



Exfoliated molybdenum disulfide for dye sensitized solar cells



Edwin O. Ortiz-Quiles, Carlos R. Cabrera*

Department of Chemistry, P.O. Box 70377, University of Puerto Rico – Río Piedras Campus, San Juan, PR 00936-8377, United States

ARTICLE INFO

Article history:

Received 29 July 2016

Revised 9 January 2017

Accepted 10 January 2017

Keywords:

Molybdenum disulfide

Exfoliation

Dye sensitized solar cells

TiO₂

Photoelectrochemistry

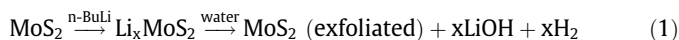
ABSTRACT

Molybdenum disulfide (MoS₂) is a layered material with promising photo-electroactive properties with possible application in solar cell devices. In this work, exfoliated MoS₂ (E-MoS₂) was produced using a chemical intercalation and exfoliation process. After an exhaustive characterization of the material, two different solar cell arrays were studied for the photoanode using the synthesized exfoliated MoS₂, as sensitizer and thin film. Normalized incident photon-to-current conversion efficiency and electrochemical impedance spectra were generated to further understand the photocurrent and electron transition behavior in the dye sensitized solar cell array. An increase in normalized incident photon-to-current conversion efficiency (IPCE) for E-MoS₂/TiO₂ hybrids and layered films was observed when compared to TiO₂. The results provide evidence of device enhancement after using exfoliated MoS₂ by increasing photocurrent efficiencies and lowering charge transfer resistance.

© 2017 Elsevier BV. All rights reserved.

Introduction

Photochemical properties of transition metal dichalcogenides have been studied for more than 30 years, providing promising results as photocatalysts for energy applications [1–5]. Recent works on these layered materials, particularly on molybdenum disulfide (MoS₂), demonstrate that structural changes provoke different electron transitions in the system [6–8]. MoS₂ is a non-precious metal, relatively earth abundant, and stable, which possess three main crystalline structure types: 2H, 3R and 1T; with hexagonal, rhombohedral, and trigonal unit cells, respectively [9]. The thermodynamically stable 2H phase can be affected by chemical reactions such as the intercalation of small molecules [10,11]. A common reactive used to complete this intercalation is n-butyllithium (n-BuLi), since lithium ions strongly interact with MoS₂ layers [12]. The quantity of lithium ions inside the layers may fluctuate depending on the duration of the reaction and the concentration of n-BuLi. This interaction produce a Li_xMoS₂ specie that can react with water to exfoliate the MoS₂ layers [10].



MoS₂ chemical treatments can affect the oxidation state of MoS₂ and its photoabsorption behavior, hence altering its physicochemical properties [13–15]. These changes provide the opportu-

nity to produce new materials and interfaces, improving properties such as radiation absorption and electron mobility range [16–18]. These two characteristics make exfoliated MoS₂ an excellent material to be tested in dye-sensitized solar cells (DSC), especially for the photoanode of this device [19–21]. Solar cells normally use expensive organometallic ruthenium based dyes, which decompose under high temperature [22,23]. In contrast, exfoliated MoS₂ (E-MoS₂) is a stable inorganic compound, which can also absorb in the visible region where a relatively high concentration of sunlight photons are available [24–26]. A recent study by Lynch et al. suggest enhancement in DSSC electron transfer processes when MoS₂ is added to graphene at the counter electrode. [27]

Two approaches are studied in this work; 1) the use of exfoliated MoS₂ as enhancer for electron transfer reactions and 2) as a substitute of ruthenium based dyes. Exhaustive physicochemical characterization of the MoS₂ during the intercalation and exfoliation process was accomplished using X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS), Raman Spectroscopy and Ultraviolet and Visible Absorption (UV/Vis). The E-MoS₂ was further tested in a dye sensitized solar cell. Finally, Electrochemical Impedance Spectroscopy (EIS) was done to obtain an insight of the electron process occurring in these two approaches. Previous results provide evidence of the potential use of exfoliated MoS₂ in this photovoltaic devices [2,10,18,25,28,29]. This study provides two strategies using E-MoS₂, prepared by wet chemistry techniques, for photovoltaic applications.

* Corresponding author.

E-mail address: carlos.cabrera2@upr.edu (C.R. Cabrera).

Experimental details

Materials

Molybdenum sulfide (powder <2 μm , 99%), n-butyllithium (~ 1.6 M in hexane), lithium iodide (crystalline powder, 99.9% trace metals basis), iodine (ACS reagent, $\geq 99.8\%$, solid), and graphite rod (L 150 mm, diam. 6 mm, 99.995%) were bought from Sigma-Aldrich. Sulfuric acid (Optima™) was obtained from Fisher Chemical; acetonitrile (ACS Grade, low water) from BDH; copper grids (300 mesh) from TedPeco; polycarbonates filters (Isopore™ membrane filters, polycarbonate membrane) and titanium dioxide (nanoparticles paste) from Arbor – Scientific.

Exfoliated MoS₂ synthesis

To complete MoS₂ lithium intercalation, 10 g of MoS₂ were mixed with an excess of n-butyllithium for 168 h in a LABCONCO protector glove box. The powder was then filtered and washed with 200 mL of hexane, and left until dried inside the glove box. Afterwards, it was sealed and stored for exfoliation. MoS₂ exfoliation was induced by adding 200 mg in 20 mL of nanopure water (18.2 M Ω ·cm and pH = 6.8). Lithium species were removed after centrifuging three times for 20 min in a Cole-Parmer centrifuge at 3400 rpm. The resultant powder constituted the exfoliated MoS₂. Suspensions of E-MoS₂ 0.06 M in nanopure water were produced to be tested in a DSC setup.

MoS₂ characterization

Raman results were obtained using a DXR™ Raman Microscope with a 532 nm source at 10 μm working distance. X-ray diffraction (XRD) patterns were generated using a RIGAKU SmartLab diffractometer in reflectance Bragg-Brentano geometry at 40 kV and 44 mA power, equipped with high speed 1D detector (D/teX Ultra). PDXL software was employed to fit the obtained patterns and paired with data base card: 2H-MoS₂ (01-071-9809), LiMoS₂ (00-018-0752), and 3R-MoS₂ (01-074-0932). Scanning electron microscopy (SEM) images were produced in a SEM JSM-7500F – field emission SEM in copper grids at 2 kV. XPS binding energy spectra were produced using a PHI QUANTUM spectrometer equipped with an Al K α polychromatic X-ray source with a pass energy of 58.70 eV. The binding energies were corrected using the carbon 1 s peak at 284.8 eV. The deconvolution was completed with Multi-Pak software version 9.4.0.7. All ultraviolet and visible light absorption spectra were obtained in an aqueous media using a quartz cell and a Shimadzu UV-2550. Cyclic voltammetry was completed using a PAR STAT 2273.

Solar cells preparation and measurements

Commercial TiO₂ paste was deposited dropping 1 mL and dispersing it with a glass rod over a 2.5 \times 2.5 cm² fluorine doped tin oxide glass (30 Ω), of 0.4 thickness, previously immobilized with Scotch tape. Afterwards, the sample was heated to 500 °C for 3 h to produce the photoanode. The same deposition and dispersion technique was employed to produce the MoS₂ film, but it was heated for only 15 min at 500 °C instead. The hybrid production consist of mixing 1 mL of the commercial paste with 1 mL of 0.06 M of the exfoliated sample producing a 1:10 mass ratio of MoS₂ to TiO₂ respectively. Soon after, it was deposited and dispersed in the same manner as the TiO₂ paste. The graphite bar (amorphous carbon (aC)) was mechanically deposited over the surface to produce the cathode. Both electrodes were assembled and a drop of the electrolyte solution prepared in acetonitrile with

0.05 M of LiI and 0.5 M of I₂ was added. Ohmic resistance was measured previous to photoelectrochemical analyses as quality control procedure to identify if a short circuit was occurring inside the cell. After preparation, the cell was tested in a Newport Quantum Efficiency/Incident Photon-to-current Conversion Efficiency (IPCE) Measurement System with a 3000 W Xenon light source, a monochromator, and radiometer. The illuminated area on the DSC was 1 cm². The PARSTAT 2273 potentiostat was employed to obtain electrochemical impedance spectroscopy results in a frequency range of 5 kHz to 1 Hz at 5 mV excitation voltage and exposed to 130 W/cm² using an Hg phosphorescent polychromatic light source. Results obtained from this experiment were fitted using ZSimpWin 3.30 and a R(QR) equivalent circuit.

Results and discussion

Crystal orientation of MoS₂

X-ray diffraction studies were employed to characterize the different orientations in the MoS₂ exfoliation synthesis, and their respective peaks were identified using Rigaku PDXL software (Fig. 1).

Indexing of bulk MoS₂ was completed and the corresponding pattern was obtained from the literature (Fig. 1a) [30,31]. The resulting peaks are characteristic of molybdenite in the trigonal prismatic (2H) coordination. Results of the lithium intercalated MoS₂ are presented in Fig. 1b. Intercalation of the system was confirmed by a shift to the left and a reduction of intensity of the peak between 13° and 15° indicating the formations of lithiated MoS₂ crystallites. A broadening of peaks also occurs, distinctive of a reduction in MoS₂ particle size [10,32]. In Fig. 1c, a shift of the peak near 14° to the right can be detected after exfoliation and purification of lithium treated MoS₂. This displacement at higher angles has been associated to a reduction in the distance between MoS₂ layers [33,34]. Therefore, lithium removal producing the exfoliation of the MoS₂ layers has been achieved during the chemical synthesis. An additional broadening of the peak indicates the formation of smaller MoS₂ crystallites, which could be explained by the reactivity of intercalated lithium with water. This reaction could have provided enough energy to reduce the dimensions of the MoS₂ layers, possibly explaining the transformation of some layers from a 2H to a 3R coordination. Such transformation has been previously presented in the literature [33], yet there is no evidence in our results suggesting a restack process for the exfoliated MoS₂ as reported in this study. Raman results showed physical changes after the lithium intercalation process, probably due to the MoS₂ structural changes detected by XRD analysis.

MoS₂ morphology changes

Morphological changes were detected in by scanning electron microscopy. These images were produced at low acceleration voltage to focus over surface changes on MoS₂ particles (Fig. 2). Highly organized MoS₂ layers were observed for the starting material in Fig. 2a. Particles with layers length over 1 μm are multiple stacked in a well-defined array with a smoothed surface. Similar particles sizes are observed in the intercalated sample (Fig. 2b), but smaller layers are visible in the sample in comparison with the precursor. Furthermore, the particles lose their defined edges, and the surface presents more imperfection. Consequently, the well-defined layers of the particles change to a wrinkled surface. These changes are consistent with the XRD results, where the well-organized bulk MoS₂ has relative low interplanar distances than intercalated sample. This could be due to the presence of lithium ions separating the layers. The affected edges could also be explained by the

Download English Version:

<https://daneshyari.com/en/article/8917837>

Download Persian Version:

<https://daneshyari.com/article/8917837>

[Daneshyari.com](https://daneshyari.com)