Electrical Characterization of Tailored MoS$_2$ Nanostructures

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Abstract. We try to understand the photocurrent generated in the tailored Molybdenum disulphide (MoS$_2$) nanostructures which were exfoliated from bulk MoS$_2$ powder by a simple liquid phase exfoliation followed by microwave treatment. Sonication and microwave treatment led to the formation of mostly hollow tailored MoS$_2$ nano-rods and nano-spheres which consist of more metallic 1T phase than semiconducting 2H phase. In this paper the interaction of light with these nanostructures and the generation of photocurrent is of peer interest. Confinement of photon in the hollow nanostructures could be very promising to derive photocurrent which can have applications in various optoelectronic devices.

1. Introduction

The unique properties of two - dimensional (2D) materials like graphene and Molybdenum disulphide (MoS$_2$), originating from their ultrathin planar structures, such as extreme bending ability, electron-hole confinement and high transparency help in the fabrication of thinner, more flexible and more efficient devices [1], [2]. These extraordinary properties of 2D materials are providing a great promise in the next-generation electronic and photonic applications. Graphene has attracted substantial attention in optoelectronic applications due to its high carrier mobility and fast response time. However, the zero bandgap nature of graphene limits its application in electronic devices.

Recently, 2D materials are an emerging branch of new materials which exhibits entirely different properties from their 3D counterparts, with a wide range of electrical and optical applications. After graphene, the discovery of other 2D materials like MoS$_2$, WS$_2$ etc. with a semiconducting nature, is now gaining great attention.

MoS$_2$ is a typical member of layered material belonging to the family of transition metal dichalcogenides (TMDs) with many properties complementary to those of graphene. Their electronic and optical properties vary drastically with layer thickness. A transition from indirect bandgap to direct bandgap occurs in the monolayer regime. Hence, in contrast to graphene which shows semi metallic behavior in monolayers, MoS$_2$ shows a well-defined bandgap in the monolayer limit with the bandgap varying from 1.9 eV for monolayers (direct) to 1.2 eV in bulk (indirect). This large bandgap in addition to high electron mobility (200 cm$^2$/V$^{-1}$s$^{-1}$) and high quantum efficiency make monolayered MoS$_2$ a hot topic for research [3], [4], [5]. Wavelength dependent photosensitivity can be observed in this material owing to the thickness dependent bandgap tenability [6]. All these properties indicate that the MoS$_2$ layers are promising as new building blocks for optoelectronic devices [7], [8], [9], [10], [11], [12].

There are mainly two possible polymorphs of MoS$_2$ at normal conditions in 2D regime, the trigonal prismatic (2H) phase and octahedral (1T) phase, where the former is a honeycomb like structure and the latter is a centered honeycomb like structure. The 2H phase can be obtained by different methods like mechanical exfoliation, chemical vapor deposition (CVD) or by the ultrasonication of the powered material in appropriate solvents. The 1T phase on the other hand, can be exfoliated through chemical processes like Li-intercalation, where the transition from the naturally occurring 2H phase to 1T phase occurs [13], [14].

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Research related to study the electrical properties of MoS$_2$ in the 2D regime has increased in the last few years owing to exotic physical and optoelectronic properties this material can show when fabricated in devices. Conductivity and I-V characteristic measurement studies on the mechanically exfoliated samples, by scotch tape method, chemical vapor deposition techniques (CVD), and various other exfoliation techniques like Li-intercalation [15] where the contacts were made by photo-lithography. Many studies have been done similarly on the mechanically exfoliated samples where contacts of Ti (5nm)/Au (50nm) was made by standard photo-lithographic method and metal evaporation techniques [16], [17], [18].

Ambient light sensing is deeply entwined with our day to day life. It forms part of almost all the consumer electronic equipment including digital cameras, television, printers etc., and the list goes endless [19]. Efficient light absorption and electron hole pair generation can take place under photo-excitation in monolayer MoS$_2$. As a channel material in field effect transistors, MoS$_2$ has exhibited a high carrier mobility and current ON/OFF ratio [20]. High sensitive and responsive monolayer MoS$_2$ based photodetector was realized at a wavelength of 561 nm by Sanchez-Lopaz and his co-workers [21]. Similar studies carried out on CVD grown MoS$_2$ showed a further enhanced responsivity [22]. It was observed that environmental factors often affect the performance of TMD based photodetectors [22].

For graphene based photodetectors, several strategies were investigated to enhance light absorption property. Some of these techniques include incorporation of graphene nanostructures, chemical doping, plasmonic nanostructures etc. [23], [24], [25]. For hollow nanostructures, photo-enhancement can occur through photon confinement effects as well. The use of such nanostructures in devices have shown enhanced performance [26], [27], [28] thereby emphasizing the applications of colloidal nanoparticles for large area device fabrication. Thus, nanostructures based on TMD materials can be good candidates which can show enhanced light absorption to be incorporated in optoelectronic devices.

In this study, we have used the liquid phase exfoliated sample of MoS$_2$ which has mostly tailored nano rod like- structures of 50-100 nm in diameter to understand the photocurrent generated in the structures. The need for better device fabrication has led to a sustainable approach with the use of colloidal nanostructures of 2D materials. The large scale device fabrication using nanowire [26], quantum dot [27], [28] or other 2D semiconductors is seeking great interest due to its extraordinarily high performance. The interesting properties like strong light absorption [27], band-gap modulation depending on size [30] and efficient multiple carrier generation [31] of the solution processed nanostructures which can be manufactured at a comparatively low cost, promises great development for the next generation electronic, optoelectronic and photonic applications. These nanostructures are exhibits good substrate compatibility as well, which enforce to assimilate them on transparent and more flexible substrates [32].

2. Experimental techniques

The preliminary bulk MoS$_2$ powder (<2 μm; 99% purity, 2H) was obtained from Sigma Aldrich and was used without additional processing or purification. The exfoliation process of the powdered MoS$_2$ was done using a mixture of 2 propanol and distilled water of ratio 2:3 as a solvent combination with a concentration of MoS$_2$ powder of 1mg/ml. For details about the exfoliation process, please look in to the ref [33].

Metal contacts were made by evaporating the pure Ag (99.99 % purity) under high vacuum conditions. The I-V characterization of the exfoliated MoS$_2$ nanostructures was done using a two-probe probe station connected to a power supply [Agilent, B2912A Precision source/Measure unit] and the morphological
studies of the sample was done by Scanning electron microscope (SEM) [Carl Zeiss EVO 18 Secondary Electron Microscope].

The samples was drop casted on silicon wafer with a 280 nm thick SiO$_2$ layer and then the drop casted solution was dried at around 50°C. The silver contacts of 140 nm thickness were made by using the thermal evaporation system [Fillunger, TCS - 0204] along the edges of the sample by masking a vertical portion of the drop casted sample using a 1 mm wide cover glass. The samples for SEM was prepared in a similar manner, by drop casting on silicon wafer but the sample was air dried for 12-14 hours.

3. Results and Discussions
Figure 2 shows the SEM studies carried out on the exfoliated and microwave treated MoS$_2$ samples which reveal the presence of MoS$_2$ flakes [Figure 2 (a, b)], MoS$_2$ rod-like structures [Figure 2 (c)] and MoS$_2$ rods plus spheres [Figure 2 (d)] in the sample. Formation process of these exfoliated MoS$_2$ nanostructures and their cumulative optical properties had already been discussed in ref. [31]. The diameter of the rod- and sphere- like structures is estimated to be approximately 100 nm and the length of the nano rods is in the range of a few micrometers [33]. The authors in [12] have reported the MoS$_2$ sphere like-structures with a diameter in the range of 50–100 nm and rod like- windings with a diameter in the range of 20–150 nm, and a few tens of micrometers in length with a high degree of size homogeneity [34]. Liquid phase exfoliation [35] is one of the simple and scalable method which can be controlled and standardized to obtain 2D materials and other desired nanostructures. The potential possessed by this technique to fabricate nanoparticles with wide range of application in different fields [36], [37], has attracted much attention and investigated extensively as it involves low cost solvents and it is very cost effective. The dangling bonds at the edges of the MoS$_2$ flake is the reason for the curving mechanism which results in the formation of the rod like structures observed as suggested by Mukherjee et al.[30], [32] It was also proposed that the spheres elongate or conglomerate to form the rod like structures [34].
Figure 2. SEM images of the exfoliated MoS$_2$ which exhibits the presence of: a) flakes of MoS$_2$, b) and c) rod like structures and d) Rod and sphere

Figure 3. TEM images of exfoliated MoS$_2$(a) hollow tube, (b) folding of the flakes

Figure 3 shows transmission electron microscopy (TEM) images which corroborate the presence of hollow nanotube structures in the exfoliated MoS$_2$ samples. The TEM micrographs shown in Figure 3 are taken from our own previous results [33]. Outer and inner peripheries of the nanotube are marked as black dotted lines in Figure 3 (a) for a better visual understanding of the hollow tube formation. The
initiation of curling mechanism to form tube like structure is marked as red dotted circle in Figure 3 (b). This rolling and curling process has been suggested by various authors [33], [38] earlier.

Figure 4. The current (I) versus channel bias (V) plots of exfoliated MoS$_2$ nanostructures measured in presence of light (white) and in dark within a voltage range of -2 V to 2V. A zoomed portion from -0.4 V to 0.4 V (marked in square region) range is shown as inset. The semi-metallic behavior is evident from the inset.

In this report, we present our preliminary room temperature (RT) electrical transport measurements studies of these MoS$_2$ nanostructures. The I-V characteristics of the MoS$_2$ nanostructures was measured in dark and in the presence of white light with a 5W bulb. This data is shown in Figure 4. We could observe a significant increase in current in the presence of light. There is a significant increase in the light current compared to the dark current as can be seen in Figure 4. Although the current v/s voltage behavior looks semiconducting for a larger voltage range, a closer investigation around 0V reveals a nearly semi-metallic behavior with a minute, but proper slope in the I-V data around this point (Ohmic behavior). This nearly Ohmic characteristic of the I-V data could be attributed to the presence of metallic 1T phase of MoS$_2$ which coexists with the semiconducting 2H phase as explained in [39]. It was reported that the sample consists of 30% of 2H phase and 70% of 1T phase MoS$_2$ [37]. The inset shows the zoomed portion from -0.4V to 0.4 V of the I-V plot. A semi metallic behavior of the I-V characteristic is clearly evident from the inset of Figure 4. The presence of the 1T phase in a higher proportion as compared to the 2H phase [33] in the 30 minute microwave treated sample could be the reason for this semi metallic electrical properties of these nanostructures. It is also observed that the current flowing through these nanostructures even at a low voltage range (-2V to +2V) is reasonably high (of the order of micro ampere) owing to the larger proportion of metallic phase MoS$_2$ in the sample. The metallic behavior of the 1T phase MoS$_2$ thus dominates over the semiconducting nature of 2H MoS$_2$ thereby showing an overall semi-metallic behavior. Also, presence of nano-rods and nano-spheres observed in the exfoliated samples are expected to be good light harvesting material due to electron confinement [33] ability. Hollow nanostructures can further confine photons under light irradiation which can have interesting applications in various optoelectronics devices. All these parameters may directly/indirectly contribute to the observation of semi metallic I-V characteristic of the exfoliated MoS$_2$ samples.
On comparing the current v/s voltage behavior of our as synthesized nanostructures in dark (black curve) and under white light illumination (red curve), there is a difference in the measured currents which can be seen in Figure 4. However, the increase in photo current generation under white light illumination may not appear as significant as we thought it would be compared to the dark current within the voltage range scanned (-2V to +2V). At +2V, the enhancement in photo current compared to dark current is only about 4 micro ampere, whereas, at -2V the increase in current is almost negligible as can be seen in Figure 4. Enhancement in photocurrent upon light illumination would depend on various factors as discussed below:

- The generated photocurrent in a sample has a direct dependence on the area of illumination and in our case it is only about 1 mm x 3 mm wide region of the sample which was exposed to white light. This small area of illumination can considerably reduce the number of photo generated carriers in the sample.

- According to the discussions in recent articles by Jie Sun et al [40] and S Reshmi et al [33], the presence of 1T phase can show a severely suppressed transmission probabilities in the valence band as well as in the conduction band. It will lead to the reduction of current flow as the transmission probabilities depend on the availability of conduction channels of various energy bands [40]. As a result, it can happen that the charge carriers generated in presence of light exposure will not be carried through a proper channel.

- There could also be a decrease in charge carrier mobility due to the p-doping effect caused by the air adsorption in the case of few layer MoS2 according to the investigations carried out by Wenjing Zhang et al [41]. They have done a comparison study of current measured in vacuum and in air, where the current had a reasonable increase when measured in vacuum, i.e., in absence of air.

- The contact barrier in the junctions too will play significant role to regulate the photocurrent generated in the system [42]. Observation of a lower increase in the photocurrent in this case could be due to increase in the height of contact barriers as well [42].

All the above mentioned factors individually or cumulatively may influence the photocurrent generation in our 1T-2H mixed samples. The experimental observations obtained so far, directly correlates with the proportion of 1T and 2H phase MoS2 present in the sample [39]. A small increase in the photo current compared to the dark current in Figure 4, might be due to the existence of the hybrid 1T-2H phase where a much larger proportion of metallic 1T phase (~70%) exists compared to the 2H phase (~30%). An increase in photo current in this case may mainly be associated with the carriers generated in the 2H phase which could flow through the conduction band [40] to give the small increase in the photo current as seen in Figure 4. The semi metallic nature of the I-V characteristics of the sample can be explained with the help of a recent theoretical study carried out by Jie Sun et al [40] and his coworkers which claims the increase in metallic behavior of hybrid 1T-2H MoS2 by increasing the concentration of 1T phase up to ~70%. A detailed study related to the generation of photocurrent in the exfoliated nanostructures is presently under way and will be published later.

4. Conclusion
The I-V characteristics of the MoS2 nanostructures was measured by making 140 nm thick silver contacts. The photo current and dark current measurements of the same sample were observed in a voltage range of -2V to +2V. The I-V spectrum obtained from the nanostructures exhibits nearly metallic behavior with a reasonable increase in the photo-current. These results are in agreement with the recent work carried out in the refs. [39] and [40] which discuss the existence of a hybrid phase in the sample with a higher proportion of metallic 1T phase compared to the semiconducting 2H phase. We attribute
the small increase in the photo current and a nearly metallic behavior of the I-V curve to the presence of more 1T phase in the sample than the 2H phase. A small increase in the photocurrent that has been observed [Figure 4] might be mainly due to the photo carriers generated in the 2H semiconducting phase present in the sample. The contact resistance [42] and the doping effect of the air molecules [41] could also be the reasons of not getting an enormous increase in the photocurrent which needs more introspection in terms of experiments to confirm. This will be done in our future course of studies.

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