Transparent-Reflective Switchable Glass Using Multi-layered Transition Metal Dichalcogenides

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***Abstract*— The molybdenum disulfide (MoS_2) offers high charge density and well-ordered layer structure for good charge balance in the transparent-reflective switchable glass. The electrically actuated device with MoS_2 counter electrode shows large modulation in the light reflectance between the reflective mirror and transparent bleached states. Under zero power consumption, 95 % of light reflectance of the mirror-state device can be maintained for 80 minutes, paving it a promising technology for energy-efficient applications.**

Keywords*— *Transition metal dichalcogenides, transparent-reflective, switchable, counter electrode

I. Introduction

In view of the importance of dynamic sunlight management system for energy-saving building facades, reversible electrochemical mirror (REM) devices have recently attracted researchers' attention as the devices could switch its transparent/reflective state with controlled electrical signals [1]. Different from the traditional electrically responsive systems based on electrochromic (EC) materials, such as transition metal oxides [2] and polymers [3], REM devices modulate the light intensity based on light reflection, rather than absorption which would prevent extra heating through the window and rooftop glazing. Despite the outstanding attributes, REM devices still suffer from short mirror memory effect (> 50 % drop in light reflectance in less than 1 hour) and small optical modulation in light reflectance (< 50 %), which could be originated from the poor charge balance between the electrodes consisted of the transparent conducting oxide (TCO).

Among various counter electrodes, the advances of the intercalation chemistry in the multiple-layered transition metal dichalcogenides (TMDCs) have gained a lot of attention [4]. The layered structure of TMDCs could endow the efficient electron/ion transport pathways for fast charge transfer [5] by providing the large-area and intimate electrode-electrolyte contact surface. In this work, we integrate the TMDCs (multiple-layered molybdenum disulfide (MoS_2)), on top of TCO as a counter electrode with the aim of improving the optical contrast upon switching the REM device. The high ion charge density (~ 11 mC/cm^2, which is 40 % higher than that of standalone TCO) with reversible Na^+ intercalation/de-intercalation reactions of TMDCs counter electrode provides the good charge balance for the reversible electrodeposition of Ag at the working electrode.

II. Experimental

A. Preparation of the FTO substrates

Firstly, the FTO substrates were ultrasonically washed with DI water, acetone and isopropanol for twenty-five minutes each. Then, the FTO substrates were then purged with a nitrogen gas gun till dry before being treated under an oxygen plasma for fifteen minutes under oxygen flow rate of 8 sccm and RF power of 30 W.

B. Growth of Multi-layered MoS_2 Film on FTO substrates

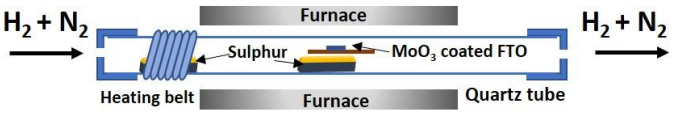

Figure 1. Schematic diagram of the furnace system.

Figure 1 indicates the configuration of two-zone furnace for the sulfurization process of the pre-sputtered 5 nm molybdenum oxide (MoO_3) on a transparent fluorine-doped tin oxide (FTO) coated glass. The MoO_3 coated FTO substrate was purged under forming gas (95 % H_2 + 5 % N_2) for 3 hours before sulfurization at atmospheric pressure. The optimized growth condition for the multi-layered MoS_2 included: (1) providing sulfur source (99.999% in powder form) from two locations: one is located in upstream with weight of 1600 mg, another one is right underneath the holder where the substrate being placed. The temperature of 220 °C and 550 °C was set for heating the sulfur and the substrates respectively. The growth was completed in ten minutes under a heating ramp rate of 50 °C/min and constant flow rate (50 sccm) of forming gas.

B. *Characterizations of Multi-layered MoS_2 Film*

For structural characterization, Raman measurement was performed by WITec alpha300S Raman imaging system with monochromatic laser source (λ of 532 nm). With a 100x objective lens (NA=0.9), 600 gratings/mm was used for PL measurement at room temperature. The cross-sectional image of MoS_2 was captured by using FEI Titan 80/300 Scanning/TEM (200 kV).

C. *Assembly of REM Device with MoS_2 coated FTO*

The two-electrode based EC devices were constructed by sandwiching the liquid electrolyte between bare ITO (working electrode) and the MoS_2 coated FTO (counter electrode) with a 300 μm thick double-sided adhesive spacer tape. The liquid electrolyte was comprised of silver nitrate (0.1 M) and sodium chloride (0.12 M) in solvent MeOH. The electrolyte was filtered before the usage.

III. RESULTS AND DISCUSSIONS

The multi-layered feature of MoS_2 is confirmed by a combination of Raman spectrum and cross-sectional high-resolution TEM image as shown in Figs 2 and 3 respectively. Two distinctive Raman peaks located at ~382.8 cm^{-1} and ~407.8 cm^{-1} were detected, which are corresponding to the Raman features E_{2g} and A_{1g} vibrational modes of the MoS_2 respectively. The wider frequency difference between these two Raman peaks (ΔA_{1g}-E_{2g}) ~25 cm^{-1} indicating more than 5 layers of MoS_2 are grown, comparing with that of the monolayer MoS_2 (ΔA_{1g}-E_{2g} < 20 cm^{-1}) as reported in the literature [6]. In agreement with Raman spectrum, the TEM image shows the clear multi-layered structure of MoS_2 with the interlayer spacing of 0.61 nm (Fig. 3). The basal plane of the MoS_2 film is not parallel to the substrate surface, suggesting the edge-terminated structure has been grown under our growth process. The electrode with such layered structure is expected to enable effective accommodation of ions with fasten ion diffusion property and provide good charge balance in the REM devices.

Having confirmed the multi-layered nature, we next evaluate the charge density behavior of MoS_2. Figure 4 shows the high ion charge density of MoS_2 (~ 11 mC/cm^2, which is 40 % higher than that of standalone TCO) with relatively stable reversible Na^+ intercalation/deintercalation behavior. Under repeated charge-discharge cycling tests (1-40th cycles), the stable ion storage behavior is observed after 30th cycles. However, we also note that an early drop in the charge density was observed in the first 30 cycles, suggesting that more investigations are needed to provide active edge sites for Na^+ intercalation without causing destruction of structure integrity of MoS_2 due to volume expansion.

Next, we investigate the switching behavior of REM device based on dual-FTO electrodes configuration (MoS_2 coated FTO was used as counter electrode, while another bare FTO was used as working electrode) with electrolyte mixed with MeOH containing 0.1 M $AgNO_3$ and 0.12 M NaCl. The Ag^+-containing electrolyte had been filtered before the usage. The REM device is an electrochromic application that rely on the electrodeposition and dissolution of the Ag metal layer to achieve spectrum control. The two-electrode REM device was constructed by sandwiching the Ag ions based liquid electrolyte between the MoS_2 counter electrode and the ITO working electrode. The operation of the Ag-based REM device involves the reversible Ag dissolution and Ag

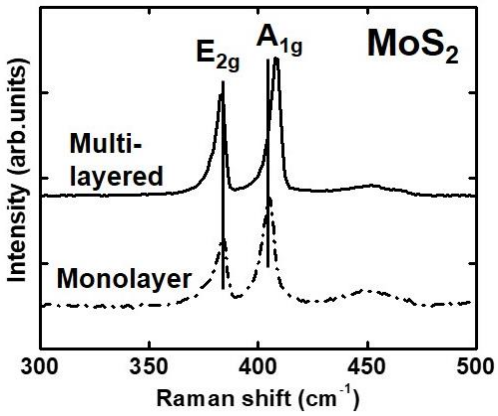

Figure 2. Raman spectrum of multi-layered MoS_2 film. For comparison, Raman feature of monolayer MoS_2 is also indicated (dashed line).

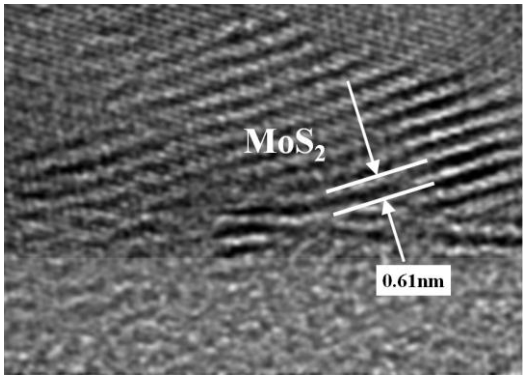

Figure 3. Cross-sectional HRTEM image of MoS_2.

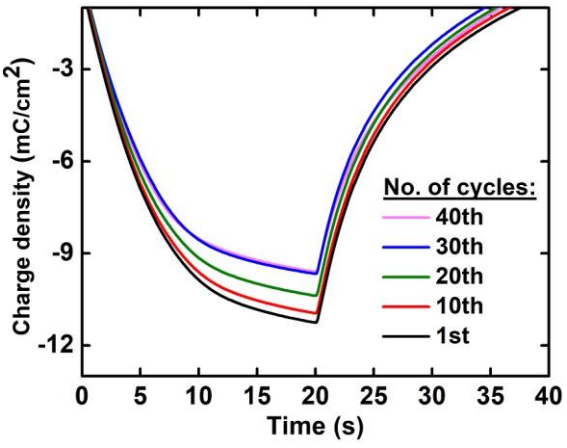

Figure 4. Charge density of MoS_2 being evaluated from the integration of the charge-discharge curves at 1st, 10th, 20th, 30th and 40th cycles in the electrolyte of 0.12M NaCl/ MeOH.

electrodeposition on the working electrode, at the transparent bleached state and mirror state respectively as shown in Figure 5. By modulating the potential across the two electrodes, the reflective Ag metal with a thickness of ~ few tens of nanometers would be either formed on the ITO working electrode or dissolved into the electrolyte, making the REM device becomes reflective-transparent switchable. The charges release/consumed during the oxidation/reduction

reactions occur on the working electrode must be compensated effectively by those involved in the reduction/oxidation reactions happen on the counter electrode.

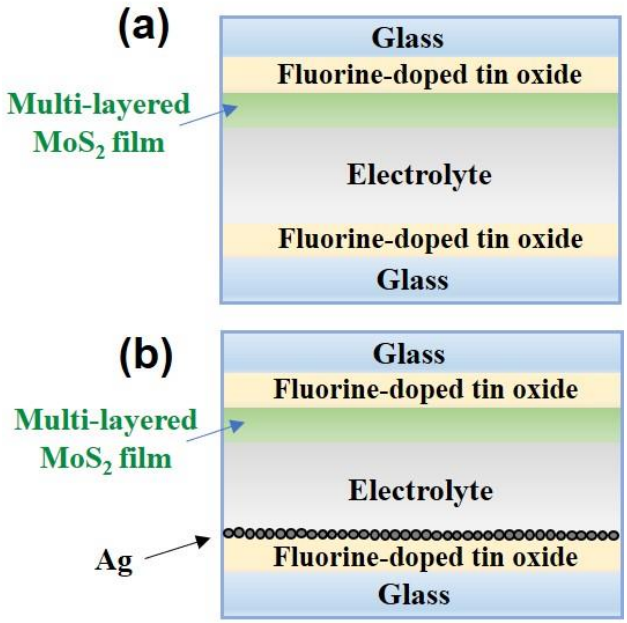

Figure 5. Schematic drawings of reversible electrodeposition mirror device in (a) bleached and (b) mirror state with multi-layered MoS_2 counter electrode.

As shown in Fig. 6, the wide dynamic control in the light reflectance (67 % and 6.6 % in the mirror and bleached states at wavelength of 650 nm respectively) can be measured upon switching the Ag-based REM device with MoS_2 counter electrode between -3.0 V and + 1.6 V. The MoS_2 counter electrode with high charge storage behaviour is the ideal ion storage layer in REM, considering it can balance the charges required for the electrochemical reactions happen during the device switching.

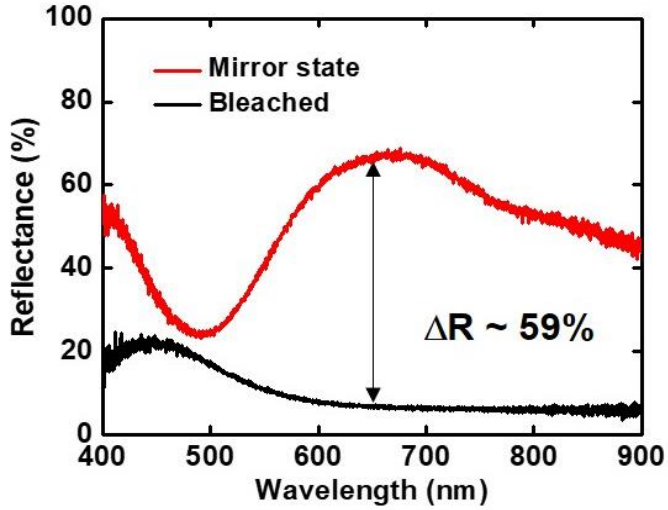

Figure 6. The optical reflectance of REM device upon switching under different bias: -3.0 V (Ag mirror formation) and + 1.6 V (Ag mirror dissolution).

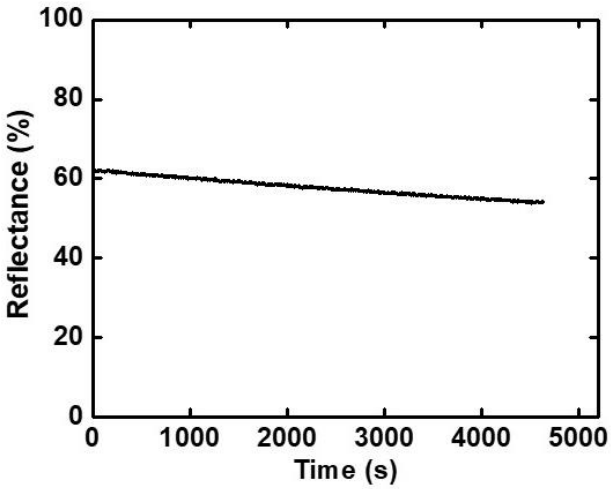

Figure 7: Mirror retention behavior of REM device. Under open circuit state, 5 % of light reflectance at wavelength of 650 nm was dropped after 80 minutes.

Ideally once the mirror is formed, the mirror state still can retain even after powering off the REM device. However, one of the most challenging issues of REM windows is the self-erasing of the mirror in the power off state, which will increase the power consumption in retaining the mirror state. Further mirror retention test was carried out here in order to investigate the memory effect of MoS_2-based REM device. As shown in Fig. 7, only a small drop of reflectance (5 %) was observed under open circuit state. The mirror state can maintain for longer than 80 minutes, which is comparable to the previous reports [7-12]. From the application point of view, the large optical modulation in the light reflectance (ΔR ~59 %) with stable mirror retention suggests the REM device with MoS_2 counter electrode can meet the energy-saving requirements in smart glass applications.

IV. CONCLUSION

A facile sulfurization method for the preparation of multi-layered MoS_2 on the transparent conductor is presented. The layered structure of MoS_2 could endow the efficient electron/ion transport pathways for fast charge transfer. Together with the good ion storage behavior, the MoS_2 pursues its potential in electrochemical applications.

V. ACKNOWLEDGMENT

The authors gratefully acknowledge financial support from the Institute of Materials Research and Engineering (IMRE) under the Agency for Science, Technology, and Research (A*STAR) via Career Development Fund/C210112032.

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