

MoS₂ quantum dots interfaced with hydroscopic polyelectrolyte for water gated devices

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Abstract

Molecular gating (*via* electric field from molecule's dipole-moment) is an effective route to dope two dimensional (2D) nanomaterials for specific electronic applications. Here, we show that molybdenum disulphide (MoS₂) interfaced with a microfiber of hygroscopic polyelectrolyte can be reversibly doped with water molecules by changing the local humidity. In this work, the p-doping water absorbed by the polymer microfiber reduces the electron density in the n-type MoS₂ quantum dots. This change in the carrier concentration ($5.24 \times 10^{11} \text{ cm}^{-2}$) is confirmed by electrical measurements. Further, Raman spectra have been analyzed to understand the bonding of molecular groups on MoS₂ quantum dots and their self-assembly on the microfiber. The work provides an avenue to explore interfacing 2D quantum dots interfaced with other polymers for specific sensing applications.

Keywords: MoS₂; Quantum dots; Electron tunneling; Humidity sensor; Microfibers; Nano assembly

1. Introduction

As a semiconducting analog of graphene, MoS₂, a member of 2D material class, has received great attention recently [1, 2]. MoS₂ monolayer is a three-atom-thick layered transition-metal dichalcogenide, composed of a stratum of molybdenum atoms covalently bonded with two layers of sulfur atoms in a trigonal prismatic (or antiprismatic) lattice. Weak van der Waals interaction [3, 4] between MoS₂ layers renders its monolayer crystal to be exfoliated mechanically and chemically [1, 3]. Furthermore, during this structural transition (thinning), MoS₂ thin sheets exhibit remarkable electrical and optical properties [1, 5]. While bulk MoS₂ possesses an indirect band-gap of 1.2 eV, monolayer MoS₂ has a direct band-gap of 1.8 eV, with enhanced photoluminescence. Single layer MoS₂ field effect transistors (FETs) possess a charge mobility of $0.5 - 15 \text{ cm}^2/(\text{Vs})$ with a high on/off current ratio (10^3 to 10^8) [6]. Due to these emergent properties, MoS₂ has demonstrated a wide range of applications, including molecule sensing [7], energy harvesting [8], battery electrodes [9, 10], and photo-electronic applications [11-13].

In 2D materials, the surface per unit volume is extremely high, making them ultrasensitive. Further, the quantum confinement in the lateral dimensions in 2D quantum dots enhances MoS₂ sensitivity at the interface due to a change in environment (pressure, water humidity, molecular doping). Subsequently, via interfacing other nanomaterials and molecules, band gap semiconductor MoS₂ can be selectively doped: either p-type or n-type [7, 14-16]. Hence, the molecular dipole moment generates an electric field applied through the quantum capacitance to modulate a large carrier density (doping). This change in the electrical carrier density has been employed to build various types of extremely sensitive sensors [16-19]. Though applications of MoS₂ sheets are extensive, it is important to note that there are very limited reports on electronic and sensor applications of MoS₂ quantum dots

(MoS₂-QDs), except MoS₂-QDs for catalysis [20]. Here, we developed a facile process to fabricate a novel robust MoS₂-QDs based electronic device/sensor by interfacing MoS₂-QDs with microfiber spun from polyelectrolyte solution.

2. Experimental Details

To synthesize a suspension of MoS₂-QDs, MoS₂ powder (from Sigma-Aldrich) was sonicated for 8 hours in 1-methyl-2-pyrrolidone (NMP) at a concentration of 1 mg/mL followed by centrifugation at 5000 rpm for 10 min to remove the remaining bulk MoS₂ and yield a supernatant of exfoliated MoS₂-QDs solution. These MoS₂-QDs are expected to have edges defects, which promotes the density of sulfur dangling bonds. Subsequently, the thiol bridge (S-S) is formed between dangling sulfur bonds of MoS₂-QDs [21, 22] and the thiol groups (S-H) of thiol glycolic acid (TGA) by dissolving the exfoliated MoS₂-QDs solution in 0.1 M aqueous TGA. Previous studies have shown that the thiol groups have a tendency to chemically bind with MoS₂'s dangling sulfur groups/defects [21, 22]. In order to enhance the density of sulfur defects, the solution is further sonicated overnight. Since the polyelectrolyte is polyallylamine hydrochloride (PAH), which is positively charged, MoS₂ is made negatively charged by covalently bonding TGA to the MoS₂-QDs. The PAH fiber was spun *via* a process explained in our earlier work [23]. Briefly, a drop of thick aqueous PAH solution (~ 20% PAH) was placed between fingers (gloved) and the fingers were drawn back and forth till visible fibers were observed. These fibers were then placed on the chip with predeposited electrodes, baked at 120 °C for 1.5 hrs. The prepared PAH fiber-chip was submerged in the MoS₂ TGA solution (prepared earlier) for 48 hours, and then removed, rinsed continuously with water, and air dried. This process facilitated the self-assembly of negatively charged MoS₂-QDs/TGA on positively charged PAH microfibers as shown by the schematic in Figure

MoS₂-QDs Self-Assembly Process

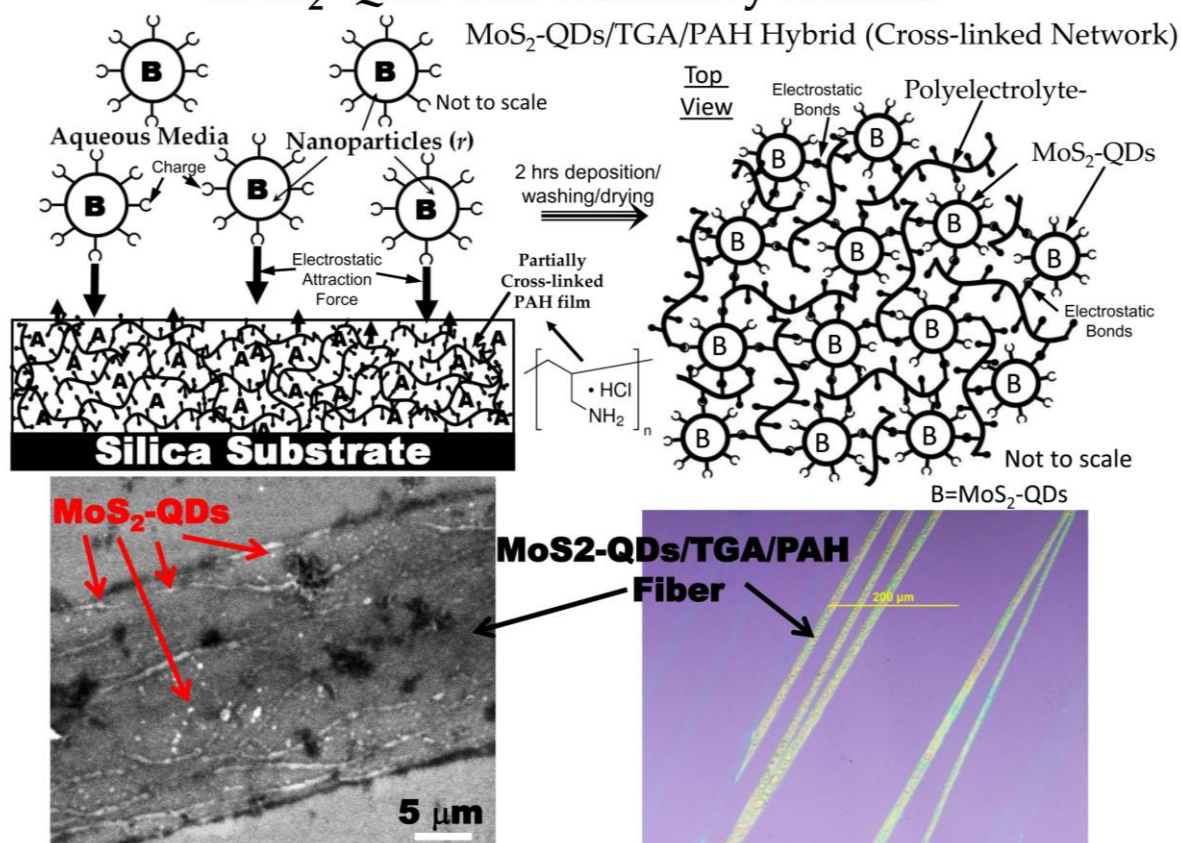


Figure 1. Schematic of the electrostatic self-assembly process for deposition of negatively charged MoS₂-TGA on positively charged PAH fiber (the chemical structure is included). The top left inset shows the pre-attachment scenario of solution dispersed MoS₂-QDs coming in contact with the polyelectrolyte fiber on the substrate. The top right inset shows the schematic of crosslinked MoS₂-QDs between PAH strands. The bottom inset shows the SEM image (right) and optical image (right) the MoS₂-QDs/PAH-fiber ensemble.

1. The fabricated nano/micro composite fiber was laid between gold electrodes 5 microns apart for further electrical measurements (explained later).

3. Results and Discussion

As a powerful tool for 2D crystal characterization, Raman spectroscopy was employed to analyze the lattice vibrations in MoS₂-QDs [24]. Raman spectra were acquired for different composites and phases: MoS₂-QDs, MoS₂-QDs bonded with TGA, and MoS₂-QDs/TGA assembled on PAH fiber (MoS₂-QDs/TGA/PAH) (left inset of Figure 2). All Raman spectra obtained were average of 5 runs [24, 25] (5 sec acquisition time; spot-size = 5 μm, 100X, NA = 0.9). Since, PAH-microfibers did not show interference on the Raman signal from MoS₂, MoS₂-QDs exhibited E_{2g}¹ (392 cm⁻¹) and A_{1g}¹ (~417 cm⁻¹) peaks, which correspond to the in plane (2 S atoms moving in opposite direction to the Mo atoms) and out of plane (S atoms in opposite directions) vibrations in right inset of Figure 2. As discussed above, MoS₂-QDs exhibit defects around the edges, which provide free dangling bonds of sulfur, hence enhancing thiol bridge bonding (S-S) between MoS₂-QDs and TGA. This thiol bridge bonding is confirmed by a clear red shift of E_{2g}¹ (~384 cm⁻¹) and A_{1g}¹ (~409 cm⁻¹) MoS₂-QDs peaks [15]. Furthermore, this red-shift (8.1 cm⁻¹ and 8.3 cm⁻¹ for E_{2g}¹ and A_{1g}¹, respectively) of features indicates stiffening of MoS₂-QDs [15, 26], speculatively due to the repelling negative charges from TGA on the edges of

MoS₂-QDs. Due to positive charge of PAH fibers, MoS₂-QDs/TGA interacts with PAH fibers through electrostatic bonding. This charge-neutralization reduces the repulsion between edge-functionalized TGA groups and softens the lattice creating a slight blue-shift (1.3 cm⁻¹ and 1.1 cm⁻¹ for E_{2g}¹ and A_{1g}¹, respectively) of MoS₂-QDs/TGA/PAH peaks, E_{2g}¹ (~385 cm⁻¹) and A_{1g}¹ (~410 cm⁻¹).

To incorporate MoS₂-QDs into practical applications, the facilely fabricated device is necessary. Here we demonstrate a molecular-doping modulation based sensor *via* self-assembly of MoS₂-QDs on PAH microfibers. As mentioned above, the humidity sensor device was fabricated by spinning PAH into microfibers, depositing these fibers onto a silica chip with pre-deposited electrodes (made of gold 5 μm apart), and lastly, by anchoring the MoS₂-QDs on the fiber.

The electrical measurement of MoS₂-QDs/TGA/PAH device suggests that the assembly of MoS₂-QDs creates a percolating network linked *via* PAH junctions (MoS₂-QDs/PAH/MoS₂-QD) as shown in the top inset of Figure 3. Under the influence of the electric field, the electron carriers tunnel through the PAH barrier from one MoS₂-QDs to the next. These measurements were conducted by connecting the chip-electrodes with probes linked to a Keithley sourcemeter unit to measure the current versus voltage and the transient response with respect to humidity and pressure. In order for equilibrated settlement of MoS₂-QDs on the PAH fibers, all devices prepared by the above process were electrically annealed (applied a potential of 5 V for 30 min) prior to the

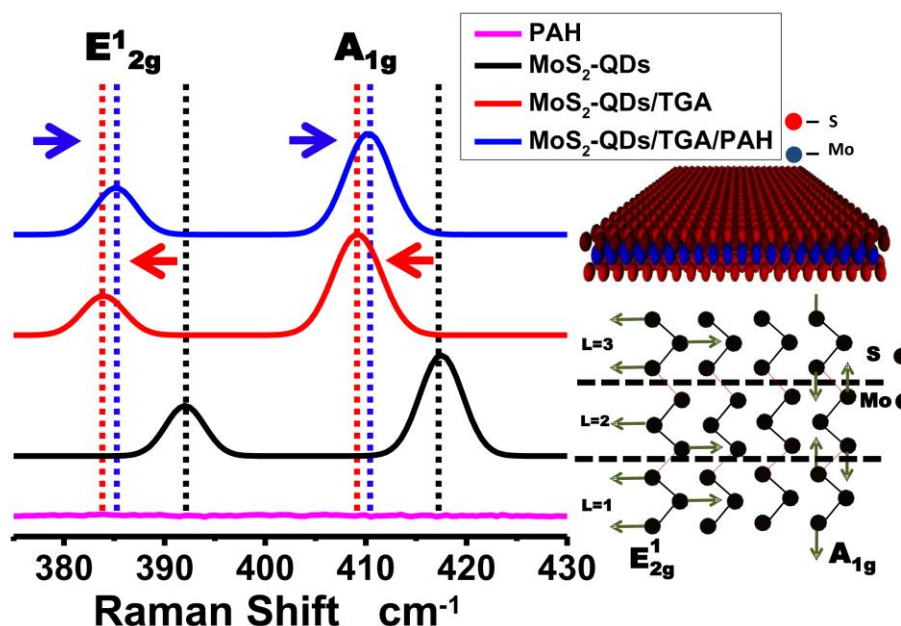


Figure 2. The left inset shows Raman spectra comparison between PAH fiber, MoS₂-QDs, MoS₂-QDs/TGA and MoS₂-QDs/TGA/PAH samples show the stiffening of the MoS₂ lattice after edge-functionalization of negatively-charged TGA (red-shift). The interaction with positively-charged PAH compensates some of the negative charges on MoS₂-QD-TGA to soften the lattice (blue-shift). Furthermore one layer of MoS₂ structure is shown in the top right inset. The bottom right inset illustrates relevant modes of vibration in MoS₂.

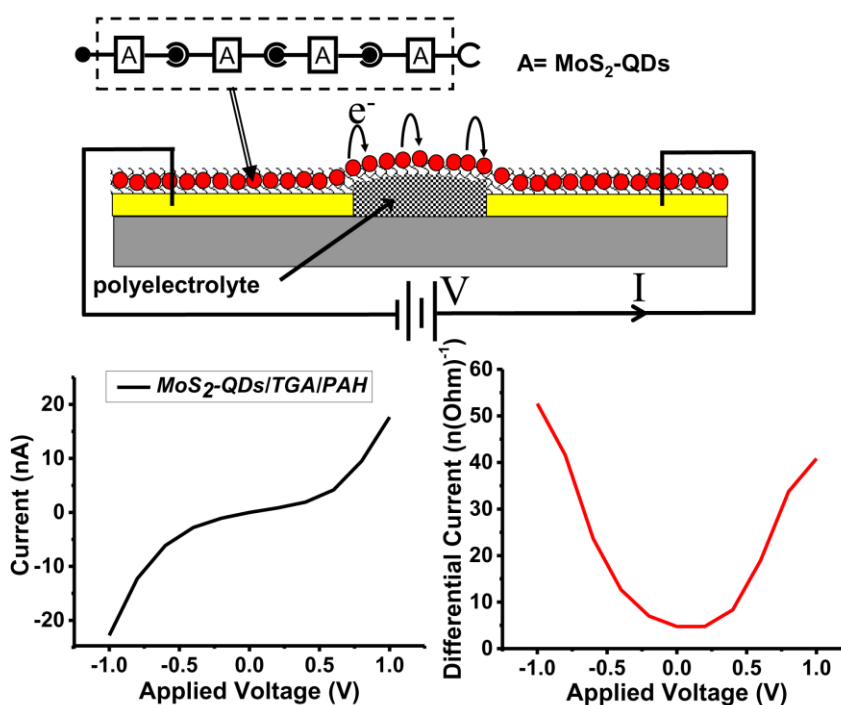


Figure 3. Top inset shows the electron transport model between MoS₂-QDs via PAH junctions. The bottom left insets is the nonlinear IV measurement, which confirms the electrons transports through semiconductor materials (MoS₂-QDs). In the bottom right inset shows differential conductance (dI/dV) with applied voltage. The barrier to electron transport reduces with increase in voltage thus increasing differential conductance.

measurements. Once the equilibrium is reached, every device exhibits a robust conductivity and response.

After the annealing process, the current-voltage (I-V) characteristic of the device is generated via a two point conductivity measurements with voltage ramping from -1 V to 1 V with a step size of 200 mV. As shown in the bottom left

inset of Figure 3, the IV curve of the fabricated device exhibits nonlinear behavior. This is an indication of electron transport through a semiconductor material, where the barrier to electron transport reduces with increase in voltage thus increasing differential conductance (dI/dV) with applied voltage (bottom right inset of Figure 3). Please note that due to electrical

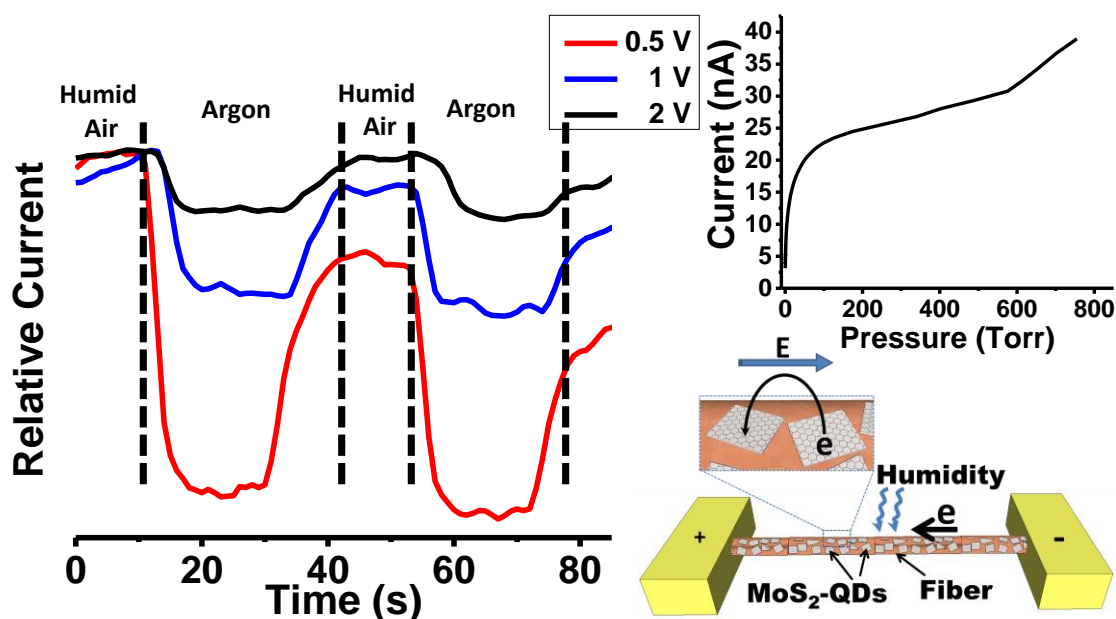


Figure 4. The left inset shows the electrical Response with humidity and pressure. The conductivity of the device was measured at fixed voltage while changing the atmospheric humidity by flowing ultra-pure Ar over the device. The decrease in the conductivity is via the reduction in p-doping due to water desorption from the PAH fiber. The difference between the relative change in conductivity at different voltages is due to higher Joule heating induced desorption at higher voltages. The top right inset shows the current vs pressure behavior. As the surrounding pressure decreases, the doping water desorbs from the MoS₂-QDs/TGA/PAH, causing the reduction in current. The bottom right inset shows model of MoS₂-QDs self-assembling on PAH fiber. The charge transports between these MoS₂-QDs.

annealing, the device shows capacitive response and the IV shown has been modified by subtracting the base current at zero volts. This is appropriate since the measurements were conducted at a fast rate (~ 5 seconds for the whole scan). For slow conductivity measurements, the device will show hysteresis.

The device's response to humidity was also tested by measuring the transient current at a fixed voltage with changing local humidity. This was accomplished by replacing the humid, atmospheric air around the device with argon gas. The conductivity of the device decreased during intervals of Ar exposure and increased while exposed to humid air consistently at three different voltages as shown in left inset of Figure 4. This implies that the n-type MoS₂-QDs network gets p-doped with water adsorbed by the interfaced PAH fiber [15]. This is also consistent with the previous studies on doping with water [27]. At higher voltage, the MoS₂-QDs/TGA/PAH is subjected to increased Joule heating leading to an additional driving-force for water desorption. Therefore, at higher voltage the water content in PAH is lower causing reduced doping, and thus a decreased conductivity. Here, the dipole moment of water (1.85 Debye) interfaced with the MoS₂-QDs applies a potential and dopes MoS₂-QDs through its quantum capacitance [28]. The change in the electron density due to modulation of humidity at 0.5 V is $5.24 \times 10^{11} \text{ cm}^{-2}$ as calculated from: $\Delta\sigma = e\mu\Delta n$, where $\Delta\sigma$ is the change in conductivity between dry air and humid air, e is the electron charge, μ is the charge mobility (assumed to be $1 \text{ cm}^2/\text{Vs}$), $\Delta n (\text{cm}^{-2})$ is the change in the electron density. Furthermore humidity response from the MoS₂-QDs was evaluated by exposing MoS₂-QDs/TGA/PAH to different levels of vacuum (vacuum probe station). The current response to the change in external pressure for MoS₂-QDs/TGA/PAH is shown in top right inset of Figure 4. Here too, the removal of water

molecules under vacuum cause the doping levels to drop, thus causing a reduction in currents.

4. Conclusions

We show that MoS₂-QDs can be prepared via a simple process and can be self-assembled on a PAH microfiber to produce a composite electrical device, the conductivity of which can be modulated with humidity. The Raman spectra result demonstrated that the edge-functionalization of the MoS₂-QDs with negatively charged TGA lead to lattice stiffening, which is partially compensated by the attachment with positively charged PAH fiber. Further, the electrical studies show a typical semiconductor response, where the device can be reversibly gated with water absorbed from the atmosphere. The self-assembled structure shown here can be employed to develop the next generation MoS₂-QD devices self-assembled on polymeric scaffold sensitive to other stimuli to build respective sensors.

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