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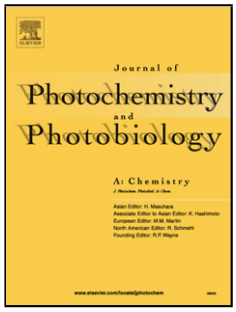

Structural and Photoelectrochemical Characterization of Heterostructured Carbon Sheet/Ag_2MoO_4-SnS/Pt Photocapacitor

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Structural and Photoelectrochemical Characterization of Heterostructured Carbon Sheet/Ag_2MoO_4-SnS/Pt Photocapacitor

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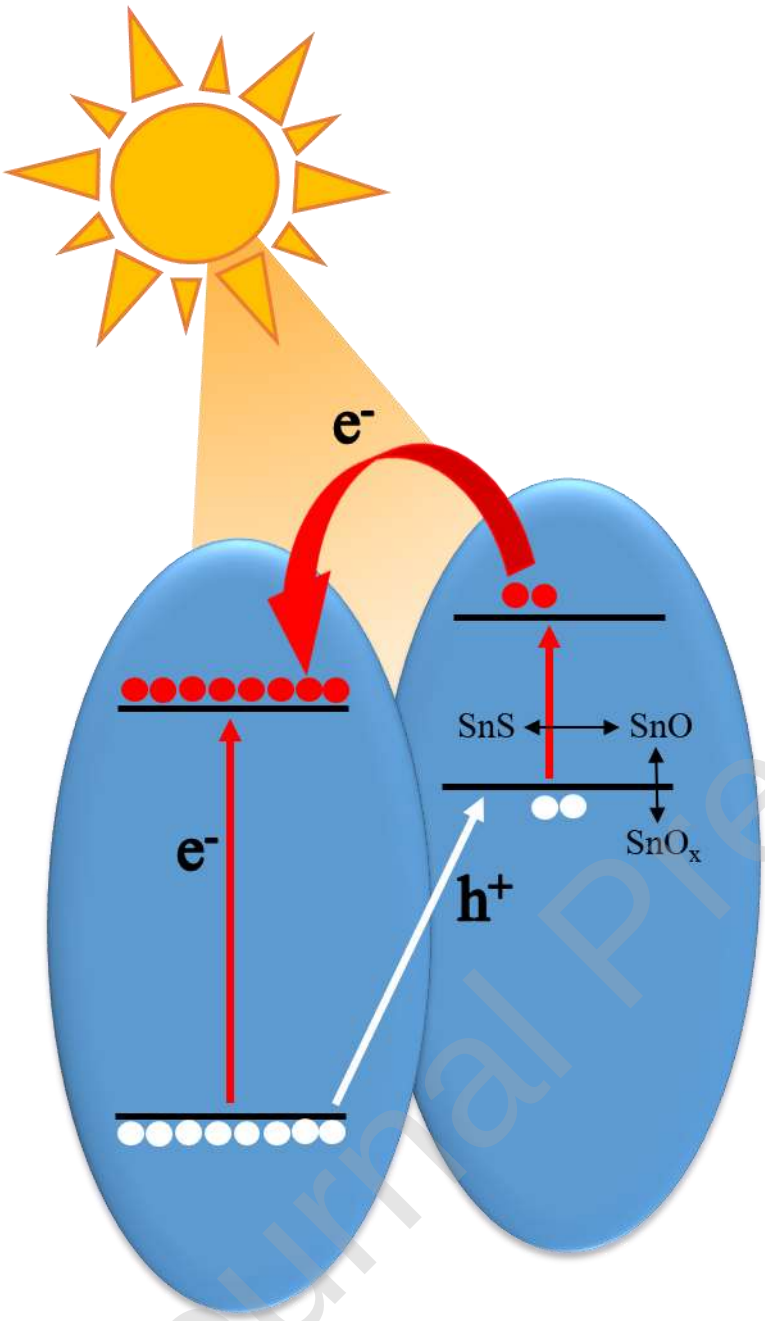
Graphical abstract



Highlights

- Novel heterostructured Ag_2MoO_4-SnS film has been coated on carbon sheet by employing hydrothermal and spray coating techniques.
- Carbon sheet/Ag_2MoO_4-SnS/Pt heterostructured photocapacitor exhibits high specific capacitance of 340 F/g in the presence of high light intensity (1 sun).

- Carbon sheet/Ag_2MoO_4-SnS/Pt heterostructured photocapacitor responds to diffused light as well.

Abstract: Photocapacitors can harvest solar energy and store it in the form of electrical energy and are expected to solve the problem of unstable power output of solar cells under fluctuating sunlight. In the present study, a novel heterostructured Carbon sheet/Ag_2MoO_4-SnS/Pt photocapacitor was developed. In this photocapacitor, SnS nanoparticles act as capacitive platform *via* redox pseudocapacitance, whereas Ag_2MoO_4 molecules act as the active core of the photocapacitor. The crystalline structure and the surface morphology of Ag_2MoO_4-SnS film on carbon sheet was examined by powder X-ray diffraction method (XRD) and Scanning Electron Microscopy (SEM), respectively. The XRD pattern indicates that Ag_2MoO_4 film on carbon sheet is in β phase with respect to Ag_2MoO_4. The SEM images reveal Ag_2MoO_4 film on carbon sheet composing of cubic structures, and SnS film on Carbon sheet/Ag_2MoO_4 composing of spherical nanoparticles. The Carbon sheet/Ag_2MoO_4-SnS/Pt heterostructured photocapacitor, when subjected to visible light illumination, showed a specific capacitance of 340 F/g with an open circuit potential of 1.25 V *vs.* Ag/AgCl electrode. The high capacitance obtained with this novel device may be attributed to the large specific area and high conductivity of the Ag_2MoO_4-SnS film. This research study has opened a new avenue for an effective heterostructured photocapacitor.

Keywords: Photocapacitor, photoelectrochemical characterization, specific capacitance, silver molybdate, carbon sheet

1. Introduction

Solar radiation acts as the energy input in the growth of energy systems in the present world which can meet the future global energy demand [1,2]. The energy can be stored by two different approaches, batteries and capacitors. Batteries convert and store the electrical energy as chemical energy; but capacitors store the electrical energy and give this energy back to the circuit whenever necessary [3]. Capacitor is a special class of energy storage device which consists of electrode materials, separators, and electrolytes. They can be categorized into different types: electric double layer capacitors (EDLC), pseudo capacitors, hybrid capacitors, *etc.* [4]. EDLCs are known as super capacitors as they provide high levels of electrical power and possess long operating lifetime [5]. Pseudocapacitors are based on the redox reactions of electrodes, such as conductive polymers or transition metal oxides. Hybrid capacitors are a combination of EDLCs and pseudo capacitors. Recently, a type of capacitor that can be charged by solar radiation has been developed and named as 'photocapacitor'. Photocapacitors (PCs) are charged utilizing solar light, which allows for direct storage of solar energy [6,7]. In photocapacitors, electrons in the valence band of a semi-conducting material absorb solar energy and get excited to the conduction band leaving positive holes behind. These charged particles, positive holes and negative electrons, are free charge carriers that can mediate electrical current [3].

In the past decade, some interesting approaches have been reported to harvest solar radiation with photocapacitive devices, as novel models of energy conversion and storage. In the general scheme, solar radiation charges the photocapacitor and the discharging process takes place in the dark. Over the past few years, titanium dioxide (TiO_2) has been utilized in photocapacitors due to its non-toxicity, low cost, relatively high chemical stability, and strong oxidizing power [8,9]. However, practical applications of TiO_2 in photocapacitors are limited owing to its wide band gap (3.2 eV) [10], which results in utilization of the UV radiation that amounts only to 5% of the solar

spectrum [11]. In order to harvest the solar energy more efficiently, the n-type silver molybdate, Ag_2MoO_4, has been identified as a promising photoanode material for different photo-electro-chemical applications like photo-catalysis including degradation of dyes [12–14] and photo-switches [15] due to its unique properties that include environmental friendliness, photoluminescence, high electrical conductivity, good photocatalytic activity, and remarkable electrochemical energy storage performance [16–18]. This material can be excited under UV and Visible light irradiation [19]. To improve the photoelectrochemical performance of this material, different strategies like doping [20,21] or heterostructuring [22–25] with other semiconductors have been developed. The Bi_2S_3 sulfide semiconductors are found to be ideal candidates to form heterojunction structures with other semiconductors and to be employed as photosensitizers in water splitting [26]. Further construction of heterojunction is an efficient way to harvest solar energy effectively [14]. In this regard, SnS with the direct band gap of 1.8 eV being the absorbent requires an n-type wide band gap transparent semiconductor as the heterojunction partner in photovoltaic applications [27].

In the present study, Ag_2MoO_4 (band gap~3.24 eV) [28] material is employed as the photoactive core of a novel photocapacitive system, to generate electrons and holes by absorbing solar radiation. The photogenerated holes are subsequently stored in a capacitive SnO_x layer. This storage stand is obtained through photo oxidation of SnS spherical nanoparticles. The combination of both materials provides a singular hetero-structured system (Ag_2MoO_4-SnS), capable to convert and store solar energy without applying any electrical bias only under solar illumination.

2. Materials and Methods

2.1. Materials

The chemicals used for coating of Ag_2MoO_4 are silver nitrate [$AgNO_3$] (≥99%), sodium molybdate dihydrate [$Na_2MoO_4.2H_2O$] (≥99%), urea [$CO(NH_2)_2$] and ammonium hydroxide [NH_4OH] (28.0-30.0%) whereas tin (IV) chloride pentahydrate [$SnCl_4 \cdot 5H_2O$] (98%), thiourea [$CS(NH_2)_2$] (≥99.0%), and acetone [$(CH_3)_2CO$] (≥99.0%) were used for SnS coating. All the chemicals were of AR grade purchased from Sigma-Aldrich and used without any processing. The carbon sheet was attained from Veermak Industries. The phosphate buffer solution (PBS) was prepared from Na_2HPO_4 and NaH_2PO_4 of HPLC grade and all the required solutions were prepared using deionized water (DI water).

2.2. Synthesis

The heterostructured Ag_2MoO_4-SnS was synthesized by coating carbon sheet with Ag_2MoO_4 followed by SnS using hydrothermal and spray coating techniques, respectively.

Prior to the synthesis of Ag_2MoO_4, carbon sheet substrate was ultrasonically washed with deionized water followed by ethanol and acetone. The Ag_2MoO_4 was prepared by stirring silver nitrate and sodium molybdate in the presence of urea for 30 minutes. The resultant white precipitate was dissolved in water-ammonia mixture, heated at 150 °C for 6 h in an autoclave containing pre-cleaned carbon sheet and then it was allowed to cool to room temperature subsequently. The resultant silverish grey coloured Ag_2MoO_4 film on carbon sheet was washed with DI water and acetone.

The precursors of SnS, tin (IV) chloride pentahydrate and thiourea, were dissolved in DI water and isopropanol separately. These two clear colourless solutions were then mixed together and stirred well. The resulted solution was spray coated on the Ag_2MoO_4 film on carbon sheet at 350 °C. The heterostructured blackish grey coloured Ag_2MoO_4-SnS film on carbon sheet was cleaned

with DI water and ethanol and dried. **Figure. 1 (a)** illustrates the schematic representation of the working electrode which consists of carbon sheet substrate, Ag_2MoO_4 and SnS.

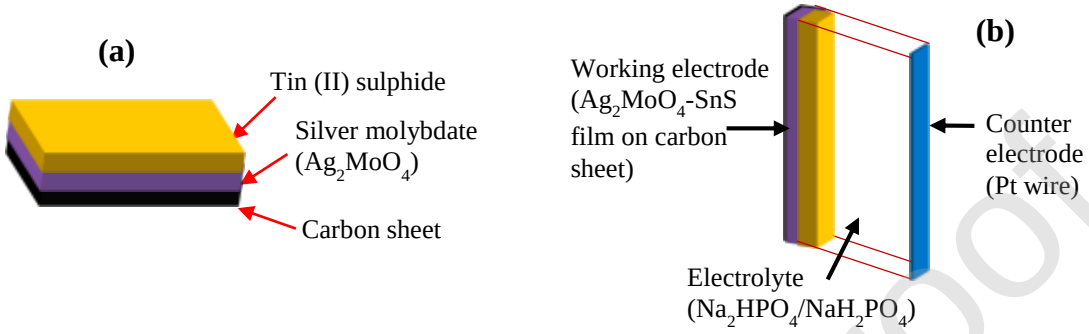


Figure. 1 (a) Schematic diagram of the working electrode and **(b)** heterostructured Carbon sheet/Ag_2MoO_4-SnS/Pt photocapacitor

The heterostructured Carbon sheet/Ag_2MoO_4-SnS/Pt photocapacitor is shown in **Figure. 1 (b)**. It was fabricated with Ag_2MoO_4-SnS film on carbon sheet (working electrode), Na_2HPO_4/NaH_2PO_4 buffer solution (electrolyte) and Pt wire (counter electrode).

2.3. Characterization

The structural properties of Ag_2MoO_4 film and Ag_2MoO_4-SnS film on carbon sheets were characterized by powder X-ray diffraction method [XRD; Rigaku Ultima IV with Cu Kα radiation (λ = 1.5408 A°), 40 kV, 44 mA, 0.02°, 20° < 2θ < 80°]. The morphology was examined by Scanning Electron Microscopy (SEM). The elemental composition of Ag_2MoO_4-SnS film on carbon sheet was carried out by Energy Dispersive analysis of X-ray (EDX) technique. The SEM images were captured on an Oxford instrument and the EDX spectrum was analysed using Bruker EDX analyzer. Diffuse reflectance spectroscopy (DRS) were acquired using a Thermo Scientific Evolution 600 UV-Vis reflectance spectrophotometry.

2.4. Photoelectrochemical measurements

The photoelectrochemical responses, such as cyclic voltammetry (CV) and electrochemical impedence spectroscopy (EIS) of the heterostructured Ag_2MoO_4-SnS film on carbon sheet were determined by potantiostat/galvanostat Autolab (PGSTAT-302) workstation. Measurements were carried out with a three-electrode system (Figure 2) and an aqueous solution buffered to pH 7 using a 0.1 M phosphate buffer (NaH_2PO_4/Na_2HPO_4) as electrolyte. For photoelectrochemical characterization, the electrodes were illuminated using a 300W Xenon lamp and the cyclic voltammetry was carried out in the potential range from -0.6 to 1.25 V.

3. Results and Discussion

3.1. Structural analysis

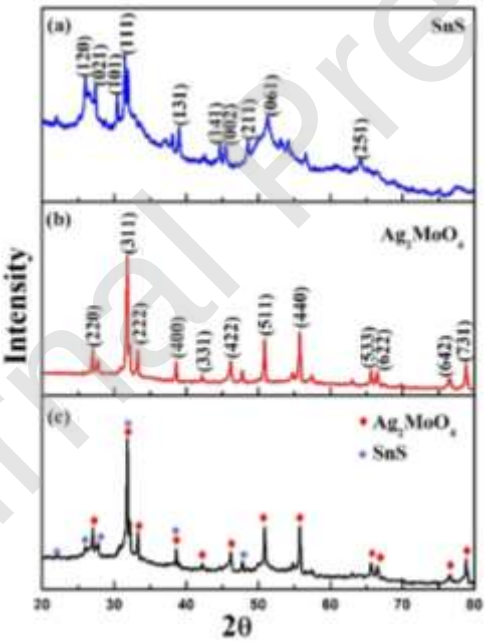


Figure. 2 XRD patterns for **(a)** bare SnS, **(b)** bare Ag_2MoO_4 and **(c)** Ag_2MoO_4-SnS films on carbon sheets

Figure. 2 shows the XRD patterns of bare SnS **(a)**, bare Ag_2MoO_4 **(b)**, and Ag_2MoO_4-SnS **(c)** films on carbon sheets. The peaks of bare SnS (**Figure. 2 (a)**) observed at 2θ values of 25.93°,

27.47°, 31.56°, 39.00°, 44.74°, 45.64°, 48.82°, 51.27° and 64.08° correspond to the planes of (120), (021), (111), (131), (141), (002), (211), (061) and (251), respectively [29,30]. Additional peaks found in the spectrum may be due to the unreacted precursors. It can be clearly seen from **Figure. 2 (b)**, that the diffraction peaks of Ag_2MoO_4 could be well indexed to a cubic structure of Ag_2MoO_4 (PDF 00-008-0473) film on carbon sheet. The peaks observed at 2θ values of 27.1°, 31.8°, 33.3°, 38.6°, 42.2°, 47.8°, 50.5°, 55.8°, 65.7°, 66.6°, 76.5°, and 78.9° are due to the d-spacing of (220), (311), (222), (400), (331), (422), (511), (440), (533), (622), (642), and (731) for bare Ag_2MoO_4 (**Figure. 2 (b)**), respectively and indicate the formation of crystalline β-Ag_2MoO_4 [19,31]. The XRD pattern of Ag_2MoO_4-SnS film on carbon sheet (**Figure. 2 (c)**) shows good resemblance with those of bare Ag_2MoO_4 and bare SnS. In **Figure. 2 (c)**, the weak peaks of SnS may be attributed to poor crystallization and low concentration of SnS in the final Ag_2MoO_4-SnS film on carbon sheet. The broader and sharper peaks observed for Ag_2MoO_4-SnS film may confirm the reduced size of the crystallites.

3.2. Surface microstructure and surface analysis

The SEM images of Ag_2MoO_4 film on carbon sheet and SnS film on Carbon sheet/Ag_2MoO_4 and cross section of SnS are shown in **Figure. 3**.

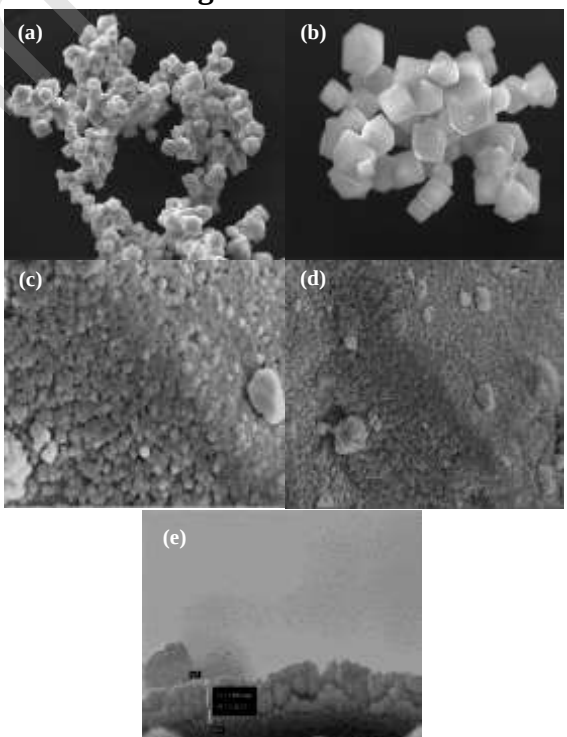


Figure. 3 SEM images of **(a-b)** Ag_2MoO_4 film on carbon sheet, **(c-d)** SnS film on carbon sheet/Ag_2MoO_4, and **(e)** Cross section of SnS

SEM measurements were employed to investigate the morphologies of different samples. These SEM images were recorded with different magnifications of about 25,000 and 50,000. **Figure. 3 (a-b)** shows the SEM images of Ag_2MoO_4 film on carbon sheet and it could be observed that it composed of nanocubes. When the surface of Ag_2MoO_4 film on carbon sheet was heterostructured with SnS, the resulting Ag_2MoO_4-SnS film on carbon sheet shows a morphology varied from that of Ag_2MoO_4 film on carbon sheet and found to be in spherical shape (**Figure. 3 (c-d)**). It can be clearly seen from the **Figure. 3 (e)** that the thickness of spray coated SnS is 650 nm; the particles are homogeneously spread and uniformly covered the whole surface of the carbon sheet.

3.3. Elemental composition analysis

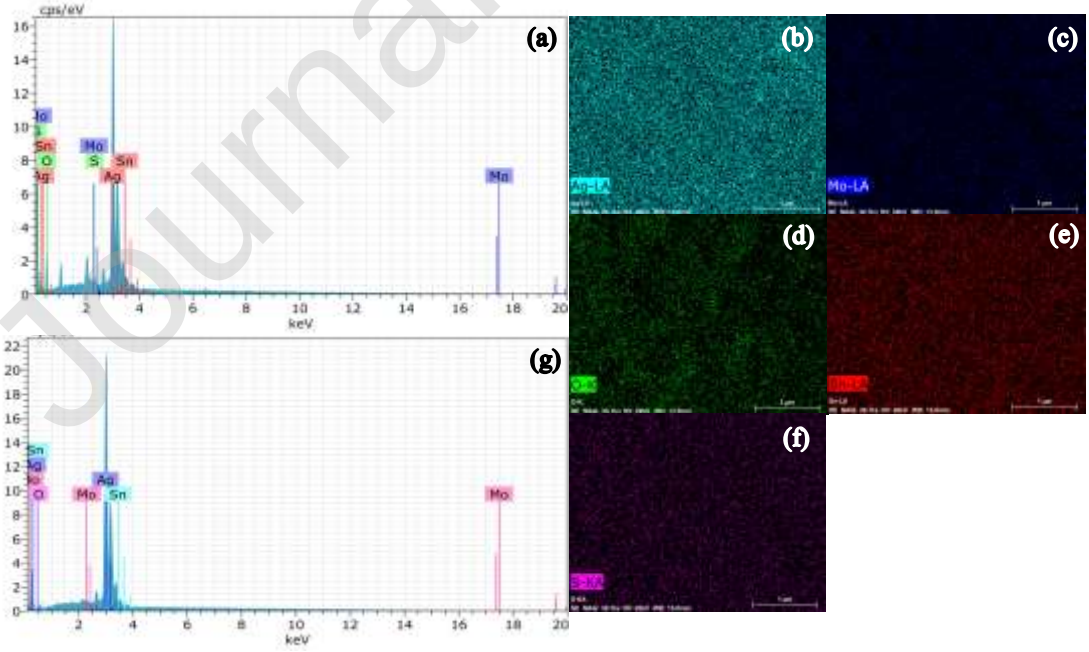


Figure. 4 EDX spectrum of **(a and g)** Ag_2MoO_4-SnS film on carbon sheet before and after cyclic voltammetry; **(b-f)** EDX-mapping of the elemental distribution before cyclic voltammetry

The elemental composition of Ag_2MoO_4-SnS film on carbon sheet was measured by EDX technique. The EDX spectrum of Ag_2MoO_4-SnS film on carbon sheet was recorded in the binding energy region of 0.0-20.0 KeV as shown in **Figure. 4 (a)**. The results show the presence of Ag, Mo and O elements, in addition to elemental Sn and S signals, which suggests that SnS had been loaded on the Ag_2MoO_4 film on carbon sheet surface. To obtain the structural information, EDX-mapping was performed and the elemental distribution of Ag, Mo, O, Sn and S were identified. **Figure. 4 (b-f)** clearly shows the signals of Ag, Mo, O, Sn and S elements in a single particle. In addition, the SnS spherical nanoparticles, loaded by the spray coating method, are found to be distributed on the surface of the Ag_2MoO_4 nanocubes.

3.4. Optical properties

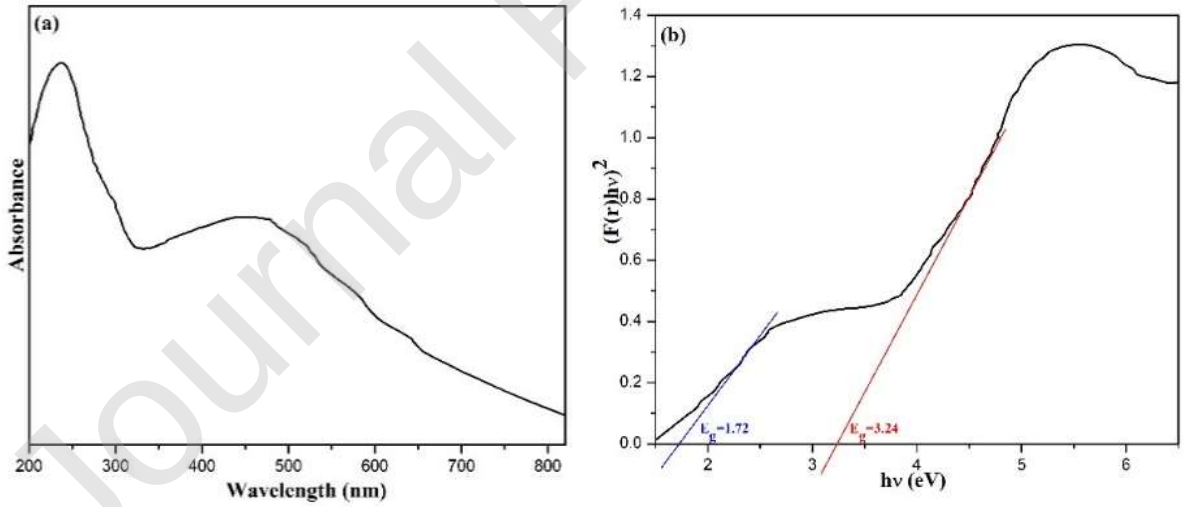


Figure. 5 UV-Vis diffuse reflectance spectra of Ag_2MoO_4-SnS coated carbon sheet

The optical properties of the Ag_2MoO_4-SnS heterostructure were evaluated by UV-Vis diffuse reflectance spectrophotometry, and the plots of absorbance *vs*. wavelength, and $[F(r)hv]^2$

vs. hν of Ag_2MoO_4-SnS coated carbon sheet was shown in **Figure. 5 (a)** and **(b)**, respectively. The Ag_2MoO_4 and SnS showed an absorption edge of 450 nm and 300 nm, respectively which can be attributed to the excellent light harvesting capabilities of the photocapacitor. The optical band gaps of Ag_2MoO_4 and SnS were estimated from the intercept of the extrapolated linear fit for the plotted experimental data of $[F(r)hv]^2$ *vs.* hν near the absorption edges. This indicate direct band gap energy of 1.72 eV and 3.24 eV for SnS and Ag_2MoO_4, respectively. These values are in good agreement with those reported previously [12,32]. These results further confirm the presence of Ag_2MoO_4 and SnS in Ag_2MoO_4-SnS coated carbon sheet.

3.5. Photoelectrochemical analysis

In order to measure the specific capacitance, the cyclic voltammetry studies were carried out and **Figure. 6** illustrates the cyclic voltammetry of Ag_2MoO_4, and Ag_2MoO_4-SnS films on carbon sheets.

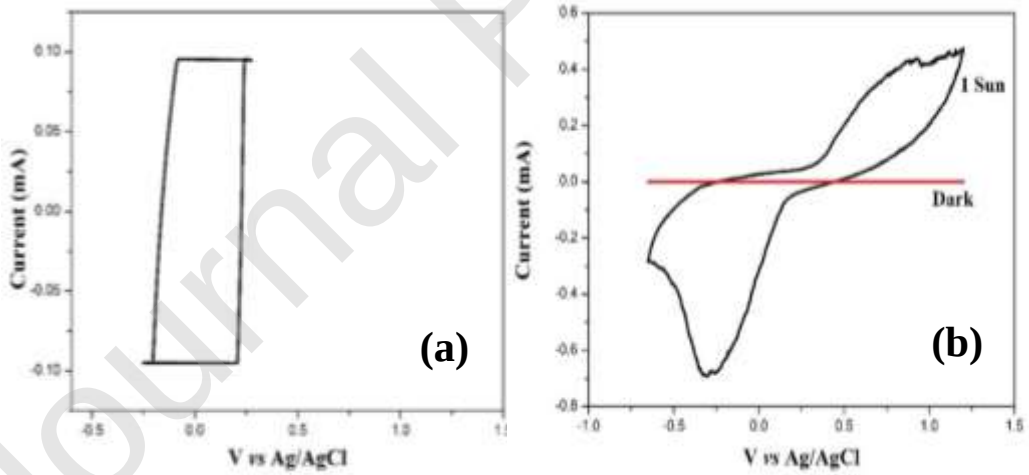


Figure. 6 Cyclic voltammetry of **(a)** Ag_2MoO_4, and **(b**) Ag_2MoO_4-SnS films on carbon sheets

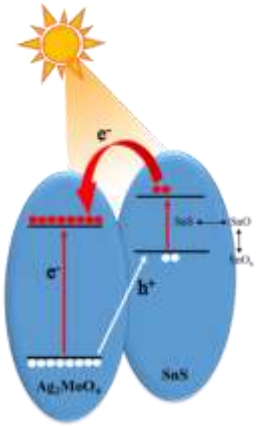
The as-synthesized heterostructured Ag_2MoO_4-SnS film on carbon sheet was conditioned by cyclic voltammetry in a phosphate buffer solution (pH≈7) with scans between -0.6 to 1.25 V *vs.* Ag/AgCl (**Figure. 6 (b)**), where the oxidation of SnS to SnO_x took place, which was confirmed by

the EDX spectrum as shown in the **Figure. 4 (g)** that indicates the absence of elemental S signal in the heterostructure. During the scan, the pristine carbon sheet/Ag_2MoO_4-SnS photoelectrode showed an anodic response, which can be related to the oxidation of SnS with capacitance. After the scan, a stable voltammogram curve with high capacitance was observed which is due to the oxidation of SnS (**Figure. 6 (b)**) to SnO_x. In contrast, no photocapacitive response was obtained when the Ag_2MoO_4 without SnS film was tested under the same conditions (**Figure. 6 (a)**). This clearly suggests a synergistic interaction between Ag_2MoO_4, and the oxidized product of SnS (SnO_x) has led to the observed photocapacitive behavior. The following simplified reactions show the evolution of the photocapacitive mechanism and the subsequent charge and discharge processes:

$$Sn^{2+} + H_2O \leftrightarrow SnO + 2H^+ \quad (1)$$

$$SnO + 2H_2O + 2xh^+ \leftrightarrow SnO_x + 2xH^+ \quad (2)$$

The stabilized voltammogram with photocapacitive behavior is believed to be related to the SnO_x/SnO redox couple. In fact, a photo-assisted oxidation of SnO (reaction 2) during the forward scan and a reduction reaction during the reverse scan had led to a typical capacitive behavior. In the dark, the conditioned Ag_2MoO_4-SnS heterostructure did not retain any capacitance as shown in **Figure. 6 (b)**, indicating that the capacitive behavior is related to the photogenerated charges at



the Ag_2MoO_4 electrode under illumination. Consequently, the suggested mechanism for the formation of the Ag_2MoO_4-SnO_x heterostructured photocapacitor is illustrated in **Figure. 7**.

Figure. 7 Proposed mechanism for the evolution of Ag_2MoO_4-SnO_x photocapacitor system

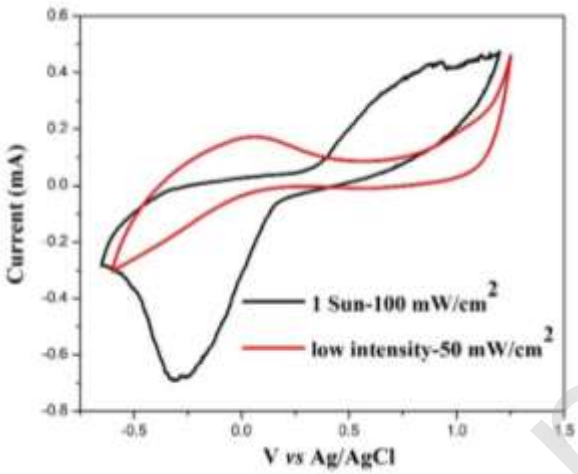


Figure. 8 Cyclic voltammetry of Ag_2MoO_4-SnS film on carbon sheet at different light intensities

The **Figure. 8** shows the cyclic voltammetry of varied specific capacitance for different light intensities. The specific capacitance was calculated as per the literature [33]:

$$C_s = \frac{\int I\,(V)\,dV}{m \times \Delta V \times v}$$

Where $\int I(V)dV$ represents the area enclosed by the CV curve; m is the active mass of the electrode material, ΔV is the potential window, and υ is the scan rate. No photocapacitance was attained with bare Ag_2MoO_4, whereas capacitances of around 340 F/g and 170 F/g were obtained with the SnS coated device under high (1 sun), and low intensity of light illumination, respectively. These values found to be relatively higher than that of reported values, especially with the $BiVO_4$-PbO_x photocapacitive device [1]. The cathodic peak is situated at around -0.6 V whereas anodic peak is at around 1.25 V for Ag_2MoO_4-SnS film on carbon sheet under both light intensities.

Light intensity (mW/cm^2)	Specific capacitance (F/g)	Specific energy (Wh/kg)
100	340	~ 40
50	170	~ 20

Table. 1 Specific capacitance and specific energy of Ag_2MoO_4-SnS film on carbon sheet

The results of the specific capacitance and specific energy are presented in **Table. 1**. The specific capacitance and specific energy of carbon sheet/Ag_2MoO_4-SnS/Pt photocapacitor enhanced with increase in light intensity. However, the specific capacitance of this integrated photocapacitor is observed to be 170 F/g at low light intensity of 50 mW/cm^2, so it can be concluded that the Ag_2MoO_4-SnS film on carbon sheet responds to diffused light as well. Specific capacitance reported for other materials are compared in **Table. 2**.

Material	Method	Specific capacitance	Reference
FeS_2 cubes	Hot injection	46 $mAhg^{-1}$ (165.6 F/g)	Maogang Gong *et al.*[7]
Mesoporous TiO_2 and microporous AC	Doctor blading	0.69 Fcm^{-2}	Tsutomu Miyasaka *et al.*[34]
$BiVO_4$-PbS quantum dots	Electro deposition and spin coating	6 $mFcm^{-2}$	Saeid Safshekan *et al.*[1]
Ag_2MoO_4-SnS film on carbon sheet	Hydrothermal and spray coating	370 F/g	Present work

Table. 2 Specific capacitance for photocapacitors using different materials: ([7], [34], [1])

Maogang Gong *et al*., worked on photocapacitor using FeS_2 cubes as photoactive material, under 1100 nm NIR (near infrared) illumination, and the specific capacitance was found to be 46 $mAhg^{-1}$ (165.6 F/g) [7]. In another study, Tsutomu Miyasaka *et al*., used mesoporous TiO_2 and microporous AC, where 0.69 Fcm^{-2} of specific capacitance was yielded under the visible light illumination [34]. Saeid Safshekan *et al*., has developed a photocapacitive device based on the heterostructured $BiVO_4$-PbO_x system that exhibits 6 $mFcm^{-2}$ under solar illumination at 100 $mWcm^{-2}$ [1]. In line with these studies, the result from our study on Ag_2MoO_4-SnS film on carbon sheet showed the specific capacitance of 370 F/g under 100 $mWcm^{-2}$.

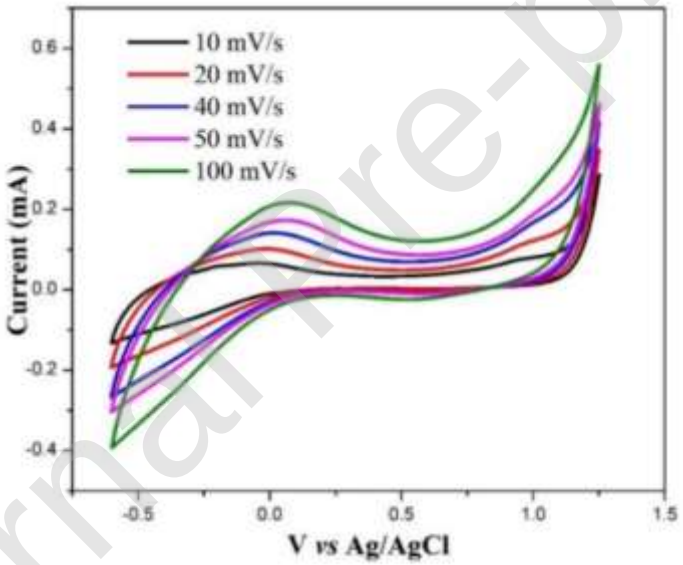


Figure. 9 Effect of scan rate on cyclic voltammetry behavior of the Ag_2MoO_4-SnS film on carbon sheet

Figure. 9 depicts the CV curves of the sample electrode at different scan rates of 10-100 mV/s in the voltage range from -0.6 to 1.25 V at low light intensity. Maintenance of a similar CV shape, and symmetric characteristics of the current response on voltage variation for the sample electrode were observed even at a high scan rate, which indicate good capacitive behavior.

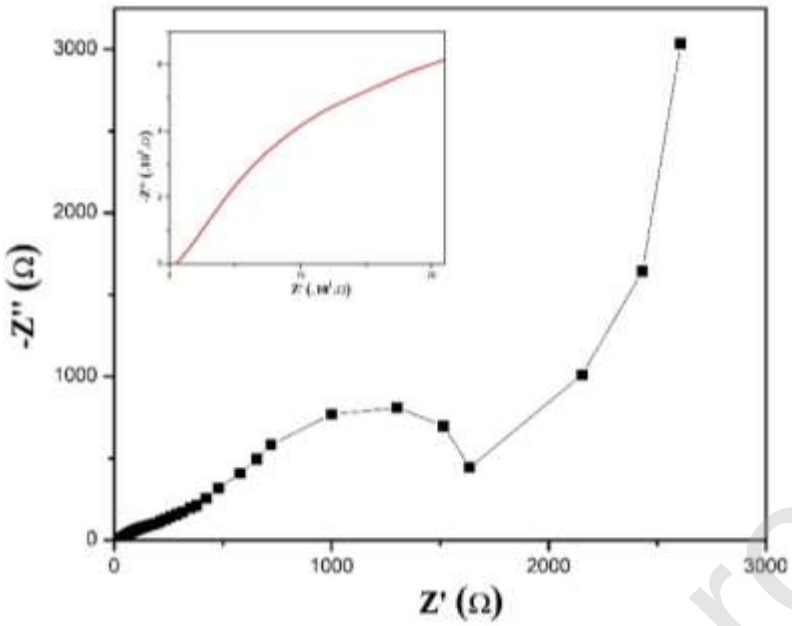


Figure. 10 Nyquist plots of Ag_2MoO_4-SnO_x film on carbon sheet in dark (inset) and under illumination

The electron transport process and the capacitive behavior of Ag_2MoO_4-SnO_x on carbon sheet system were comprehend by performing electrochemical impedance spectroscopy (EIS). **Figure. 10** depicts the Nyquist plot -Z'' vs. Z' obtained under 1 sun illumination and the inset shows the same acquired under dark condition. All the measurements were recorded at 1V. A high resistance was observed with Ag_2MoO_4-SnO_x on carbon sheet in dark, whereas a reduced resistance of ~1700 Ω was attained with 1 sun illumination. This plot consists of a semicircle in high-frequency region (charge-transfer impedance) and a vertical line in low-frequency region (purely capacitive behavior) under illumination indicating the appearance of faradaic phenomena. The charge storage in Ag_2MoO_4-SnO_x carbon sheet system is evident by observed charge transfer under illumination with high capacitance (imaginary part of the Nyquist plot) in EIS [1,35].

5. Conclusion

A novel photocapacitor system is developed based on the Ag_2MoO_4-SnS hetereostructure which evolved to Ag_2MoO_4-SnO_x on controlled oxidation. The photocapacitive mechanism stems out from the conversion of SnS into SnO_x as demonstrated by EDX measurements. Ag_2MoO_4 film and Ag_2MoO_4-SnS film on carbon sheets were successfully prepared in nano scale range using both hydrothermal and spray coating techniques. The crystal phase, elemental composition, morphology, and optical properties of heterostructured Ag_2MoO_4 and Ag_2MoO_4-SnS films on carbon sheets were confirmed by XRD, EDX, SEM, and UV-Vis Spectroscopy, respectively. Cube-like nanostructures of Ag_2MoO_4 were coated on the carbon sheet using hydrothermal method at 150 °C and spherical shaped SnS nanoparticles were then coated on Ag_2MoO_4 coated carbon sheet at 350 °C. The photocapacitive behavior of this system outperforms the most advanced device reported in the literature, showing a specific capacitance of 340 F/g with an open circuit potential of 1.25 V *vs.* Ag/AgCl in the presence of high light intensity (1 sun) and exhibits potential for construction of direct solar energy storage devices. The enhanced ion-diffusion resulting from the increased active sites of the Ag_2MoO_4-SnS heteronanostructure can be acknowledged for the excellent capacitance. This is further supported by the extended spectral response from UV to Visible region.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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