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MoS$_2$ nanosheet/Mo$_2$C-embedded N-doped carbon nanotubes: Synthesis and electrocatalytic hydrogen evolution performance†


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In situ solid and subsequent hydrothermal reactions were developed to grow ultrathin MoS$_2$ nanosheets on Mo$_2$C-embedded N-doped carbon nanotubes. As applied as electrocatalysts for hydrogen evolution, the hybrid nanotubes exhibited excellent catalytic activity.

Hydrogen, as a green fuel, is a promising candidate for traditional petroleum fuels in the future. The rare metals, such as platinum, have high efficiency in the hydrogen evolution reaction (HER), however, their high cost and scarcity limit their large scale applications. During the past few years, MoS$_2$ has attracted much attention due to its high abundance, low cost and chemical stability in the acid solution. Density functional theory calculations indicated that the edges of MoS$_2$ nanoparticles were active for hydrogen evolution, while their (0001) basal planes were catalytically inert. In terms of subsequent experimental results, T. F. Jaramillo and his coworkers demonstrated that the electrocatalytic activity for hydrogen evolution of MoS$_2$ correlated linearly with the number of edge sites on the MoS$_2$ catalyst. Thereafter, enormous efforts have been put into optimizing MoS$_2$ nanostructures to increase the amount of edges per mole MoS$_2$. As a result, the electrocatalytic performances of those optimized MoS$_2$ nanostructures were significantly improved. For example, the Tafel slope of highly ordered double-gyroid MoS$_2$ bicontinuous networks was as low as 50 mV per decade. Besides the aspect of active sites, another issue need to be also addressed well when MoS$_2$ nanostructures applied for HER catalyst, i.e., an extremely low conductivity between two adjacent van der Waals bonded S–Mo–S sheets. Resistivity through the basal planes has been measured to be 2200 times larger than that through the direction parallel to the planes, which significantly decreases the overall HER rate. Such low conductivity great limits charge transfer rate during the HER process, and consequently suppresses the total HER efficiency of MoS$_2$ nanostructures. One efficient way to solve the problem is growing MoS$_2$ nanostructures on conductive substrates, such as graphene, graphite, and carbon paper, etc. In this case, an advantageous catalyst design may be to make (0001) basal planes of MoS$_2$ nanostructures perpendicular to the conductive surface. However, most of the conductive substrates are inert for HER, which significantly decreases the density of active sites of MoS$_2$ nanostructures. Thus, increasing both the conductivity and active sites of MoS$_2$ nanostructures simultaneously for efficient HER electrocatalysts still remains a challenging task.

In this work, we describe a strategy based on in situ solid reaction and subsequent hydrothermal reactions to grow MoS$_2$ nanosheets on N-doped carbon nanotubes (NCNTs) with Mo$_2$C nanoparticles embedded in the NCNT walls. Compared with other MoS$_2$ based heteronanostructures, the synthesized MoS$_2$ composite applied as HER catalyst offers the following advantages: (i) The composites possess abundant active sites for HER because the thickness of MoS$_2$ nanosheets is in range of 1–5 nm, and the MoS$_2$ nanosheets grown on the surface of N-doped carbon nanotubes with an angle that allows more active edge sites exposed to electrolyte. Besides, the spacing (002) of the basal planes of MoS$_2$ nanosheets are expanded. This leads to rich-defect in MoS$_2$ nanosheets, which provides additional active edge sites for HER. (ii) NCNT in the composite can significantly improve the whole conductivity of the electrocatalyst, and thus increases charge transfer rate during the HER process. (iii) Mo$_2$C nanoparticles are active for HER, and thus the introduction of NCNTs in the composite would not decrease the density of the active sites of the electrocatalyst significantly.

![Scheme 1 Illustration of the growth processes of MoS$_2$/Mo$_2$C-NCNTs.](image)

The growth of MoS$_2$ nanosheets on Mo$_2$C-embedded NCNTs (named as MoS$_2$/Mo$_2$C-NCNTs for convenience) is based on in situ solid and subsequent hydrothermal reactions, as illustrated in Scheme 1. MoO$_3$/polyaniline (MoO$_3$/PANI) hybrids were first fabricated by our previous method with a modification. After the hybrids were annealed at 700°C for 2 h under an Ar flow, interesting tube-like nanostructures were obtained, in which the inner and outer walls consist of MoO$_2$ and amorphous N-doped carbon material with crystalline Mo$_2$C nanoparticles embedded in the carbon material, respectively (for convenience, this product is named as MoO$_3$/Mo$_2$C-NCNTs). Under a hydrothermal condition with the presence of thiourea, MoO$_2$/Mo$_2$C-NCNTs can be transformed into MoS$_2$/Mo$_2$C-NCNTs at 200°C for 48 h. The detailed synthesis processes are also described in the Electronic
Fig. 1 Structural characterization of MoO$_3$/Mo$_2$CkNCNTs. (a) TEM image, the left inset showing amorphous N-doped carbon layer, and the right inset showing HRTEM image of crystalline Mo$_2$C embedded in amorphous carbon layer, (b) HRTEM, and (c) EELS spectrum.

PANI has been demonstrated to be able to grow readily on the surfaces of various inorganic materials as various forms, such as nanorods, nanoparticles, and thin films, if the polymerization conditions are controlled properly. In the present work, by tuning polymerization temperature and the concentration of aniline, PANI thin films were uniformly coated on the MoO$_3$ nanowires. The as-synthesized products were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). A typical SEM image (Fig. S1) clearly shows that MoO$_3$/PANI hybrids were synthesized in high yields with lengths and diameters of about several micrometers and 400 nm, respectively. An in situ solid reaction for the formation of MoO$_2$/Mo$_2$CkNCNTs was carried out by heating the MoO$_3$/PANI hybrids at 700°C for 2 h at an Ar atmosphere. X-ray diffraction (XRD) (Fig. S2) reveals that the products contain crystalline Mo$_2$C (JCPDs PDF no. 77-0720) and MoO$_2$ (JCPDs PDF no.86-0135). SEM image (Fig. S3) shows that the diameter of the open MoO$_2$/Mo$_2$CkNCNTs decreases down to about 320 nm. A low-magnification TEM image (Fig. 1(a)) clearly demonstrates that the thickness of the walls the hybrid NCNTs are about 135 nm. From the TEM image, light and dark regions can also be identified in the walls of the hybrid NTs, implying that the hybrid NTs are composed of different materials. The lattice distance in the dark region (inner wall) from high-resolution TEM (HRTEM) image (Fig. 1(b)) is 0.35 nm, corresponding to (110) plane of Mo$_2$C. The XRD and TEM analyses show that the inner wall of the NTs is MoO$_2$, and the outer wall is composed of amorphous carbon material and crystalline Mo$_2$C. In order to further determine the composition of the hybrid nanotubes, line-scan electron energy loss spectroscopy (EELS) was carried out, as shown in Fig. 1(c). It can be clearly found that the C and N elements are distributed in the whole regions of the NTs, whereas the Mo and O elements are mainly distributed in the inner walls. X-ray photoelectron spectroscopy (XPS) further confirms the presence of N element in the NTs, and its percentage is determined to be 20 at% (Fig. S4). On one hand, the results above further confirms the tubular character of the products; on the other hand, it demonstrates that the outer wall is composed of N-doped and Mo$_2$C embedded-amorphous carbon material, and the inner wall is crystalline MoO$_2$.

Fig. 2 Structural characterization of MoS$_2$/Mo$_2$CkNCNTs. (a) SEM, (b, c) TEM, and (d) HRTEM images, the inset in (d) showing SAED pattern of basal plane of MoS$_2$ nanosheets.
These results above imply that the interesting MoO\(_2\)/MoO\(_2\)-NCNTs can be successfully obtained by the simply annealing of the MoO\(_2\)/PANI hybrids at an Ar atmosphere. The formation of the tubular structures is similar to those of hollow inorganic nanocrystals based on a method through the nanoscale Kirkendall effect.\(^\text{10}\) The key process for hollow structure preparation through the nanoscale Kirkendall effect is the formation of a so-called “core–shell” structure at the initial stage. A net vacancy diffusion towards the interior with the reaction process processed if the diffusion of core material is faster than that of the shell material, which gradually leads to void space at the core–shell interface, and eventually the formation of a hollow structure. In the present work, both MoO\(_2\) and PANI are instable thermodynamically. At a high temperature, the diffusion rate of MoO\(_2\) core is faster than that of the PANI shell. With the chemical reaction between MoO\(_2\) and PANI proceeded, most of MoO\(_2\) material was reduced into Mo\(_2\) phase, accompanying with the formation of a hollow region in the center of the products. Due to its faster diffusion rate MoO\(_2\) would further diffuse through the core-shell interfaces into shell region, and react with PANI. Consequently, produced Mo\(_2\)C nanoparticles would be embedded in the outer wall of the NCNTs. It is worth noting that the N elements in PANI cannot be removed completely at the temperature of 700°C, which leads to in situ N-doping in the outer walls of the hybrid NTs.

The hydrothermal reaction for the preparation of MoS\(_2\)/MoO\(_2\)-NCNTs was carried out by heating an aqueous solution contains the MoO\(_2\)/MoO\(_2\)-NCNTs as precursors and thiourea as the sulfur source at 200°C for 48 h. During the heating process, O\(^2\) ions in MoO\(_2\)/MoO\(_2\)-NCNTs were replaced with S\(^2\) ions, leading to the transformation of MoO\(_2\) to MoS\(_2\). XRD technique was conducted to investigate the structural information of the product. As shown in Fig. S5, besides the diffraction peaks indicated by “#” from Mo\(_2\)C, several ones from MoS\(_2\) marked by “)” are also found in the XRD pattern.\(^\text{11}\) Two broadened peaks at high-angle region (32.7 and 58.3°) are well indexed to (100) and (110) planes of 2H-MoS\(_2\) (JCPDS 37-1492). This indicates the crystalline MoS\(_2\) and MoO\(_2\) are presented in the product. It is noteworthy that the diffraction peak of 2H-MoS\(_2\) at 2\(θ\)=14.4° shifts to low-angles of 2\(θ\)=8.5 and 13.8°, suggesting that the interlayer distance of (002) plane of MoS\(_2\) is expanded.\(^\text{11}\) Using the Bragg equation, the corresponding expanded d spacings are 1.04 and 0.64 nm, respectively. Moreover, all of the diffraction peaks from MoS\(_2\) are broadened, suggesting its low crystallinity. In addition, the small peak at 2\(θ\)=26.0 corresponds to (011) plane of MoO\(_2\), suggesting that small parts of MoO\(_2\) still present in the final product. The structure of the MoS\(_2\)/MoO\(_2\)-NCNTs is further characterized by SEM and TEM observations. SEM image (Fig. 2(a)) shows the MoS\(_2\)/MoO\(_2\)-NCNTs have interesting hierarchical morphologies, i.e., many ultrathin nanosheets grown almost perpendicularly on the surfaces of one-dimensional nanostructures. The lengths and diameters of MoS\(_2\)/MoO\(_2\)-NCNTs are about 3.5 μm and 500 nm, respectively. The low-resolution TEM image (Fig. 2(b)) reveals that the products are still of tubular character with the ultrathin nanosheets surrounding outside. The cross-sectional TEM image (Fig. 2(c)) reveals that the thickness of MoS\(_2\) nanosheets is in the range of 1–5 nm. In the corresponding HRTEM image (Fig. 2(d)), most of the edges of MoS\(_2\) nanosheets have large spacing of 1.02 nm, which is consistent with the result from XRD analysis. The corresponding selected-area electron diffraction (SAED) (the inset in Fig. 2(d)) of the basal plane of MoS\(_2\) nanosheets show that the atomic arranging manners on the basal surfaces are disordered. As previously demonstrated, the expanded spacings of (002) plane were attributed to oxygen incorporation in MoS\(_2\).\(^\text{3}\) First-principle calculations and experimental data further proved that the oxygen incorporation could effectively regulate the electronic structure, improved the intrinsic conductivity of MoS\(_2\), and consequently enhanced its HER activity significantly.

![Image](https://example.com/image1.png)

**Fig. 3** XPS spectra of MoS\(_2\)/MoO\(_2\)-NCNTs. (a) Mo 3d, (b) S 2p, (c) N 1s, and (d) C 1s spectra.

![Image](https://example.com/image2.png)

**Figure 4.** (a) Polarization curves, and (b) Tafel plots of Pt, bulk MoS\(_2\), MoS\(_2\) nanoflowers, and MoS\(_2\)/MoO\(_2\)-NCNTs, (c) Cycling stability of MoS\(_2\)/MoO\(_2\)-NCNTs at an overpotential of 220 mV, and (d) Polarization curves showing that negligible degradation of HER activity of MoS\(_2\)/MoO\(_2\)-NCNTs after 1000 cycles and continuous hydrogen production for 10,000 s at an overpotential of 220 mV.

The surface electronic state and composition of the MoS\(_2\)/MoO\(_2\)-NCNTs were further investigated by X-ray
The cathodic current density of the hybrid NTs is larger than those of other MoS$_2$ nanoflowers, the MoS$_2$/Mo$_3$C-NCNTs exhibit excellent HER activity with small onset overpotential of 145 mV, a large exchange current density of 21 µA cm$^{-2}$, and a large cathodic current density of 280 mA cm$^{-2}$ at $\eta = 300$ mV due to more active edge sites for HER and very high conductivity of carbon nanotubes. Our results demonstrate that the NTs are very promising for HER electrocatalysts.

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### Notes and references

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* † Electronic Supplementary Information (ESI) available: [Experimental processes, SEM image of MoO$_3$/PANI hybrids, XRD, SEM, and XPS of MoO$_2$/Mo$_3$C-NCNTs, XRD, EELS spectrum for MoS$_2$/Mo$_3$C-NCNTs, electrochemical impedance spectroscopy of MoS$_2$/Mo$_3$C-NCNTs, and structural characterization of MoS$_2$ nanoflowers]. See DOI: 10.1039/b000000x/