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COMMUNICATION

Creating a synergistic interplay between tubular MoS\(_2\) and particulate Fe\(_3\)O\(_4\) for improved lithium storage†

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A novel three-dimensional MoS\(_2@Fe_3O_4\) nanohybrid, composed of tubular MoS\(_2\) uniformly and densely decorated with particulate Fe\(_3\)O\(_4\), is constructed which exhibits significantly improved lithium storage performances through an impressive synergistic interplay between the two active materials.

Inorganic graphene analogues (IGAs) such as transition metal dichalcogenides (e.g., MoS\(_2\) and WS\(_2\))\textsuperscript{1,2} and oxides (e.g., MnO\(_2\))\textsuperscript{3} are emerging as fascinating anode candidates for next-generation, high-power lithium-ion batteries (LIBs) due to their rich resources, low toxicity and extraordinarily high theoretical capacities arising from a unique “conversion reaction” mechanism. In this mechanism, 4–8 Li\(^+\) ions can be stored per formula unit since the oxidation state of a high-valance transition metal compound is fully utilised. It is worth noting, however, that these layered materials are all featured by strong interlayer van der Waals forces giving rise to a huge tendency to restack. If so, large quantities of active sites for lithium storage are sacrificed, and poor cycle and rate performances are inevitable. Therefore, various hollow micro/nanostructures of IGAs are being pursued for improved electrochemical performances.\textsuperscript{4}

MoS\(_2\), as a typical member of transition metal dichalcogenides, is composed of a layer of molybdenum atoms sandwiched between two layers of sulphur atoms, which are covalently bonded to form a nanosheet. The reasonably high theoretical capacity (670 mA h g\(^{-1}\)) of MoS\(_2\), resulting from a conversion reaction of MoS\(_2\) + 4Li\(^+\) + 4e\(^-\) → Mo + 2Li\(_2\)S, may rank it as a promising substitute for graphitic carbon — the current anode material of LIBs that has a relatively low theoretical capacity (372 mA h g\(^{-1}\)). Unfortunately, the MoS\(_2\) nanosheets suffer from huge volume expansion as well as serious restacking during repeated lithiation/delithiation, which are major reasons for the poor cyclability especially at high rates. One possible solution is to employ different spacers such as graphene nanosheets,\textsuperscript{5} carbon nanotubes,\textsuperscript{6} carbon nanospheres,\textsuperscript{7} noble metal nanoparticles,\textsuperscript{8} and transition metal oxide nanoparticles,\textsuperscript{9} which can physically isolate the MoS\(_2\) nanosheets for reversible lithium and electron transport. Another strategy is to construct higher-level hollow assemblies from the MoS\(_2\) nanosheets, e.g., nanotubes,\textsuperscript{10} nanoboxes,\textsuperscript{11} and hollow nanospheres,\textsuperscript{12} which are expected to improve the reversible capacity of MoS\(_2\) by alleviating the restacking of the nanosheets. For example, in a recent report, Wang et al. have fabricated interesting tubular architectures from the MoS\(_2\) nanosheets, which deliver a ~40% higher reversible capacity after 50 charging–discharging cycles at a current density of 100 mA g\(^{-1}\).\textsuperscript{13} However, it should be stressed that the cycle stability of tubular MoS\(_2\) is still not satisfactory due to a certain degree of aggregation, exhibiting an obvious and steady capacity decay from the very beginning. In this regard, further improvement is necessary to achieve better cycle and rate performances.

![Fig. 1](image-url)

**Fig. 1** — (a) SEM, (b and c) TEM, and (d) HRTEM images of as-synthesised tubular MoS\(_2\).

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\textsuperscript{4} Electronic Supplementary Information (ESI) available: [Experimental details and supplementary figures]. See DOI: 10.1039/x000000x

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*J. Name.*, 2013, **00**, 1-3 | 1
Here we report a novel hybridisation design, by which a second active material, i.e., particulate Fe$_3$O$_4$ is hierarchically assembled on tubular MoS$_2$ by a facile, one-step approach based on van der Waals interactions. The resulting three-dimensional (3D) MoS$_2$@Fe$_3$O$_4$ nanohybrid, composed of tubular MoS$_2$ uniformly and densely decorated with particulate Fe$_3$O$_4$, exhibits significantly improved reversible capacity and rate capabilities through a synergistic interplay between the two active materials. On one hand, tubular MoS$_2$ serves as a matrix that can provide abundant mesopores and hollow interiors to facilitate lithium transport and storage, and buffer the structural stress during the cycling processes. On the other hand, particulate Fe$_3$O$_4$ acting as a spacer can isolate tubular MoS$_2$ from aggregation, thereby increasing the intertube distance for easy lithium access. Moreover, compared to other spacers such as nanocarbons and noble metals, Fe$_3$O$_4$ is particularly attractive due to its high theoretical capacity (928 mAh g$^{-1}$), making it an important electrochemical contributor. A strikingly high reversible capacity of 1113 mAh g$^{-1}$ is delivered after 100 charging–discharging cycles, ~44% higher than that of tubular MoS$_2$. This value warrants our 3D MoS$_2$@Fe$_3$O$_4$ nanohybrid as an appealing choice for high-performance LiB anode.

Tubular MoS$_2$ is synthesised by a hydrothermal method, and its morphological information is provided in Fig. 1a and S1 (ESI†). From these SEM images we can clearly see uniform tubular architectures with ripple-like surfaces and hollow interiors, whose outer diameters are ~200 nm and lengths are above 1 μm. The same morphology is confirmed by TEM characterisation, as shown in Fig. 1b. Under closer examination (Fig. 1c), a wall thickness of ~50 nm can be recognised. Ambiguously, the tubular architectures are constructed from numerous MoS$_2$ nanosheets, most of which are indeed single layers since the observed wrinkles marking these MoS$_2$ nanosheets are randomly distributed without obvious "stacking" traces (Fig. 1d). Moreover, the measured interlayer distance of ~0.6 nm further proves the presence of single-layer MoS$_2$ nanosheets. The XRD result of tubular MoS$_2$, as presented in Fig. S2 (ESI†), is in good agreement with TEM characterisation. The diffraction peaks located at 2θ = 26° and 59° are assigned to the (100) and (110) planes of 2H–MoS$_2$ polytype, respectively. The absence of (002) diffraction peak, different from that of bulk MoS$_2$, indicates that the well-stacked layers have been successfully exfoliated.

Particulate Fe$_3$O$_4$ with an average diameter of ~6 nm is synthesised according to our previous report. For the hierarchical assembly, the two building blocks are mixed in tetrahydrofuran (THF) under sonication, during which particulate Fe$_3$O$_4$ is spontaneously attracted to the naked surfaces of tubular MoS$_2$ by strong van der Waals forces. As explored by us previously, the solvent property plays a key role in determining the assembly result: since THF is a bad solvent for MoS$_2$, the high surface energy of this layered material cannot be compensated for in an unsolvated state, and a huge tendency to aggregate exists. Once organically modified particulate Fe$_3$O$_4$ featured by a low surface energy is introduced, it is spontaneously attracted to the naked surfaces of tubular MoS$_2$ by strong van der Waals forces, thereby serving as a spacer to isolate the latter from aggregation as well as reducing the total free energy. It should be stressed that this assembly approach based on van der Waals interactions is facile and cost-effective compared to those based on hydrothermal reactions and complexation interactions. Fig. 2 shows TEM and HRTEM images of the resulting 3D MoS$_2$@Fe$_3$O$_4$ nanohybrid at an Fe$_3$O$_4$/MoS$_2$ wt ratio of 1/2. As seen from the TEM images, tubular MoS$_2$ is uniformly and densely decorated with particulate Fe$_3$O$_4$. Note that the hierarchical assembly is highly efficient since no free nanoparticles are seen dissociated from tubular MoS$_2$. Fig. 2d presents an HRTEM image of the 3D MoS$_2$@Fe$_3$O$_4$ nanohybrid. The coexistence of the two building blocks can be easily identified, with measured lattice fringe distances of ~0.48 and ~0.6 nm corresponding to the (111) and (002) planes of spinel Fe$_3$O$_4$ and 2H–MoS$_2$, respectively. This novel hybridisation design can fully exploit the merits of the two building blocks through a synergistic interplay: 1) tubular MoS$_2$ serves as a matrix to provide abundant mesopores and hollow interiors, thus facilitating lithium transport and storage; 2) particulate Fe$_3$O$_4$ acts as a spacer to effectively isolate tubular MoS$_2$ from aggregation, thereby increasing the intertube distance for easy lithium access. Moreover, the extremely high theoretical capacities of the two building blocks rank them as excellent active materials whose combination may lead to optimised lithium storage performances. For comparison, the Fe$_3$O$_4$/MoS$_2$ wt ratio is further elevated to 1/1, and typical TEM images are presented in Fig. S4 (ESI†). It can be seen that the distribution of particulate Fe$_3$O$_4$ on tubular MoS$_2$ is much denser than the case shown in Fig. 2. Besides, large quantities of free nanoparticles unbound to the naked surfaces of tubular MoS$_2$ can be observed, which demonstrates that particulate Fe$_3$O$_4$ is excess relative to tubular MoS$_2$, and an "over-saturated" situation is therefore reached at this wt ratio. As such, we conclude that an Fe$_3$O$_4$/MoS$_2$ wt ratio of 1/2 is the optimum value for uniform and complete coverage without "over-dosing".

To further explore the interactions between tubular MoS$_2$ and particulate Fe$_3$O$_4$ in the 3D MoS$_2$@Fe$_3$O$_4$ nanohybrid, we present high-resolution Mo 3d, S 2p, Fe 2p and O 1s XPS spectra in Fig. 3. It can be seen that for tubular MoS$_2$, the Mo 3d spectrum has
two major peaks at 232.2 and 228.7 eV, which are attributed to the doublet Mo 3d_{5/2} and 3d_{3/2} orbitals; the peaks corresponding to the S 2p_{1/2} and 2p_{3/2} orbitals of divalent sulphide (S^2-) are observed at 162.6 and 161.7 eV. The binding energy profiles and positions of Mo and S in tubular MoS_2 are very similar to what are reported for neat MoS_2 nanosheets. As to particulate FeO, the two distinct peaks at 724.5 and 710.5 eV corresponding to the Fe 2p_{1/2} and 2p_{3/2} orbitals, and the peak at 530.5 eV corresponding to the O 1s orbital are also similar to the XPS spectra of neat FeO nanoparticles. There is no satellite peak located at ~719 eV, thus ruling out the presence of maghemite (Fe_3O_4). The XPS results demonstrate that our facile, one-step assembly approach based on van der Waals interactions is non-invasive without altering the chemical nature of the two building blocks.

The electrochemical characteristics of the 3D MoS_2@FeO x nanohybrid can be figured out by analysing its CV curves, as shown in Fig. 4a. The reduction peaks at 1.28 and 0.76 V in the 1st cathodic scan originate from the formation of Li$_2$FeO$_4$ and Li$_4$MoS$_2$ due to Li$^+$ intercalation. The reduction peak at 0.40 V corresponds to the conversion of FeO into Fe. The strong reduction peak at 0.28 V is related to the kinetically activated electrolyte degradation as well as the conversion of MoS$_2$ to Mo (accompanied by the formation of a Li$_3$S matrix). In the subsequent cathodic scan, the obvious peak at 0.28 V is negatively shifted to 0.12 V and becomes very small, indicating that the solid-electrolyte interface (SEI) film has been built perfectly. The reduction peak at 0.40 V is positively shifted to 0.69 V due to the structural modification after the 1st cycle. The weak reduction peak at 0.76 V even disappears. Note that during the 2nd cathodic scan, a new reduction peak at 1.44 V arises, which is related to the conversion of S to Li$_2$S. In summary, the reduction peaks at 0.12, 0.69 and 1.44 V can be ascribed to the following three conversion reactions: MoS$_2$ + 4Li$^+$ + 4e$^- \rightarrow$ Mo + 2Li$_2$S, FeO$_2$ + 8Li$^+$ + 8e$^- \rightarrow$ Fe + 4Li$_2$O and 4Li$^+$ + 2S + 4e$^- \rightarrow$ 2Li$_2$S. In the anodic scans, the reversible oxidation peak at 2.41 V corresponds to the conversion of Li$_2$S to Li$_3$S. The broad oxidation peak at 1.54–1.90 V is the overlapping of two peaks that stand for the partial oxidation of Mo to MoS$_2$ and the oxidation of Fe to Fe$_3$O$_4$, respectively. Since the polarisation (1.52 V) between reduction and oxidation of the Mo$^{4+/3+}$ redox couple is much higher than that (0.97 V) of S/S$^2$, the conversion between Li$_2$S and S should be the major reaction mode here. Therefore, the major reaction mechanisms of the 3D MoS$_2@$FeO x nanohybrid are the conversion reactions of 4Li$^+$ + 2S + 4e$^- \rightarrow$ 2Li$_2$S + Mo and FeO$_2$ + 8Li$^+$ + 8e$^- \rightarrow$ 3Fe + 4Li$_2$O. These results are in good agreement with the corresponding charging–discharging curves (Fig. 4b).

To confirm the superiority of the 3D MoS$_2@$FeO x nanohybrid over tubular MoS$_2$ in the lithium storage performances, we compare their cycle behaviours in Fig. 4c. Clearly, tubular MoS$_2$ delivers an initial capacity of 1369 mAh g$^{-1}$, even higher than its theoretical value due to abundant mesopores as well as defect sites (arising from low crystallinity) for lithium storage. However, an obvious capacity decay is witnessed, and the capacity drops to 772 mA h g$^{-1}$ after 100 charging–discharging cycles, accounting for a cycle retention of only 56%. This phenomenon is in consistent with the previous report and is probably due to a certain degree of aggregation originating from strong intertube van der Waals forces. After aggregation, a substantial fraction of active sites are no longer available. To address this inherent deficiency, particulate FeO is hierarchically assembled on tubular MoS$_2$, thus forming the 3D MoS$_2@$FeO x nanohybrid to achieve a synergistic interplay between the two active materials. By this novel hybridisation design, tubular MoS$_2$ serving as a matrix can provide abundant mesopores and hollow interiors to facilitate lithium transport and storage. The introduction of particulate FeO as a spacer can isolate tubular MoS$_2$ from aggregation, thereby increasing the intertube distance for easy lithium access. Moreover, we stress that compared to other spacers, FeO is particularly attractive due to its excellent electrochemical activities. In consequence, the 3D MoS$_2@$FeO x nanohybrid possesses enhanced cyclability, delivering a reversible capacity up to 1113 mAh g$^{-1}$ at the end of 100 charging–discharging cycles which accounts for a cycle retention up to 71%. This value is ~44% higher than the reversible capacity of tubular MoS$_2$.

Furthermore, the 3D MoS$_2@$FeO x nanohybrid also exhibits significantly improved rate capabilities, delivering fairly high reversible capacities of 1183, 1110, 1019 and 910 mA h g$^{-1}$ when cycled at current densities of 100, 200, 500 and 1000 mA g$^{-1}$. At the highest current density of 2000 mA g$^{-1}$, the reversible capacity is still as high as 800 mA h g$^{-1}$. It is worth mentioning that even after deep cycling at 2000 mA g$^{-1}$, the reversible capacity can return to 1101 mA h g$^{-1}$ immediately when the current density is recovered to 100 mA g$^{-1}$, further confirming enhanced cyclability due to the unique structural arrangement between tubular MoS$_2$ and particulate FeO. In contrast, when tubular MoS$_2$ alone is tested under the same current densities, it delivers reversible capacities of 1070, 944, 824, 641 and 484 mA h g$^{-1}$, significantly lower than those of the 3D MoS$_2@$FeO x nanohybrid. The superior cycle and rate performances of the 3D MoS$_2@$FeO x nanohybrid therefore justify an impressive synergistic interplay between tubular MoS$_2$ and particulate FeO. In this sense, our hybridisation design lays a basis for elaborate combination of different active materials into multifunctional nanohybrids with significantly improved lithium storage performances over single-component anode systems.
In conclusion, an impressive synergic interplay between tubular MoS$_2$ and particulate Fe$_3$O$_4$ is created, resulting in a novel 3D MoS$_2$@Fe$_3$O$_4$ nanohybrid. On one hand, tubular MoS$_2$ serving as a matrix can provide abundant mesopores and hollow interiors to facilitate lithium transport and storage and buffer the structural stress during the cycling processes. On the other hand, particulate Fe$_3$O$_4$ acting as a spacer can isolate tubular MoS$_2$ from aggregation, thereby increasing the intertule distance for easy lithium access. The 3D MoS$_2$@Fe$_3$O$_4$ nanohybrid delivers a reversible capacity as high as 1113 mA h g$^{-1}$@100 mA g$^{-1}$, ~44% higher than that of tubular MoS$_2$. This interesting hybridisation design may open the door to a new class of multifunctional nanohybrids as appealing choices of high-performance LIB anodes.

We thank NSFC (21304053) for financial support. X.-D.Z. is grateful to the Natural Science Foundation of Heilongjiang (B2012 02), the Fundamental Research Funds for the Central Universities (HIT.NSRIF.2013.059) and the Postdoctoral Science–Research Development Foundation of Heilongjiang (LBH-Q11130).

Notes and references


