A binder-free CNT network–MoS$_2$ composite as a high performance anode material in lithium ion batteries$^\dagger$

Congxiang Lu,$^\dagger$ Wen-wen Liu,$^\dagger$ Hong Li$^a$ and Beng Kang Tay$^{*,\dagger}$

A carbon nanotube (CNT) network and molybdenum disulfide (MoS$_2$) are rationally architected into a novel type of anode material in lithium ion batteries (LIBs), without the necessity for any binders. Enhanced structural stability and reaction kinetics provide the high and stable capacity as well as superior rate capability.

Lithium ion batteries (LIBs) nowadays serve as the most important power source for portable electronics and are also identified as a promising power solution for future electric vehicles. 1 However, development of LIBs is now bottlenecked by the graphite anodes, due to their limited specific capacity of 372 mA h g$^{-1}$. As such, novel anode materials with higher capacity without compromising the cyclability have become the subject of intensive research worldwide. Among the emerging materials, MoS$_2$ has attracted particular attention, because of much smaller volumetric changes in the lithiation–de-lithiation processes.$^2$–$^14$ Therefore, it could provide the potential for less degradation during cycling and better rate capability.

However, the performances of anodes made of bulk MoS$_2$ materials are still far from ideal, providing only limited capacities and suffering from severe capacity fading. One reason is their intrinsically poor electric and ionic conductivities which hinder efficient charge transfer.$^6$ Besides, the typical conversion of MoS$_2$ to Li$_2$S and Mo happening during lithiation$^3,15$ is likely to degrade the electrodes, if no anchoring sites are provided. In addition, in bulk forms of MoS$_2$, capacities are often significantly constrained due to the difficulty of the internal portion of the material to be fully lithiated.

Making MoS$_2$ into nanostructures and compositing them with other nano materials, especially those from a carbonaceous family like graphene$^5,10,11$ or CNTs,$^4,6$–$^8,16$ are considered as promising solutions for the problems. CNTs exhibit superior properties such as excellent electrical$^{17}$ and thermal conductivity$^{18}$ and structural stability.$^{19,20}$ Therefore, it is expected that by combining the merits of CNT and MoS$_2$, the CNT–MoS$_2$ composite can act as a promising anode material in LIBs. Highly conductive CNTs facilitate charge transfer during cycling while their hollow structure and mechanical strength enable them to act as an excellent volume buffer for MoS$_2$ during lithiation–de-lithiation.

There have been a number of reports on the synthesis of CNT–MoS$_2$ composites.$^2$–$^4,8$ It may be noteworthy that although the synthesis methods as well as morphology control of such composites definitely play significant roles in the performance, yet, how the material is assembled onto the current collector may also be of high importance. In particular, direct conductive pathways constructed between active materials and current collectors have proven to be beneficial to the effective charge transfer.$^{21,22}$ However, to the best of our knowledge, there have not been such reports on CNT–MoS$_2$ composites so far. Active materials have to be mixed with polymer binders before electrochemical testing. If there is a method to exclude these less conductive additives, it could be a step further in the development of CNT–MoS$_2$ anode materials. In this regard, we develop a method to synthesize a MoS$_2$ material on the surface of CNTs which are grown on the metal current collectors and self-assembled into networks (see ESI† for experimental details). The obtained composite can be directly used for LIB testing without binders. This novel architecture exhibits greatly improved electrochemical performances including high reversible capacity, excellent capacity retention and rate capability.

Fig. 1(a) displays the CNTs successfully grown on the stainless steel (SS) substrate by the CVD method. The length of the CNTs is about several tens of micrometers while the diameters are in the range of 10 to 50 nm. As shown in Fig. S1 (ESI†), CNTs consist of tens of walls, indicating their multi-walled characteristic. Interestingly, CNTs are self-assembled into a sparse network, leaving a notable space inside, which is beneficial for the access of electrolyte and lithium ions during charge–discharge. CVD-prepared CNTs often come with hydrophobic surfaces.

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Thus, these CNTs obtained are treated by O2 plasma to ensure complete wetting. As shown in the insets of Fig. 1(a), the contact angle changes from 142° to below 10° after O2 plasma treatment, indicating the change from super hydrophobic to hydrophilic. After the hydrothermal reaction and annealing process, the surface of the CNTs is completely covered by MoS2 nanoflakes, as displayed in Fig. 1(b) and (c). The connection of the CNT network to the substrate is so strong that it survives the harsh conditions during the long-duration hydrothermal reaction. This is also advantageous for the stability of the anode. Compared to those of bare CNTs, diameters of the composite nanowires increase to be 100 to 200 nm, but the porosity among the CNT network is still maintained to a large extent. Such a structure could facilitate the electrolyte to come into contact with the active material and ensure all of its portions into electro-chemical reactions. In the TEM image of Fig. 1(d), the core–shell structure of the CNT–MoS2 nanowire is clearly presented. As indicated in the HRTEM image of Fig. 1(e), carbon layers that construct CNTs are separated by ca. 3.4 Å, matching the wall separation in multi-walled CNTs. The surrounding MoS2 flakes consist of several (<10) layers, in between which the distance is around 6.4 Å, close to the interlayer distance of the (002) plane orientation in MoS2. In addition, energy-dispersive X-ray spectroscopy (EDX) line scan analysis (see ESI†) manifests the element distribution from the shell to core parts of the nanowires.

Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) are also employed to further characterize the CNT–MoS2 composite. As shown in Fig. 2, the Raman spectrum of as-synthesized CNTs exhibits a G peak at 1581 cm\(^{-1}\) and a D peak at around 1347 cm\(^{-1}\), consistent with previous reports.\(^2,24\) After the hydrothermal reaction, two characteristic peaks of MoS2 appear at 379 and 405 cm\(^{-1}\), which belong to the E\(_{2g}\) and A\(_{2g}\) modes, respectively.\(^25,26\) In the meantime, both D and G bands of the CNTs diminish significantly, probably due to the screening effects of the covering MoS2 flakes.\(^2\) Furthermore, XPS reveals that the stoichiometric ratio between Mo and S is 1: 1.86, further confirming the successive synthesis of MoS2 (see Fig. S3 of ESI† for details).

To evaluate its performance as an anode material, the CNT–MoS2 composite on SS chips is directly assembled into half cells for electrochemical testing without the usage of any binders or additives. The representative cyclic voltammetry (CV) curve for the first three cycles is shown in Fig. 3(a). In the first cycle, two distinct peaks are observed on the CV curve at 1.0 and 0.4 V, consistent with previous reports.\(^3,10,27\) The cathodic peak at 1.0 V can be assigned to insertion of Li ions into the interlayer of MoS2, transforming its phase from Mo in trigonal prismatic to Mo in octahedral coordination.\(^3,7\) The subsequent sharp peak located at 0.4 V is associated with the further reaction between MoS2 and Li\(_+\), resulting in LiS\(_2\) and Mo metallic particles, following the reaction of \(4\text{Li} + \text{MoS}_2 \rightarrow \text{Mo} + 2\text{Li}_2\text{S}\).\(^7\) It should be mentioned that both the reduction peaks disappear in the following cycles, suggesting irreversibility in the conversion of MoS2 into Li2S and Mo.\(^3\) Meanwhile, a remarkable cathodic peak appears at 1.8 V, which is indicative of the lithiation process of S into Li2S. Therefore, in the following cycles, reactions may take place between lithium and sulfur. In anodic sweeps, a broad peak at around 1.5 V can be attributed to the partial oxidation of Mo to MoS2 (ref. 28) and/or de-lithiation of residual lithium intercalates (Li\(_x\)MoS2).\(^2\) The subsequent pronounced peak at 2.3 V corresponds to conversion of Li2S to S\(_2\).\(^4\)
In the initial lithiation profile tested at 200 mA g⁻¹ as shown in Fig. 3(b), two voltage plateaus at around 1.1 and 0.6 V can be observed, corresponding to the formation of Li₂MoS₂ and reduction of MoS₂ into Mo particles embedded in the Li₂S matrix, respectively. In the de-lithiation plots, well-defined plateaus at 2.2 V can be attributed to extraction of lithium from Li₂S. These plots are in line with aforementioned CV measurements. Initial lithiation and de-lithiation capacities at 200 mA g⁻¹ of the CNT–MoS₂ composite are 1715 and 1305 mA h g⁻¹, respectively, corresponding to a columbic efficiency of 76.1%. The irreversible capacity loss of 23.9% is probably caused by formation of the solid electrolyte interface (SEI), which is almost inevitable in nanosized anode materials. Nevertheless, the efficiency is maintained at nearly 100% in the subsequent cycles and the composite demonstrates an impressively high de-lithiation capacity of 1456 mA h g⁻¹ after 50 cycles. This is among the highest capacities as well as best cyclic performances of CNT–MoS₂ composites ever reported at a current density of 200 mA g⁻¹ and also much better than the performance of commercial MoS₂ powder with binders in the control group (see Fig. S6 of ESI† for details). Rate capability is another important criterion to evaluate the performance of an anode material. As shown in Fig. 3(d), a de-lithiation capacity of 1450 mA h g⁻¹ is obtained after 10 cycles at a charge–discharge current of 200 mA g⁻¹, consistent with the value shown in Fig. 3(c). When the current densities are increased to 400, 600, 800 and 1000 mA g⁻¹, the corresponding de-lithiation capacities are 1431, 1367, 1302 and 1224 mA h g⁻¹ after 10 cycles, respectively, demonstrating high capacities and plausible cycling behavior even at high current density. Eventually, when the current is set back to 200 mA g⁻¹, the de-lithiation capacity recovers to 1535 mA h g⁻¹, indicating excellent rate capability of the composite.

The outstanding performances including high capacity, excellent cycling retention and rate capability are enabled by the rational design in material selection, compositing and also architecting. Improved structural stability as well as efficient reaction kinetics is realized in this hierarchical assembling of a CNT network and MoS₂ flakes. Firstly, the network of CNTs provides a strong skeleton for the composite, avoiding aggregation of the active material, retaining its inter-space and also large surface area to a considerable extent. Secondly, the internal cavity and flexibility of the CNTs can help to absorb or buffer the mechanical stress induced by volume variation of MoS₂ upon repetitive lithium insertion–extraction. Meanwhile, voids inside the composite not only provide space to accommodate volume change but also shorten the diffusion pathways, enabling fast Li⁺ transport and hence improved rate capability. Furthermore, highly conductive CNTs are widely known as good pathways for charge transfer in nanocomposites. In this CNT network–MoS₂ flake composite, charge transfer can be further enhanced because of the direct rooting of the CNT network onto the metal current collector as well as binder-free architecting.

In summary, an approach to fabricate a binder-free CNT network–MoS₂ composite anode material has been successfully developed. It consists of CVD growth of CNTs on a metal substrate and hydrothermal preparation of MoS₂ nanoflakes. Because of reinforced structural stability and also enhanced reaction kinetics, the obtained CNT–MoS₂ composite demonstrates impressive electrochemical performances. Encouragingly, a high and reversible capacity of over 1300 mA h g⁻¹ is retained for 50 cycles at a current density of 200 mA g⁻¹, while excellent rate performance is also delivered. This method offers a new idea to optimize the CNT–MoS₂ composites under intensive research. Moreover, the binder-free construction and usage of a CVD-grown CNT network on a metal substrate instead of dispersed CNTs may not be limited to CNT–MoS₂ composites. They may also be of potential for the improvement of other CNT-based composite anode materials.

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Notes and references