electrode (CE) material for next-generation photovoltaics, such as dye-sensitized solar cells (DSSCs) [12–18]. DSSCs are regarded as potential alternatives to conventional silicon solar cells due to the low cost of materials, their high conversion efficiencies, the simplicity of their fabrication, and potential flexibility [19–25]. To obtain a highly efficient DSSC, the CE should efficiently catalyze the reduction of the redox couple in the electrolyte. Pt is the conventional CE material, and it is currently the electrode with the best electrocatalytic activity toward the iodide/triiodide redox couple (I^-/I_3^-) used in DSSCs. However, the high cost and rarity of Pt limit its practical use [21,26–29].

Therefore, various Pt-free CEs have been suggested as possible alternatives to the high cost Pt CE. For instance, the CEs based on metal sulfides (FeS_2, NiS_2, WS_2) [12,30,31], carbides (WC, MoC) [32] and nitrides (TiN, NiN) [33,34] exhibited reasonable conversion efficiencies around 7–8%. In addition, alloy CEs including Co-Ni [35], Fe-Se [36], Co-Se [37], Ru-Se [38] showed promising conversion efficiencies above 8%. Furthermore, several CEs based on conducting polymers or carbon materials demonstrated high conversion efficiencies around 9–10% with iodine or cobalt redox couples [39-42]. Among those materials for Pt-free CEs, MoS_2 is one of the most promising alternatives to Pt because of its low cost, abundance, chemical stability, and excellent catalytic activity.

Currently, MoS_2 CEs are generally prepared *via* chemical reactions that are carried out at 200–800 °C [12,14–18], followed by post-sintering at 300–500 °C to crystallize the MoS_2 [12,13,16]. However, the generation of these harsh conditions is expensive, and high temperatures are not compatible with flexible plastic substrates [21,25,43]. If truly low-cost photovoltaics are to be realized, both material and processing costs must be reduced [25,44]. To this end, we have developed a rapid and simple fabrication process for MoS_2 electrocatalytic CEs. In our process, MoS_2 was synthesized at a relatively low temperature (70 °C), followed by rapid sintering (about 1 min) at room temperature using a near-infrared (IR) pulsed laser. Despite the rapid and simple fabrication process, the laser-sintered MoS_2 CE showed a higher conversion efficiency than that of the heat-sintered CE; furthermore, it had a comparable conversion efficiency to that of the conventional Pt CE when used in DSSCs. To reveal the electrocatalytic activity of laser-sintered MoS_2 CE and the effect of laser-sintering on the electrode surface morphology, the crystal structure and chemical states of a laser-sintered MoS_2 film were investigated. Furthermore, the electrocatalytic activities of the laser-sintered MoS_2, heat-sintered MoS_2, and Pt CEs toward the I^-/I_3^- redox couple were systematically compared.

2. Experimental details

2.1. Fabrication of the MoS_2 and Pt CEs

First, fluorine-doped tin oxide glass (FTO; TEC-8, Pilkington) was sonicated while being washed sequentially with deionized (DI) water and ethanol for 20 min. Then, the FTO glass was dried under a stream of N_2. Subsequently, the FTO glass was treated with UV/ozone for 20 min at room temperature. To deposit the MoS_2 film, the cleaned FTO glass was immersed in an ethanolic solution containing 0.2 M molybdenum(V) chloride (Aldrich, 95%) and 0.2 M thioacetamide (Aldrich, 99.0%) at 70 °C for 7 h [13]. After finishing the reaction, the MoS_2/FTO electrode was washed with ethanol and dried under a stream of N_2. Then, post-treatment was carried out, either by a conventional heat-sintering method or our laser-sintering method. The heat sintering was carried out at 350 °C for 30 min under a N_2 atmosphere. For comparison, the heat sintering was also performed with the same condition in a forming gas (5 vol % H_2 in N_2). In contrast, the laser sintering was performed in air using a pulsed ytterbium-doped fiber laser system (ML20-PL-R-OEM, General Microtechnology & Photonics) with a near-infrared IR wavelength (1080 nm). The distance between MoS_2/FTO electrode and the laser source was about 22 cm. The pulse duration, pulse repetition rate, and the maximum average power output were 40 ns, 50 kHz, and 20 W, respectively. We controlled the average output power to be from 6 to 10% of the maximum value. The focused laser beam used for sintering had a diameter of 30 μm and a scanning speed of 50 cm/s. Approximately 1 min was required to scan a sample with dimensions of 1 × 1.5 cm. For comparison, a conventional Pt CE was also prepared by a thermal decomposition method. A drop of 7 mM H_2PtCl_6 solution in isopropanol was spread onto FTO glass, followed by annealing at 400 °C for 20 min in air.

2.2. Electrode assembly

For the TiO_2 working electrode, two kinds of TiO_2 pastes were prepared, as described previously [45]. Briefly, a transparent paste of hydrothermally synthesized nanocrystalline TiO_2 (20 nm diameter) was prepared. In addition, a scattering paste of TiO_2 particles with diameters of 500 nm (G2, Showa Denko, Japan) was prepared. Before the deposition of the TiO_2 pastes, the FTO glass was coated with a dense TiO_2 blocking layer by spin-casting of a 7.5 wt % Ti(IV) bis(ethylacetoacetato)-diisopropoxide solution in 1-butanol, followed by annealing at 500 °C for 10 min in air. Onto this substrate, the transparent paste was deposited by the doctor blade method, followed by annealing at 150 °C for 10 min in air. Subsequently, the scattering paste was deposited onto the layer of transparent paste by the same method, followed by annealing at 500 °C for 30 min in air. The annealed TiO_2 electrode was immersed into a 0.5 mM N-719 dye (Everlight) solution in ethanol for 12 h at room temperature. Then, the dye-adsorbed TiO_2 electrode was assembled with the CEs using hot, melted Surlyn 1702 (Dupont, 60 μm-thick). Then, a drop of the electrolyte was injected into the assembled cells through pre-drilled holes onto the CEs. The electrolyte was an acetonitrile solution containing 0.7 M 1-propyl-3-methylimidazoliumiodide (PMII, synthesized), 0.03 M I_2 (Aldrich, 99.8%), 0.05 M guanidinium thiocyanate (Aldrich, 97%), and 0.5 M 4-*tert*butylpyridine (Aldrich, 96%). The active area of the assembled cells was approximately 0.40–0.45 cm^2, measured by an image analysis program from data collected with a CCD camera (Moticam 1000).

2.3. Characterization

The morphologies of the MoS_2 films were characterized by field-emission scanning electron microscopy (FE-SEM; Hitachi S4100). The surface electronic states of the synthesized MoS_2 films were investigated by X-ray photoelectron spectroscopy (XPS; Thermo Fisher Scientific Sigma Probe) using an Al Kα X-ray source. Depth profiling was carried out using a 2 keV Ar^+ beam with an etching rate of 18 nm/min. The crystal structures of the films were confirmed using X-ray diffraction (XRD; Rigaku D/MAX 2500 V) with Cu Kα radiation. Cyclic voltammetry (CV) for each CE was carried out using a CHI440 potentiostat-galvanostat (CH Instruments Inc.) at a scan rate of 50 mV/s in an electrolyte containing