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Nanowire templated CVD synthesis and morphological control of MoS₂ nanotubes†

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Although the syntheses of molybdenum disulfide (MoS₂) nanoparticles, nanosheets, and nanotubes (NTs) have been reported for years, the synthesis and morphological control of the few-layered MoS₂ NTs are still a great challenge, where a template-assisted route is barely seen among the gas-phase reactions at elevated temperature. Here, we report the nanowire (NW) templated chemical vapor deposition (CVD) synthesis of few-layered MoS₂ NTs by utilizing a sacrificial template in the CVD process. The MoS₂ NTs exhibit good structural integrity derived from the high temperature gas-phase reaction. Moreover, the diameter of the NTs and layer number of MoS₂ are controllable. A field effect transistor (FET) device is fabricated to study the electrical property of a single MoS₂ NT, and the carrier mobility is obtained. This work provides an effective route for the synthesis of the MoS₂ NTs with only a few layers of thickness and could promote the synthesis of other one-dimensional (1-D) transition metal dichalcogenide (TMD) nanomaterials.

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Introduction

Nanotube (NT) is an important one-dimensional (1-D) nanomaterial, and it serves as a good system for exploring a great deal of novel phenomena at the nanoscale and investigating the properties depending on size and dimensionality reduction.^{1,2} Besides, many NT based devices exhibit excellent performance due to the heterostructure built on the surface or the interface between the nanotube and other nanomaterials.^{3–5} On the other hand, being a typical two-dimensional (2-D) transition metal dichalcogenide (TMD), the atomically thin molybdenum disulfide (MoS₂) nanosheet has been vigorously studied and widely used in a variety of nanodevices due to its unique properties.^{6–15} By analogy to graphene and carbon nanotubes, it is indispensable to explore the MoS₂ NT and find out the difference in properties compared to the planar structure. Since Tenne *et al.* first reported the MoS₂ NT, a number of researchers have focused on its synthesis and reported a wide range of methods.^{16–27} Consequently, the products can be uniform with a well-defined wall,^{17,18} bamboo-like,^{23,24} and nanosheet-based²⁵ in morphology when prepared with different methods, and the diameter ranges from subnanometer²⁰ to several hundred nanometers^{23–25} with the wall thickness varying from a single-layer²⁰ or few-layer¹⁷ to about 10 nanometers or more.^{18,25–27} Among these reports, the template-assisted route possesses the advantage of controlling the length and diameter of the

products.^{23–25} However, the reported templates only work at relatively low temperature (not higher than 450 °C), while a high quality few-layered product is obtained by a gas-phase reaction at elevated temperatures^{17,26} where the morphological control is barely seen. Thus, it is necessary to develop a method where a proper template is introduced to achieve the synthesis and morphological control of few-layered MoS₂ NTs.

Chemical vapor deposition (CVD) has been proven to be a reliable and effective method to synthesize high quality atomically thin MoS₂ nanosheets, and it can potentially provide a better control over the number of layers.^{28–30} With different precursors and optimizations of the system, CVD also enabled the robust growth of a series of atomically thin TMDs as well as TMD alloys, heterostructures, and superlattices.^{31,32} Its outstanding adaptability makes CVD a promising method for the synthesis of other few-layered MoS₂ nanostructures. Meanwhile, the size and morphological control of nanomaterials should also be taken into consideration, both of which are important impact factors for the properties as well as the performance of nanomaterial based devices.^{33,34} For example, the bandgap of atomically thin MoS₂ nanosheets,^{35,36} the electrical properties of single-walled carbon nanotubes,^{37,38} and the ultraviolet light sensing performance of zinc oxide nanowires³⁹ are all related to the morphology and/or size of the nanomaterials. Thus, morphological control is of great importance to MoS₂ NTs and may result in some new surface/interface-induced properties. By appropriately combining the CVD process with the template-assisted method, which excels in size control, few-layered MoS₂ nanotubes with morphological control could be obtained.

Here, we develop a template-assisted CVD process to synthesize MoS₂ NTs in which electrospun silicon dioxide (SiO₂) nanowires

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(NWs) are introduced as the sacrificial template. After removing the templates, the MoS₂ exhibits a tubular structure with a good structural integrity. The diameter of MoS₂ NTs is highly dependent on that of the SiO₂ NWs, and the layer number of the MoS₂ NTs can be modified down to 4 by shortening the growth time. The electrical property of the NT is also studied through a single MoS₂ NT based field effect transistor (FET) device. The synthesis method not only enables the availability of few-layered MoS₂ NTs, but also enlightens the preparation of the tubular structure of TMD materials.

Results and discussion

A schematic illustration of the synthesis is shown in Fig. 1. First, SiO₂ NWs are prepared by a general electrospinning and annealing method.⁴⁰ The electrospun SiO₂ NWs are annealed at 500 °C and dispersed on silicon wafer as templates, since they are uniform in shape, stable in the CVD process, and flexible for the later process. Second, MoS₂ sheets are grown on the silicon wafer with SiO₂ NWs by a double-tube CVD process, which has been reported in our previous work.⁴¹ During the reaction, the molybdenum trioxide (MoO₃) precursor is reduced by the sulfur (S) vapor to form volatile suboxide MoO_{3-x}, which subsequently diffuses to the surface of the SiO₂ NWs.^{42,43} Then, sulfidation of the reduced surface occurs under the assistance of S vapor, the Mo-S bond forms, and thus results in the SiO₂@MoS₂ structure.^{44,45} After removing the SiO₂ NWs with hydrofluoric (HF) solution, the MoS₂ shell sheets remain to form the nanotubes. Furthermore, because of the use of SiO₂ NWs as a template and the time-dependent CVD process, the diameter and layer number of MoS₂ NTs can probably be controlled. The detailed synthesis process is depicted in the Methods section.

As shown in the scanning electron microscopy (SEM) image of Fig. 2(a), the annealed SiO₂ NWs are uniform in shape and smooth with the average diameter of about 531 nm and the length of several tens of micrometers (the distribution of diameters can be found in Fig. S1, ESI†). After the CVD process,

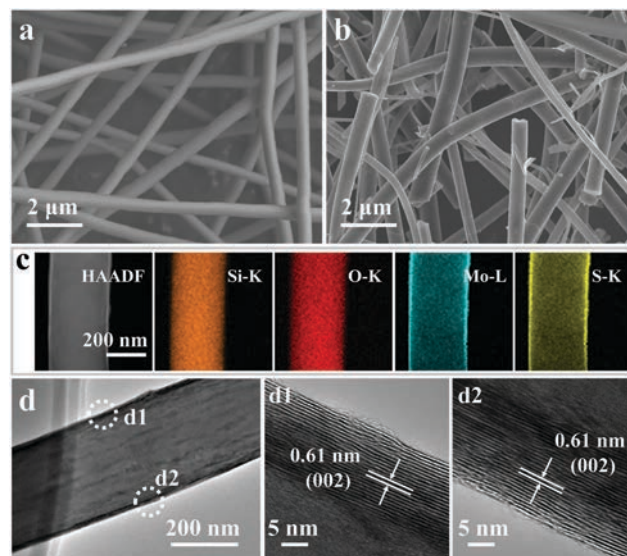


Fig. 2 (a) SEM images of SiO₂ NWs after annealing; (b) SEM images of SiO₂@MoS₂ structures; (c) HAADF-STEM image of a SiO₂@MoS₂ structure and its elemental mapping images of Si, O, Mo, and S, respectively; (d) TEM images of the same structure in (c), and (d1) and (d2) are the HRTEM images of the local parts in the corresponding areas in (d).

the surface of the NWs exhibits no obvious change (shown in Fig. 2(b)) compared to Fig. 2(a). Transmission electron microscopy (TEM) equipped with an energy disperse X-ray (EDX) spectrometer is employed to further investigate the morphology and structure of the samples. The high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image in Fig. 2(c) was taken of a piece of an as-CVD grown single NW, whose elemental mapping images demonstrate the distribution of each element. The distribution of Mo and S elements is consistent with the morphology shown in the HAADF image, which proves that the MoS₂ is formed as an external shell. The distribution of Si and O elements indicates that the SiO₂ NW acts as the internal core of the structure. Fig. 2(d) shows the TEM images of the same NW, and Fig. 2(d1) and (d2) show the high resolution TEM (HRTEM) images of the local parts in the corresponding areas of Fig. 2(d). It can be seen that the shell has a high degree of crystallinity, and clear lattice fringes with a spacing of 0.61 nm are attributed to the (002) crystalline plane of MoS₂. By contrast, the core is obviously in an amorphous state, which is in accordance with the electrospun SiO₂ NW. Based on the results of Fig. 2(c) and (d), it can be concluded that the MoS₂ sheets deposit continuously and tightly on the surface of SiO₂ NWs. Thus, the core-shell structure of SiO₂@MoS₂ is formed. Besides, the layer number of MoS₂ sheets is around 20 with a high uniformity where no abrupt change or absence can be observed.

To obtain the MoS₂ tubular structure, HF solution was employed to remove the core SiO₂ NWs. The reaction is time-dependent when the concentration of HF is fixed, and thus the removal of SiO₂ NWs can be controlled. By partially removing the SiO₂ NWs, the radial corrosion produces a space between the core and shell, where the relationship that the MoS₂ shell

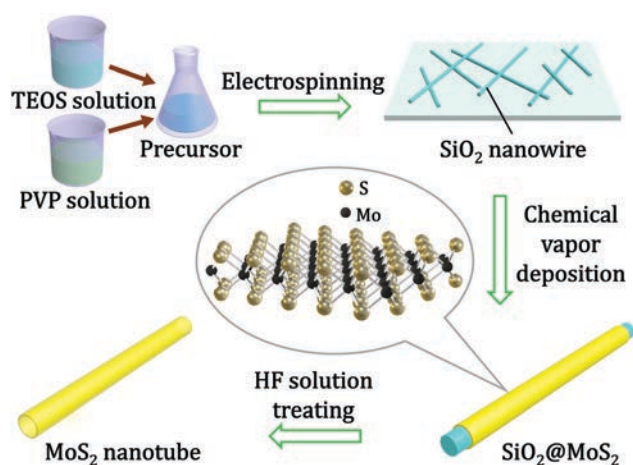


Fig. 1 Schematic illustration of the synthesis of the MoS₂ nanotube.

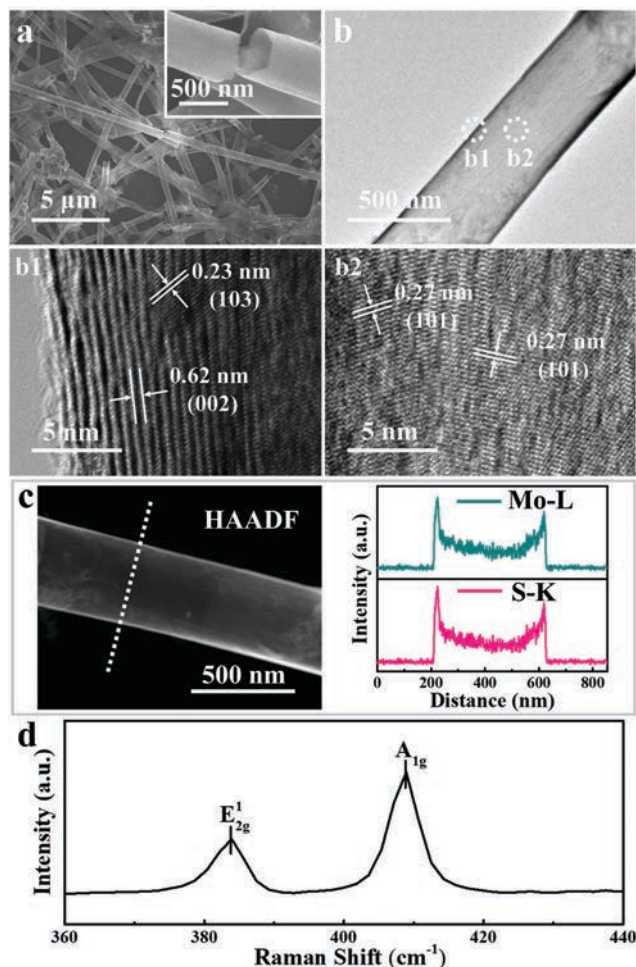


Fig. 3 (a) SEM images of the MoS₂ NTs (the inset shows a single NT broken into two); (b) TEM image of a MoS₂ NT, and (b1) and (b2) are the HRTEM images of the local parts in the corresponding areas in (b); (c) HAADF-STEM image of the same MoS₂ NT in (b) and its EDX line scan results of Mo and S elements; (d) Raman spectra of the MoS₂ NTs.

grows as per the shape of the SiO₂ core can be found (Fig. S2, ESI†). The SEM images (Fig. 3(a)) and TEM images (Fig. 3(b)) demonstrate the existence of the tubular structure. The open ends of the MoS₂ NTs can be observed (inset of Fig. 3(a)). The length of the nanotubes is several micrometers, and the average diameter is about 540 nm (Fig. S3, ESI†), which is comparable to that of the NWs shown in Fig. 2(a). The HRTEM images in Fig. 3(b1) and (b2) respectively represent the marginal and central parts on the surface of a nanotube, both of which are local parts in the corresponding areas in Fig. 3(b). The lattice fringes with spacings of 0.62 nm, 0.23 nm, and 0.27 nm are attributed to the (002), (103), and (101) crystalline planes of MoS₂, respectively, and show a high crystallinity of 2-H phase MoS₂ in a polycrystalline state (selected area electron diffraction pattern shown in Fig. S4, ESI†). The EDX line scan obtained by HAADF-STEM was applied to further investigate the distribution of S and Mo elements. As shown in Fig. 3(c), the curves of each element represent the distribution situation of a section's projection to the marked line. The sharp peaks of both curves

stand for marginal parts on the surface of a tubular structure, while the flat curves stand for central parts. Thus, the distribution of Mo and S elements is consistent with the morphology shown in the HAADF images as well as the SEM and TEM images, and the tubular structure can be verified. Therefore, the MoS₂ shell remains as a nanotube after removing the core SiO₂. Raman characterization with a 532 nm laser at room temperature is shown in Fig. 3(d), and the two peaks are at 383.9 cm⁻¹ and 408.9 cm⁻¹, respectively, which correspond to the Raman active mode of in-plane (E_{2g}¹) and out-of-plane (A_{1g}¹) vibrations of MoS₂, respectively. Moreover, the position difference of the two vibration modes is 25.0 cm⁻¹, which correlates with the reported value of MoS₂ sheets whose number of layers is 5 or more,^{46,47} and it can also be directly observed in Fig. 3(b1).

One of the most prominent advantages of the template-assisted method is the good controllability of the product's morphology, especially the diameter in this case. To verify the influence of the template NWs, the mass fraction of the solute as well as the applied voltage in the electrospinning process was varied to obtain NWs with different diameters. The characterization of the NWs can be found in Fig. S5 (ESI†), where the average diameters are about 110 nm, 210 nm, and 860 nm, respectively. After the same CVD and HF solution treating process, the MoS₂ nanotubes possess the average diameter of about 114 nm, 220 nm, and 860 nm, respectively, according to the SEM and TEM images shown in Fig. 4(a)–(c) and their insets. Based on the results above together with the NWs (average diameter of about 531 nm) shown in Fig. 2(a) and Fig. S1 (ESI†) and NTs (average diameter of about 540 nm) shown in Fig. 3(a)–(c) and Fig. S3 (ESI†), the influence of the templates on the final NTs is studied. The relationship between the diameter of NWs and NTs is shown in Fig. 4(d), where the black and orange dots represent the diameter of NWs and NTs, respectively, the error bars refer to the standard deviation of the diameter of NWs and NTs respectively, and the pink line represents the fitted result. A linear relationship between the

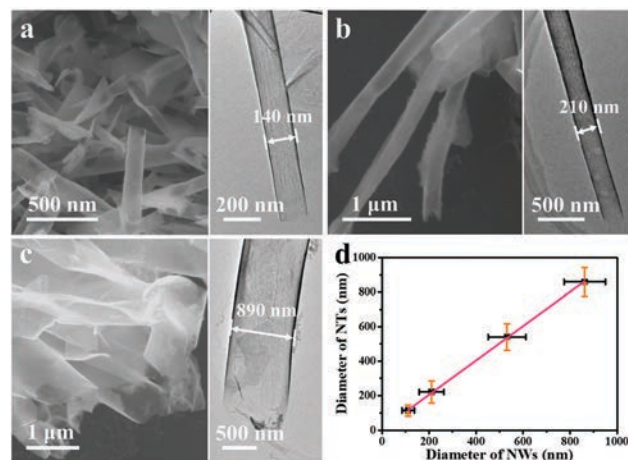


Fig. 4 SEM images of the MoS₂ NTs with an average diameter of about (a) 114 nm, (b) 220 nm and (c) 860 nm; each of the inset shows a TEM image of a typical single NT; (d) fitted relationship between the diameter of NWs and the diameter of NTs.

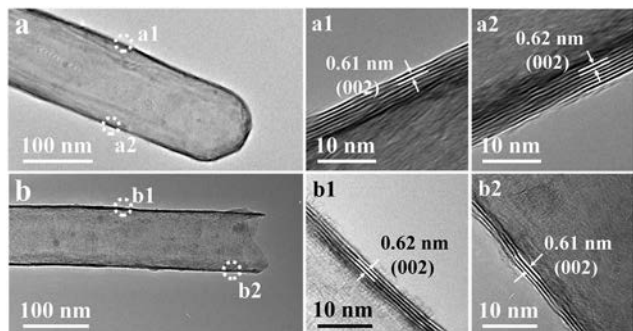


Fig. 5 (a) TEM images of a MoS₂ NT with the layer number of 7 (shown in the HRTEM images of (a1) and (a2)); (b) TEM images of a MoS₂ NT with the layer number of 4 (shown in the HRTEM images of (b1) and (b2)).

diameter of NWs and NTs can be found with the slope being 0.997 and the intercept being 4.540. The results prove that the diameter of the NTs perfectly adapts to that of the NWs, which exhibits a high controllability of this NW templated synthesis.

The influence of growth time in the CVD process was also briefly studied. After shortening the growth time with other process parameters remaining unchanged, the products obtained were observed through TEM and HRTEM. There are two NTs with similar diameters shown in Fig. 5(a) and (b). From their HRTEM images shown in Fig. 5(a1), (a2) and (b1), (b2), which show the local parts of the corresponding areas, respectively, the layer number of the two NTs is found to be 7 and 4, respectively. Based on the experimental results, when the growth time is set to 13 min, 8 min, and 5 min, respectively, the MoS₂ NTs possess the layer numbers of around 20, 7, and 4, respectively. The difference is possibly derived from less amount of deposition resulting from a shorter growth time. Nevertheless, the structural integrity of the NTs is not deteriorated compared with the thicker-walled ones. Admittedly, the influence of growth time could be more complicated and needs systematic study using kinetics and thermodynamics. The layer number should be further reduced with a shorter growth time, but the tubular structure hardly remained in our observation (Fig. S6, ESI[†]), and the reason may be owing to the capillary effect in removing the SiO₂ NWs in the liquid environment damaging the interlayer van der Waals interactions of thinner-layered NTs.

The electrical property of the MoS₂ NT was investigated by fabricating a single NT based FET device through focused ion beam (FIB) deposition, and the schematic illustration of the device is shown in Fig. 6(a). A single NT with a diameter of about 300 nm was chosen on the 300 nm SiO₂ on n++ Si substrate, and two platinum (Pt) electrodes were deposited at the two ends as source and drain, respectively. Fig. S7 (ESI[†]) exhibits a good Ohmic contact between the NT and the Pt electrodes, which could be attributed to the Pt's large work function of 5.6 eV.⁴⁸ The transfer characteristic, *i.e.* source–drain current (I_{sd}) versus gate voltage (V_g), is shown in Fig. 6(b) with an inset of the device's SEM image. When the source–drain voltage (V_{sd}) is fixed at 1 V, the FET device is switched on at a gate voltage of 9.8 V, which indicates an enhancement-mode behavior. The

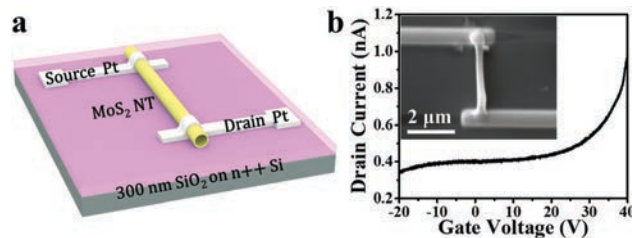


Fig. 6 (a) Schematic illustration of the single MoS₂ NT FET device. (b) Transfer characteristics of the FET based on a MoS₂ NT with the diameter of 300 nm and length of 2.8 μ m between the source and drain (shown in the inset of the device's SEM image).

following analytical expressions are used to estimate the carrier mobility (μ) of the device:^{49–51}

$$\mu = \frac{dI_{sd}}{dV_g} \frac{L^2}{C_{ox} V_{sd}} \quad (1)$$

$$C_{ox} = \frac{2\pi\epsilon\epsilon_0 L}{\cosh^{-1}[(r + t_{ox})/r]} \quad (2)$$

where L is the NT channel length of 2.8 μ m, C_{ox} is the oxide capacitance, ϵ is the dielectric constant of the gate insulator ($\epsilon = 3.9$ for SiO₂), ϵ_0 is the vacuum permittivity, r is the radius of the NT, and t_{ox} is the thickness of the oxide. According to the calculation, μ is $1.0 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is close to that of the previously reported MoS₂ NT FET.⁵¹ However, the mobility is quite small compared to the MoS₂ nanosheet, which could result from the much weaker capacitance coupled with the back gate.⁴⁹

Methods

Synthesis of SiO₂ NWs

A reported electrospinning method followed by annealing was used to synthesize the SiO₂ NWs.⁴⁰ The precursor was prepared by mixing a solution of 1.2 g of tetraethyl orthosilicate (TEOS) in 0.6 g of 0.05 M hydrochloric (HCl) acid and 0.4 g of ethanol with another solution of 1.1 g of polyvinylpyrrolidone (PVP) in 4.9 g of isopropanol (IPA) and 8.2 g of *N,N*-dimethylformamide (DMF). Thereafter, a syringe containing the precursor was placed horizontally and 25 cm away from an electrically grounded flat collector covered with aluminum foil. During the electrospinning process, a DC high voltage of 20 kV was applied to a metal needle of the syringe, and the propulsion rate was 0.002 mm s^{−1}. NWs with larger diameter can be obtained by increasing the mass fraction of TEOS and PVP, and decreasing the DC voltage to 15 kV. After being kept under ambient conditions for 48 h to allow for complete condensation of TEOS, the as-electrospun NW mat on the aluminum foil was annealed at 500 °C for 5 h at the heating rate of 2 °C min^{−1} in a box furnace in air. The SiO₂ NW mat was mechanically flexible and ready for later experiments, and the dispersed SiO₂ NWs were obtained by sonicating the mat dispersed in ethanol for 1 h.

Synthesis of the SiO₂@MoS₂ structure

The dispersed SiO₂ NWs were drop-casted onto a clean piece of silicon wafer with a hot plate underneath to evaporate ethanol.

Thereafter, the silicon wafer with SiO₂ NWs was introduced into a CVD system with a double-tube system, which has been reported in our previous work.⁴¹ A combustion boat containing 0.4 g of S was placed upstream, and a one-side sealed quartz tube was placed downstream, inside which was placed the silicon wafer with SiO₂ NWs, and a quartz boat containing 12 mg of MoO₃ was located at the bottom of the above-mentioned tube. All of the above were placed in the high-temperature area inside a 2-inch-diameter quartz tube furnace. The growth was carried out at atmospheric pressure with an argon flow of 75 standard-state cubic centimeter per minute, and the furnace was heated from room temperature to 900 °C at the heating rate of 30 °C min⁻¹. After 5, 8 and 13 minutes' preservation at 900 °C respectively, the furnace was cooled to room temperature without any operation. The time of heat preservation plays an essential role in the growth, as longer heat preservation could bring about larger layer numbers.

Removal of SiO₂ NWs

First, a mixture of HF aqueous solution (wt% ≥ 40) and ethanol (volume ratio = 1 : 2) was prepared. Then, the mixed solution was used to react with the SiO₂ NWs to remove them and get the MoS₂ NTs. After drop-casting the solution onto the mat of SiO₂@MoS₂, about 10 minutes' staying was needed for complete reaction. Then, the remains were washed 3 times with ethanol, dried, and peeled off from the silicon wafer for later characterization.

Product characterization

The morphology of SiO₂ NWs was observed *via* field emission SEM (FE-SEM, S-4800, Hitachi). The morphology and elemental distribution of the SiO₂@MoS₂ structure were investigated by using SEM, TEM and HRTEM (Tecnai G2 F30, FEI) equipped with an energy dispersive X-ray analyzer (EDAX, AMTEK Co., Ltd). SEM, TEM, HRTEM, and EDX line scanning were employed to study the morphology and elemental distribution of MoS₂ nanotubes. Raman spectra were obtained on a laser confocal micro Raman spectrometer (LabRAM HR 800, HORIBA Jobin Yvon) with an argon ion line laser of 532 nm as the excitation source.

Fabrication of the FET device

The mat of SiO₂@MoS₂ NWs was peeled off from the silicon wafer and dispersed in HF solution for 10 min. After the SiO₂ was dissolved, the mixture was centrifugated at 8000 rpm for 5 min. The sediment was washed with deionized water and centrifugated alternatively for another two times to remove the residual HF. Then, one drop of the mixture of MoS₂ NTs and deionized water was drop-casted onto a clean 300 nm SiO₂ on n++ Si substrate on a hot plate. 50 nm-thick Pt electrodes were deposited using an SEM-FIB system (TESCAN LYRA 3).

Conclusion

In conclusion, a NW templated CVD synthesis of MoS₂ NTs has been developed. The diameter of the NTs could be controlled by

changing the diameter of SiO₂ NWs, and the layer number of MoS₂ could be controlled from 4 to around 20 by varying the growth time of the CVD process. Transfer characteristics of a single MoS₂ NT based FET exhibit an enhancement-mode behavior of the device with the carrier mobility of $1.0 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This work facilitates the study of few-layered MoS₂ NTs and can enlighten further research and expand the application of other TMD NTs beyond a 2-D planar structure.

Conflicts of interest

There are no conflicts to declare.

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