Strong-coupled hybrid structure of carbon nanotube and MoS₂ monolayer with ultrafast interfacial charge transfer†

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Introduction

The free assembly of low-dimensional materials by van der Waals (vdW) interactions opens up a new era in materials research since there is no constraint in lattice matching as in conventional materials design and the resulting materials platforms become extremely rich.1–4 These artificial vdW heterostructures possess distinct properties to those of their individual components and exhibit great potential in the application of next-generation nanoelectronics, optoelectronics and photovoltaics.5–7 Currently, the prevailing building blocks for vdW hybrids are mostly limited to two-dimensional (2D) materials, mainly due to the easy fabrication of a 2D interface with controlled geometry and coupling strength via either exfoliation-transfer,8 solution stacking9,10 or direct growth techniques.11–14 Actually, there are other lower-dimensional materials, such as the very rich one-dimensional (1D) materials, that can be assembled with 2D materials, which is believed to further expand the materials platform of vdW hybrids and promote properties and applications beyond those of 2D hybrids only. For example, previous works, although very few, on 1D–2D hybrid structures have already demonstrated superior device performances, such as nanoscale resolution in a vertical point heterostructure,15 wide gate tunability in a p–n heterojunction,16 and enhanced performances in lithium-ion batteries17–19 and hydrogen evolution reaction.20,21 Despite these extraordinary properties of 1D–2D hybrids, the key interfacial geometry and coupling strength has not been controlled purposely. Therefore, there is a great demand to develop a facile and efficient method to produce 1D–2D hybrid structures with a controlled interface.

In principle, a 1D–2D hybrid structure can be easily obtained by directly stacking two components together. Unfortunately, uniform and strong interfacial coupling between 1D and 2D components is not naturally guaranteed, because the interaction area is very small, at only a nanometer in width, and is easily disturbed by exotic molecules, which is much more difficult to control than that in 2D–2D hybrids that have a larger interaction area and cleaner interface. Therefore, one needs to develop new strategies to precisely control the 1D–2D interface during hybrid component assembly.

Recently, a sequential chemical vapour deposition (CVD) method was developed to directly grow 2D hybrids (both in-
plane and out-of-plane stacked) with high-stacking-quality interfaces.\textsuperscript{12–14} The basic idea is to control the feedstock and growth conditions between the growth process of the two hybrid components. In this work, we employed and developed the sequential CVD method to construct 1D carbon nanotube-2D MoS\textsubscript{2} monolayer hybrids with strong interfacial coupling. The successful synthesis can be attributed to two key design controls: (i) hydrogen annealing between the two-component growth to eliminate amorphous contamination and ensure a clean interface and (ii) growth of MoS\textsubscript{2} after the nanotubes to make the 2D structure spread over the 1D structure and form a large interaction area. A clean interface with large interaction area leads to strong mechanical and electronic interfacial coupling, as illustrated by the phonon energy modulation and ultrafast interlayer charge transfer dynamics. The findings in this work should shed light on the mass fabrication of broad materials with a clean interface.\textsuperscript{22}

Results and discussion

To construct a hybrid structure of 1D nanotubes covered by a 2D MoS\textsubscript{2} monolayer, we designed our sequential CVD procedure, growing the nanotubes before MoS\textsubscript{2} (Fig. 1a). After using typical growth conditions for the nanotubes and MoS\textsubscript{2} (see the Methods section for growth details), scanning electron microscopy (SEM) was carried out and the SEM image shows that MoS\textsubscript{2} triangular domains prefer to nucleate on nanotubes rather than on bare substrate (Fig. 1b). Further statistical data on the relative angle \( \theta \) between the MoS\textsubscript{2} triangle and the nanotube axis \( T_{\text{NT}} \) along one individual nanotube reveals that there is no observable preference for in-plane MoS\textsubscript{2} rotation (Fig. 1c and d). In principle, one may expect some dominant MoS\textsubscript{2} rotation angles, as observed in 2D MoS\textsubscript{2}-graphene hybrid materials with a clean interface.\textsuperscript{22–24} This random angle distribution of MoS\textsubscript{2} indicates that the 1D–2D interface between the nanotubes and MoS\textsubscript{2} is not clean. Indeed, the optical images for longer MoS\textsubscript{2} growth time show obvious multi-layers of MoS\textsubscript{2} along the nanotube axis, which gives a higher contrast than on bare substrate (Fig. 1e). This multi-layered MoS\textsubscript{2} structure is further demonstrated by the much larger height in the atomic force microscopy (AFM) image (ESI Fig. S1†), greatly reduced emission intensity in the photoluminescence spectrum (Fig. 1f), and larger frequency difference between the \( E_{2g} \) and \( A_{1g} \) modes in the Raman spectrum of MoS\textsubscript{2} in the hybrid region (Fig. 1g). The formation of a multi-layer of MoS\textsubscript{2} on the nanotubes is believed to originate from the dangling bonds of amorphous carbon on the nanotubes during the growth, which act as very active nucleation centres for MoS\textsubscript{2} growth.\textsuperscript{25} Obviously, normal sequential growth cannot produce nanotube-MoS\textsubscript{2} hybrids with a clean interface due to the existence of possible amorphous carbon on the nanotube surface.

To obtain a clean interface in the nanotube-MoS\textsubscript{2} hybrid structure, the key issue is to have a clean nanotube surface before MoS\textsubscript{2} growth. In the nanotube growth field, it is known that hydrogen annealing at a proper temperature can etch the amorphous carbon away but keep the nanotubes intact (amorphous carbon is more reactive than graphitic nanotubes).\textsuperscript{26–30} In our experiment, we added a hydrogen annealing process at 700 °C for 15 min after nanotube growth but before MoS\textsubscript{2} growth (Fig. 2a). After the same procedure of MoS\textsubscript{2} growth as that in normal growth without hydrogen annealing, an entirely different growth result occurred: MoS\textsubscript{2} domains nucleated randomly on the whole substrate rather than on the nanotubes (Fig. 2b); the nanotube outlines cannot be seen in the optical images anymore but a uniform MoS\textsubscript{2} monolayer contrast on and off the nanotube (ESI Fig. S2†), no photoluminescence decrease in the MoS\textsubscript{2} on the nanotube region (Fig. 2c), and a uniform frequency difference of 19 cm\textsuperscript{-1} between the \( E_{2g} \) and \( A_{1g} \) modes of monolayer MoS\textsubscript{2} (Fig. 2d) can be observed. All of the above characteristic features illustrate clean nanotube-MoS\textsubscript{2} monolayer hybrid structures without the formation of multi-layer MoS\textsubscript{2} at the interface.

In principle, there are two possible stacking geometries in nanotube-MoS\textsubscript{2} hybrids, i.e. MoS\textsubscript{2} grows over the nanotube or the nanotubes sit on MoS\textsubscript{2}, and the first geometry is preferred as it presents a larger interaction area with strong interfacial...
coupling (Fig. 3a). To verify the vertical stacking relationship between the nanotubes and MoS$_2$, AFM was first carried out to analyse the cross-sectional profile across the nanotubes. Representative AFM images of the same nanotube on bare substrate and hybridized with a MoS$_2$ monolayer are presented in Fig. 3b. The height of the two curves are almost the same (∼1.9 nm), while in the nanotube-MoS$_2$ region, the full width at half maximum intensity (16.0 nm) is greater than in the bare nanotube region (11.0 nm) (Fig. 3c), which is a strong indication that the MoS$_2$ is growing over the nanotube. However, if the nanotube is sitting on MoS$_2$, the measured AFM width across a nanotube should be very similar (ESI Fig. S3†). We further employed a water washing method to verify the interfacial climbing-over geometry in the nanotube-MoS$_2$ hybrids. As pure MoS$_2$ can be easily washed out by water immersion but nanotubes cannot (ESI Fig. S4†), one can determine whether the nanotubes are on or under MoS$_2$ by observing whether the nanotubes are washed away with MoS$_2$ or not. If the nanotubes are washed away, the nanotubes are sitting on the MoS$_2$ and vice versa. The results show that after soaking the hybrid sample in water and taking it out, the MoS$_2$ domains are removed but the nanotubes remain (Fig. 3d and e), which confirms the climbing-over geometry between the nanotubes and MoS$_2$ at the interface.

This climbing-over geometry is against common sense. As a nanotube is typically 2 nm in diameter and a MoS$_2$ monolayer is only ∼0.7 nm in thickness, during the post-growth of MoS$_2$, one would expect MoS$_2$ to grow underneath the nanotubes instead of climbing over them. This climbing behaviour of MoS$_2$ on the nanotubes should be attributed to the interaction strength difference between the nanotubes and MoS$_2$ to the substrate. From the water washing phenomenon, it has already been revealed that the nanotube-substrate interaction is much stronger than the MoS$_2$-substrate one, so during MoS$_2$ growth on the nanotubes, it takes less energy for MoS$_2$ to climb on the nanotubes than push the nanotubes up away from the substrate (Fig. 3a). This growth mechanism is also supported by our observation that the MoS$_2$ forms a discontinuous edge at

![Fig. 2](image1.png)

Fig. 2 Carbon nanotube-MoS$_2$ hybrids with a clean interface. (a) Schematic illustration of the optimized sequential CVD process. By annealing the nanotubes before the growth of MoS$_2$, amorphous carbon can be etched away, and a clean interface is guaranteed. (b) SEM image of the randomly nucleated MoS$_2$ domains on the whole substrate. Clean nanotubes do not act as nucleation centres. (c) Photoluminescence spectra of MoS$_2$ on and off the nanotube. (d) The Raman spectra of MoS$_2$ display a uniform frequency difference of 19 cm$^{-1}$ between the $E_{2g}$ and $A_{1g}$ modes. All signatures in (c and d) illustrate that the MoS$_2$ samples are homogeneous monolayers.

![Fig. 3](image2.png)

Fig. 3 Carbon nanotube-MoS$_2$ hybrids with large interaction area. (a) Schematic illustration of the process of MoS$_2$ climbing over one nanotube. (b) AFM image of the same nanotube on bare substrate and hybridized with a MoS$_2$ monolayer. (c) AFM cross-sectional profiles along the line labelled in (b). The height of the two curves are almost the same (∼1.9 nm), while in the nanotube-MoS$_2$ region, the full width at half maximum intensity (16.0 nm) is greater than in the bare nanotube region (11.0 nm). (d) and (e) SEM images of the nanotube-MoS$_2$ hybrid structure before (d) and after (e) soaking in water. (f) SEM image of a MoS$_2$ monolayer grown across nanotubes and discontinuous edges are formed at two sides of the nanotubes. (g) Polarized SHG patterns at different positions labelled in (f), indicating that the whole MoS$_2$ domain is still a single crystal.
two sides of the nanotubes. As the MoS$_2$ climbing consumes some energy (MoS$_2$ will bend to increase the strain energy), not all of the MoS$_2$ can climb over the nanotubes at the same time, leading to unequal length (Fig. 3f). However, the whole domain is still a single crystal, as proved by the same polarized second-harmonic generation (SHG) pattern at different positions (Fig. 3g). This specific climbing growth behaviour of MoS$_2$ leads to a larger interaction area between the nanotubes and MoS$_2$ at the interface.

The clean interface with large interaction area naturally results in strong interfacial coupling in nanotube-MoS$_2$ hybrids both mechanically and electronically. This strong coupling was first demonstrated in the vibration frequency shift of the specific Raman modes of the nanotubes. The nanotube radial breathing mode (RBM), which is the in-phase collective motion of atoms along the radial direction and a characteristic Raman mode of 1D materials, is hardened by $\sim 1\text{ cm}^{-1}$ with MoS$_2$ coverage (Fig. 4a and b). This blue-shift can be attributed to the strong interlayer mechanical coupling between the nanotubes and MoS$_2$ (mechanical coupling enhances the effective force constant of RBM vibrations). The nanotube G mode is sensitive to carrier doping and its frequency is therefore an indicator of interlayer charge transfer. From the band alignment configuration, the as-prepared nanotube-MoS$_2$ hybrids naturally form a p–n junction, as pristine nanotubes are p-type, while MoS$_2$ are n-type (Fig. 4c). The electrons will transfer from the MoS$_2$ to the nanotubes through the strong electronically coupled interface. As a consequence, the G-mode Raman frequency of the nanotubes red-shifts by $\sim 2\text{ cm}^{-1}$ (Fig. 4d) (the electron transfer makes the original p-type nanotubes more neutral). It is worth noting that these Raman shifts cannot be detected for MoS$_2$ since the 2D excited area (laser spot) is two orders of magnitude larger than that of the 1D hybrid area.

The strong interfacial electronic coupling between the nanotubes and MoS$_2$ can also be demonstrated from their ultrafast charge transfer dynamics. We performed ultrafast pump–probe spectroscopy to capture this process in a temporal profile with a pulse width of 100 fs. Since the single-tube signal is too weak to be detected in the ultrafast spectroscopy, we grew MoS$_2$ on aligned dense nanotube arrays to enhance the signal (a laser spot can cover many nanotube-MoS$_2$ samples). Using a pump fluence of $12\mu\text{J cm}^{-2}$, we resonantly pumped MoS$_2$ at 680 nm and selectively probed at a longer wavelength of 820 nm (Fig. 4e). Time-resolved transient absorption (TA) signals of the pristine nanotube arrays, pristine MoS$_2$ and their corresponding hybrids are shown in Fig. 4f. The TA signals of the nanotubes and MoS$_2$ are consistent with those in previous reports and the understanding is that the nanotube signal rises up quickly and then decays to

![Fig. 4](image-url)
zero in the next few picoseconds and no time-resolved signal is detected in MoS₂ since the probe photon energy is smaller than the MoS₂ bandgap. As for the nanotube-MoS₂ hybrids, the TA signal is enhanced by ~50% compared with that of the pristine nanotube arrays. We attribute the enhanced signal to the interfacial charge transfer: after photoexcitation of MoS₂, both electrons and holes will transfer to the nanotubes due to their type I band alignment. The charge transfer signal (Fig. 4g, where the dashed line corresponds to the laser cross correlation function), obtained by subtracting the TA signal of the nanotubes from the hybrid structure, rises a little slower compared with that of pristine nanotubes and reflects that the charge transfer process is ultrafast and on the time scale of only ~100 fs (the fittings are obtained by deconvolution analysis). This ultrafast charge transfer time facilitates the fabrication of fast photoelectric conversion with a speed limit of up to 10,000 GHz.

Conclusions

In conclusion, we have demonstrated a strong-coupled 1D nanotube-2D MoS₂ monolayer hybrid structure through a controlled sequential CVD growth. The post hydrogen annealing before MoS₂ growth is the key to creating a clean interface and the climbing-up growth behaviour of MoS₂ over the nanotubes ensures a large interaction area at the interface, which together lead to strong interfacial coupling both mechanically and electronically. Our work opens up an avenue for assembling low-dimensional materials with controlled interfacial geometry and coupling strength by utilizing complex 2D, 1D and 0D components, therefore it will push the exploration of high-performance device applications of vdW nanomaterials with higher spatial resolution and faster response speed.

Experimental

Carbon nanotube growth

Carbon nanotubes were grown using a CVD method on a 300 nm SiO₂/Si substrate. We used argon bubbled ethanol as a carbon precursor and a thin ion film (0.2 nm) as a catalyst. Before the growth, the catalyst was annealed in air at 700 °C for 5 min, and the system was flushed using ultrahigh purity Ar gas for 10 min. Then, the furnace was ramped to 930 °C with 350 sccm H₂ and 100 sccm Ar passed through ethanol for the synthesis of the nanotubes for 30 min.

Growth of MoS₂ on nanotubes

We grew MoS₂ on nanotubes by atmospheric pressure CVD method using MoO₃ and S powder as precursors. 10 mg of MoO₃ powder was placed at the centre of a tube furnace and 30 mg of S powder at the upstream side, 15 cm from the MoO₃ powder. The substrates with as-grown nanotubes or annealed nanotubes were placed downstream of the position of MoO₃. Before the growth, the system was flushed with ultrahigh-purity Ar gas for 30 min. The temperature of the furnace was then ramped to 750 °C with 15 sccm Ar gas flow for 40 minutes, and then kept at 750 °C with 250 sccm Ar gas flow for 5 min, and then naturally cooled to room temperature with 200 sccm Ar gas.

Optical measurements

Photoluminescence and Raman spectra were recorded using self-built equipment with a laser excitation wavelength of 532 nm. The laser power was set as 1 mW, and the integral time was 1 s for the photoluminescence measurements, 30 s for the Raman measurements. Optical images were taken by an Olympus microscope (Olympus BX51). The pump–probe was measured with femtosecond pulses (~100 fs, 80 MHz) generated by a Ti:sapphire oscillator (Spectra-Physics Mai Tai laser) and an OPO laser. The TA signal, ΔR/R = R_{w/pump}/R_{w/o pump} - 1, was recorded using photomultiplier tubes and lock-in amplifier with reflective geometry. More details about the pump–probe setup can be found in our previous work.

Conflicts of interest

The authors declare no conflict of interest.

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References

6. M. Massicotte, P. Schmidt, F. Vialla, K. G. Schadler, A. Reserbat-Plantey, K. Watanabe, T. Taniguchi,