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To cite this article: Muhammad Imran Ahmed et al 2016 Mater. Res. Express 3 045022

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Materials Research Express

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RECEIVED 5 February 2016

REVISED 4 April 2016

ACCEPTED FOR PUBLICATION 7 April 2016

PUBLISHED 27 April 2016

TiO_2/MoS_2 nanocomposite electron selective contact

Absorption enhancement in CH₃NH₃Pbl₃ solar cell using a

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Keywords: perovskite solar cells, titanium dioxide, molybdenum disulfide, transition metal dichalcogenides (TMD)

Abstract

In the present contribution, perovskite absorbers have been combined with few layer thick MoS_2 semiconductor to put together a solar cell allowing broad spectrum harvesting of solar radiations. Such modification allows to achieve solar light harvesting at the band edges, addressing a drawback of $CH_3NH_3PbI_3$ absorbers. We recorded an improved efficiency from 3.7% to 4.3% on the back of this methodology. We have also worked out a novel methodology to synthesize TiO_2/MoS_2 nanocomposite by *in situ* dispersion of liquid exfoliated MoS_2 sheets in the sol gel reaction.

Introduction

Since the nascent advent of perovskite solar cells, they have achieved impressive milestones [1, 2]. Manufacturing protocols have evolved to improve efficiencies [3, 4]. Research has been focused at improving the performance through structural ordering [5], composition modification [6–8] and innovations enabling flexible cells with transparency and color tailoring [9]. Environmental concerns for lead have been addressed with alternate absorbers [10, 11].

An aspect to improve the performance of these solar cells can be to increase light absorption without increasing the film thickness or complicating the device architecture [11, 12]. Though strong absorption of 1.5×10^4 cm⁻¹ at 550 nm [13], drop down in absorption around the band edges affords a possibility of increasing performance by absorption enhancement at these edges. Metallic nanoparticles in different configurations have been reported for absorption enhancement near long wavelength edge [14–16] and have also been credited with lowering the exciton binding energy and improving charge transfer at the electron selective interface [17]. Absorption enhancement over the short wavelength edge remains open for investigation.

Broad spectrum absorption demands continuously tuneable band gap. Since band gap is determined by the chemical composition and the organization of crystal lattice, efforts have been directed at achieving continually tuneable band gap by semiconductor alloying and generating superlattices. Though introduction of Brillouin zones in thin semiconducting layers generated by atomic scale deposition of thin layers allows realization of specific band gap for a particular application, they cannot be dynamically varied during operating conditions. This method is not only challenging to design but also introduces unwanted defects due to variation in mixing ratios and lattice mismatch [18].

Layered 2D semiconductor transition metal dichalcogenides (TMD) have been explored extensively and have the potential to replicate the wonder material properties of graphene. Interplaner weak van der Waals forces ensure efficient exfoliation using micromechanical cleavage and liquid phase exfoliation [19, 20]. Strong planer bonding offers unique properties allowing the optical and electrical properties of MoS₂ to vary between bulk and single/few layers owing to quantum mechanical confinement. Stability of MoS₂ under photoexcitation is derived from the 4d orbital determining Mo conduction and valance band positions in bulk [21]. During exfoliation to nanosize, edge located Mo atoms are freed from the influence of MoS₂ inert basal plane, resulting

in continually shifting optical band gap with the sheet thickness allowing for wide spectrum harnessing of solar spectrum [20].

In bulk form it is an indirect band gap semiconductor and in single layer it is a direct band gap semiconductor allowing virtually continuous tuning of the band gap between 1.2 eV of bulk to 1.85 eV of single layer [22–24]. Investigation of quasi particle band structure of MoS_2 through STM concluded a band gap of 2.34 eV, 0.44 eV higher than the optical band gap [25]. Consistent conclusions have also been drawn from the determination of band gap under the effect of dielectric environment resulting in a 0.3 eV increase over optical band gap [26, 27]. These observations validate the experimental evidence for the photocurrent reported for MoS_2 between 350 to 800 nm. Mobility values vary between 517 cm² V⁻¹ s⁻¹ and 200 cm² V⁻¹ s⁻¹ for bulk [28] and single layer [29]. Strong quenching allows for one order of magnitude higher absorption for MoS_2 in solar cell applications allowing for enhanced optical absorption and improved charge transport at the interfaces. Use of metal sulfides as nanocomposite with TiO₂ in perovskite solar cell systems is reported as a blocking layer of Sb₂S₃ at the interface between TiO₂ and CH₃NH₃PbI₃ enhancing the stability of the system by addressing the interface degradation mechanisms [30].

We report here a perovskite absorber based solar cell employing hole transport layer free design. Synthesis was performed under ambient air conditions of high humidity by modifying the synthesis protocol. TiO_2/MoS_2 nanocomposite was developed using a novel sol gel synthesis method allowing *in situ* incorporation of MoS_2 sheets in the TiO_2 particles matrix. Nanocomposite allowed higher efficiency on the back of greater light harvesting by few layer thick MoS_2 and higher mobilities and reduced interfacial recombination because of the nanocomposite.

Materials and methods

Materials

All the chemicals except CH_3NH_3I were purchased from Sigma Aldrich and were used without further purification. CH_3NH_3I , (MAI) was sourced from Dysol (MS101000-50). Indium doped tin oxide (ITO) was used as front contact. At 10 mm × 10 mm it had a resistivity of 15 Ω cm⁻². ITO coated slides were detergent cleaned, washed with flowing ultra pure water and ultrasonicated in ethanol for 20 min. They were subsequently dipped for one minute in piranha solution, rinsed in flowing ultra pure water and dried by blowing hot air.

Experimental details

Titania nanoparticles were synthesized by sol gel route. Titanium isopropoxide (<97%), 2- methoxyethanol (99.9+ %) and ethanolamine(99+ %) were mixed in 1: 4: 0.5 molar ratio. The mixture was refluxed in a three necked flask in an inert environment, stirred at room temperature for 1 hr, 80 °C for 1 h and finally at 120 °C for 2 h under constant stirring. Light yellow color of the sol indicated the dissolution of isopropoxide precursor in methoxyethanol solvent aided by ethanolamine as linker. Bulk MoS₂ was exfoliated using liquid phase exfoliation technique employing *N*-Methyl-2-pyrrolidone (NMP) as solvent. Probe sonicator was used for exfoliation spanning over 66 h while a chiller was used to maintain temperature of the bath at 2 °C. Suspension thus achieved was centrifuged at 4000 rpm. Supernatant was removed and filtered with 0.22 micron nylon filter. Two methods were used to prepare composite. In the first method, MoS₂ containing filter was sonicated in 2-methoxyethanol and this dispersion was added in TiO₂ sol. In the second method MoS₂ containing filter was sonicated mass fraction of MoS₂ in final TiO₂ sol.

Devices were synthesized by spin coating titania composite over pre cleaned ITO coated glass slides at 2500 rpm for 20 s. TiO_2 coated slides were dried in oven at 500 °C for 2 h with a heating rate of 10 °C per min and were allowed to cool in furnace. $CH_3NH_3PbI_3$ was deposited by a modified two step solution processing method. Lead iodide was dissolved in DMF to obtain a 1 M solution. MAI was dissolved in iso-propanol at 7 mg ml⁻¹. Lead iodide solution was spin coated on TiO_2 coated slides at 3000 rpm for 20 s. Lead iodide coated slides were annealed for 3 min at 40 °C and then at 100 °C for 5 min. They were removed from the oven and then mounted on the spin coater and MAI was coated at 3000 rpm for 20 s. Slides were again annealed for 3 min at 40 °C and 5 min at 100 °C in a laboratory oven. Au was thermally evaporated by a mask to define an active area for the device of 0.11 cm².

Characterization

Microstructures and film morphologies were investigated using scanning electron microscope (JEOL JSM6490A) and atomic force microscope (JEOL SPM 5200). X-Ray diffraction (XRD) studies were done on STOE Stadi MP in θ -2 θ mode using Cu K α source under tube acceleration voltage of 40 KV and tube current of



20 mA. Measurements were recorded with a step size of 0.04° and dwell time of 3 s for each step. ECOPIA HMS-5000 system was used for Hall Effect measurements employing the van der Pauw principle. Contacts were made with silver paste on the samples and gold coated spring loaded contacts were used for measurements. Nanovea PS 50 optical profilometer was used to determine the film thicknesses employing Mountains 2D software suite. Impedance spectroscopy was performed using Biologic EC Lab work station. EC-Lab V10.40 software was used for simulation of impedance data. J–V parameters were obtained on Keithley 2400 source meter. Newport 67005 solar simulator with AM 1.5 G filter was used at an irradiance intensity of 100 mW cm⁻². Voltage step was 10 mV with a step time of 40 ms.

Results and discussion

Pristine MoS₂ dispersions on silicon wafers were investigated under AFM to reveal extent and quality of exfoliation (figure 1). The images revealed that single layers of MoS₂ were obtained in the dispersion with thickness distribution of 0.939 nm. Addition of exfoliated MoS₂ in as prepared TiO₂ sol resulted in poor quality dispersions and formed agglomerates instead of evenly dispersed sheets, critical to obtain broad spectrum harvesting of solar spectrum. Another shortcoming was the difficulty in sustaining the sol once we adopted this technique for the synthesis of nanocomposite. On addition of MoS₂, it was sonicated for even dispersion which resulted in gel formation in most instances. We devised a novel method for better quality dispersion of MoS₂ sheets by dispersing them in the solvent in the sol gel reaction. This allowed uniform distribution of MoS₂ sheets with complete imbedding in the particle matrix. We investigated different wt% and best quality dispersion were achieved for 20 wt% of MoS₂ loading in TiO₂ sol. Higher concentrations resulted in redundant MoS₂ particles on the surface, detrimental to the performance of the final devices. More importantly, higher concentrations resulted in agglomerations causing conduction band of the MoS₂ to decrease below the conduction band of the TiO₂ and thus hampering the very basis of the electronic structure of the devices.

 MoS_2 dispersion in TiO₂ sol was investigated for dispersion quality and restacking effects. Investigation of TiO₂/MoS₂ composite under AFM (figure 2(a)) and SEM (figures 2(b), (c)) confirmed that MoS₂ was completely imbedded in the particle matrix allowing for coverage of sheets with TiO₂ particles. This allowed uniform film structure with mean square roughness of the order of 6.41 nm critical for well functioning solar cells since they allow homogeneous coverage of the perovskite sensitizer and avoid short circuiting of the devices. Both SEM and AFM profiles testify to the effectiveness of the *in situ* method of MoS₂ dispersion in the sol gel synthesis of TiO₂ nanoparticles.

Quantitative validation of MoS_2 dispersion in TiO_2 was obtained through Raman spectroscopy (figure 3(a)) where peak at 146 cm⁻¹ confirmed the anatase titania. Raman signature peaks for MoS_2 are reported at 383 cm⁻¹ for E1 2 g mode associated with antiphase parallel oscillations of sulfur and molybdenum atoms in crystal plane and at 409 cm⁻¹ for A1g mode for sulfur atoms in out of plane antiphase oscillations. We observed peaks at 383 cm⁻¹ and 406 cm⁻¹. Since monolayer of MoS_2 gives a signature peak at 405 cm⁻¹, this suggests that our dispersions consist of monolayers and few layer stacks. The wave number shift is attributed to quantum



Figure 2. (a), (b) AFM micrograph of TiO_2/MoS_2 dispersions showing sheets imbedded in particle matrix, (c), (d) SEM micrographs of TiO_2/MoS_2 nanocomposite.



confinement effect with decreasing layer thickness and also confirms the shifting optical band gap associated with few and monolayer MoS₂ dispersions [31]. XRD studies at figure 3(b) present a characteristic peak at 13.58 attributed to MoS₂, contributed by (002) plane of hexagonal lattice [32]. Small particle distribution is demonstrated by the peak broadening in the diffractogram. Peaks at 25.58, 37.38, 48.25, 54.2, 55.48, 62.98 are associated with (101), (004), (200), (105), (211) and (204) planes of anatase TiO₂ (JCPDS 21-1272) respectively.

Figure 4 represent the UV–vis spectrum recorded for pure TiO_2 and TiO_2/MoS_2 nanocomposite. Spectrum recorded for pure TiO_2 indicates an efficient absorption at wavelengths lower than 400 nm associated with UV activation at the recorded band gap of 3.2 eV of anatase TiO_2 . By linear extrapolation from the inflection point on the curves to the base line, absorption onsets were determined. Incorporation of MoS_2 results in considerable



absorption over the whole visible light spectrum with red shift, visible in the composite spectrum over pure TiO₂. This red shift can be due to the chemical bonding between the nanocomposite constituents.

CH₃NH₃PbI₃ films were deposited on the optimized TiO₂/MoS₂ nanocomposite. CH₃NH₃PbI₃ was made with a modified approach to the reported procedure for high relative humidity environment [33]. Briefly, we introduced an intermediate step to wet the lead iodide coated films with iso-propanol and simultaneously with MAI solution in iso-propanol while the samples were spinning on the spin coater. They were then soaked in MAI solution in iso-propanol and allowed a soaking time of 20 s before further spin coating and annealing. Details of the synthesis procedure are outlined in the methods section.

Large area SEM and AFM images (figures 5(a), (b)) reveal uniform coverage for CH₃NH₃PbI₃ particles, an indication of the efficiency of the synthesis protocol under high humidity. Other researchers have also concluded that appropriate humidity levels during film formation are prerequisite for obtaining pin hole free films with improved optoelectronic and mass transport properties. It has been reported that films grown under nitrogen filled glove box conditions introduce pin holes and grain boundaries [34], a source of energetic disorder impeding the photovoltaic performance. Films annealed in air were found to increase the grain size resulting in reduced grain boundaries and improved mass transport. Therefore, a proper humidity level during film formation introduces moisture assisted grain boundary creep, resulting in larger grains, avoiding pin holes and improving carrier lifetimes [34, 35]. Additional charge carriers may be generated by autoionization of adsorbed water molecules at the surface into hydroxyl and proton ions creating surface OH⁻ sites. Protons may migrate between these sites and act as additional carriers.

The diffraction pattern presented in figure 5(c) is consistent with the tetragonal phase of the CH₃NH₃PbI₃ with sharp peaks at 14.0, 24.3, 28.4, 31.7, 40.5, 43.0, and 50.3° , corresponding planes have been indexed in figure 4 [3, 36–38]. Some residual lead iodide is also evident and is considered to be beneficial for the photovoltaic performance by improving carrier lifetime. This residual lead iodide at the grain boundaries is also attributed to reduced recombination at the absorber electron selective contact interface.

Figure 6(b) shows a schematic of the device operation. In order to obtain necessary photoexcitation and afford efficient electron uptake by TiO_2 , it is imperative that the conduction band of MoS_2 be kept higher than the conduction band of TiO_2 which can be ensured by keeping MoS_2 sheets to few layer thickness in the composite. Theoretical calculations have suggested that band gap of MoS_2 is dictated by the interaction between S-Mo-S dictating a variation in CB with the variation of thickness while VB remains virtually fixed. Thus, if efficient exfoliation is not achieved or the layers restack during dispersion in TiO_2 matrix, this could result in CB edge of MoS_2 lying lower than the CB of TiO_2 , disrupting the energy scheme of the complete device.

Photoexcitation occurs simultaneously in MoS_2 and $CH_3NH_3PbI_3$ with photoexcited electrone injected into the conduction band of TiO_2 . We have estimated that small weight fraction of MoS_2 does not have a detrimental effect on the photons reaching the $CH_3NH_3PbI_3$ layer, allowing efficient light harvesting by both the sensitizers in respective active regions of the solar spectrum. Photons reemitted by MoS_2 can be another factor in improving the photovoltaic performance for the devices using TiO_2/MoS_2 blend as electron transport layer. MoS_2 thus







augmenting the performance of the device allowing for improved efficiency of 4.43% from 3.74% for the TiO₂ only device (figure 6(a)).

Absorption spectra of completed devices are compared in figure 7. MoS₂ composite based devices present a broader absorption spectrum spanning the visible range over 350 nm to 800 nm. This increase is associated with MoS₂ nanosheets providing additional quenching. These observations are in good agreement to the reported



Figure 7. UV–Vis absorption spectra of completed devices based on pure TiO₂ and TiO₂/MoS₂ electron selective contacts.



photoabsorption and photocurrent response of MoS_2 in the visible spectrum driven by the shifting band gap associated with single and few layer thick sheets. This corresponds to the theoretical calculations for monolayer MoS_2 absorption at photons energy of 1.9 eV. Strong absorption is observed for wavelengths of the order of 500–530 nm. Some photons between 1.9 to 2.4 e V can be reemitted to be subsequently absorbed by $CH_3NH_3PbI_3$ further enhancing the absorption.

 MoS_2 is credited with improved mobility values to the tune of $200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $517 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for mono and multilayer systems. We estimated that incorporation of MoS_2 in the TiO₂ matrix will allow for improved charge transport at the interface between $CH_3NH_3PbI_3$ by reducing the interfacial resistance. To validate this idea and to obtain quantitative measure of the interfacial charge transport processes, we performed impedance spectroscopy of the completed devices. Impedance spectroscopy is a versatile technique to decipher the interfacial electronic processes and has been extensively employed in the study of solar cells [39–43]. Impedance response was obtained between 100 mV to 800 mV for frequency range of 1 MHz to 500 mHz at a perturbation of 20 mV. Obtained data was analyzed through Biologic analysis software using a modified transmission line equivalent circuit [44] depicted in figure 8. It involved two RC elements and a series resistance component. Graphical trend of circuit element values obtained through simulation of Impedance response is presented in figure 8. Nyquist plots consist of typical arc associated with the impedance response for such devices and are presented in figure 9.

Rs is the resistive contribution from circuit wires and ITO, one RC circuit is used to model the electron selective contacts and an additional RC element to model the shunt resistance and capacitance associated with



the active layer. Constant phase elements are used instead of ideal capacitors to obtain a better fit. Two characteristic arcs can be identified from the Nyquist plots, an intermediate frequency feature and an additional low frequency feature. The intermediate frequency feature is ascribed to recombination in the active layer while the source of additional low frequency feature is still debated. This is differently attributed i.e. some consider it having no bearing on the physics of the device and therefore leaving it out of the curve fitting parameters [45] while others have identified its origin as charge accumulation by ferroelectric domain walls with slow time constants [46]. Distribution of trap states in CH₃NH₃PbI₃ band gap itself has also been attributed to the generation of two distinct impedance features [39]. A contrary hypothesis suggests the difference in electron affinities of the contacting materials as a source for the generation of this characteristic response [47]. This low frequency feature is a characteristic of the DSSCs and has been associated with ionic mobility in liquid electrolyte. Ionic mobility in CH₃NH₃PbI₃ devices has also been established [48, 49] and can be a possible source for this low frequency feature in these devices.

Values for Rs, Rsc and Rrec are presented in figure 8. Total series resistance is a combination of Rs and Rsc [47] and with the addition of MoS_2 in titania, the total series resistance decreases. This decrease in series resistance is the cause of increased FF for devices with titania MoS_2 composites. Higher charge carrier mobilities for the composite ($2.3 \times 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) over pure $\text{TiO}_2(9.49 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ is considered to be the reason for decreased series resistance.

The intermediate frequency feature in the Nyquist plot is associated with Rrec [47]. Recombination rate is inversely proportional to the recombination resistance. The higher the recombination resistance, the lower the recombination rate and vice versa. Recombination in perovskite is primarily an interfacial phenomenon owing to long diffusion lengths of excitons in CH₃NH₃PbI₃. MoS₂ in the nanocomposite offers a superior charge transport pathway in the form of a two dimensional framework lowering the recombination rate. Passivation of defects in the TiO₂ matrix can be another source of decrease in recombination rate. Recombination resistance decreases with increase in applied bias voltage. This decrease is attributed to the higher concentration of charge carriers at higher voltages resulting in greater recombination. Recombination rates are associated with the Voc and higher recombination rate decreases with the applied bias. The value of Rrec is higher for titania MoS₂ composite. This increase of Rrec with the concurrent decrease of the slope with increasing voltage presents quantifiable evidence of increased Voc for devices employing titania MoS₂ as electron selective contacts over pure titania.

Conclusions

We have demonstrated enhance optical absorption and higher efficiency for CH₃NH₃PbI₃ devices using TiO₂/ MoS₂ nanocomposite as electron selective contact. Higher absorption results in higher Jsc, allowing for better solar spectrum harvesting toward the lower wavelength region. Higher mobilities associated with MoS₂ results in decrease in the series resistance component, verified through impedance spectroscopy which provides additional verification for increase in the Voc for the improved devices. All the synthesis was performed under ambient air conditions of high humidity employing HTL free device architecture. Though this method did not present record efficiencies, it has the potential of lowering the processing cost of this technology, paving the way for its rapid commercialization. Employing MoS₂ with exceptionally large absorption can give us a very large weight specific energy advantage. CH₃NH₃PbI₃ with a band gap of the order of 1.5 eV, using few and monolayer MoS₂ with band gap varying between 1.3 to 1.9 eV could be an effective way to enhance the optical absorbance. Furthermore, for such systems, coupled with extremely high optical absorbance coefficient of TMDs, very small quantities of materials can be used to augment the performance without employing complicated device architectures.

Acknowledgments

We thank staff at National Nanotechnology Research Centre Institute of Materials Science and Nanotechnology, Bilkent University Turkey for help with J–V characterization. This research was funded by Higher Education Commission Pakistan through grant number 213-58732-2EG2-014(50023541).

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