

Cite this: *Nanoscale Adv.*, 2019, 1, 1957

# The rational design of hierarchical MoS<sub>2</sub> nanosheet hollow spheres sandwiched between carbon and TiO<sub>2</sub>@graphite as an improved anode for lithium-ion batteries†

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Molybdenum disulfide (MoS<sub>2</sub>) shows high capacity but suffers from poor rate capability and rapid capacity decay, which greatly limit its practical applications in lithium-ion batteries. Herein, we successfully prepared MoS<sub>2</sub> nanosheet hollow spheres encapsulated into carbon and titanium dioxide@graphite, denoted as TiO<sub>2</sub>@G@MoS<sub>2</sub>@C, via hydrothermal and polymerization approaches. In this hierarchical architecture, the MoS<sub>2</sub> hollow sphere was sandwiched by graphite and an amorphous carbon shell; thus, TiO<sub>2</sub>@G@MoS<sub>2</sub>@C exhibited effectively enhanced electrical conductivity and withstood the volume changes; moreover, the aggregation and diffusion of the MoS<sub>2</sub> nanosheets were restricted; this advanced TiO<sub>2</sub>@G@MoS<sub>2</sub>@C fully combined the advantages of a three-dimensional architecture, hollow structure, carbon coating, and a mechanically robust TiO<sub>2</sub>@graphite support, achieving improved specific capacity and long-term cycling stability. In addition, it exhibited the high reversible specific capacity of 823 mA h g<sup>-1</sup> at the current density of 0.1 A g<sup>-1</sup> after 100 cycles, retaining almost 88% of the initial reversible capacity with the high coulombic efficiency of 99%.

Received 12th January 2019  
Accepted 19th March 2019

DOI: 10.1039/c9na00019d

rsc.li/nanoscale-advances

## Introduction

Lithium-ion batteries (LIBs) have attracted extensive attention as potential power sources for significant application in electric vehicles because of their long cycle life and high power density.<sup>1–3</sup> Currently, graphite is predominantly used as an anode material for commercial LIBs. However, due to the relatively low theoretical capacity of graphite (around 372 mA h g<sup>-1</sup>), the commercial LIBs cannot meet the energy storage requirements for large-scale electric vehicles in the future.<sup>4,5</sup> Thus, it is highly desirable to exploit alternative anode materials with higher capacity and excellent cycling stability. Transition metal oxides and sulfides as promising anode materials have shown striking electrochemical performance in LIBs.<sup>6–8</sup> Among these alternatives, a two-dimensional (2D) layered material, molybdenum disulfide (MoS<sub>2</sub>), has received

significant attention due to its open framework facilitating the insertion of Li<sup>+</sup> reversibly; this leads to high reversible capacity.<sup>9–11</sup> However, bare MoS<sub>2</sub> electrodes exhibit poor rate capability and fast capacity fading caused by low conductivity, huge volume variation and aggregation during cycling.<sup>12–16</sup> In addition to MoS<sub>2</sub>, TiO<sub>2</sub> is considered as one of the most potential alternative anode materials owing to its excellent cycling stability, low cost and environmental friendliness. Several MoS<sub>2</sub>/TiO<sub>2</sub> composites have been reported with improved electrochemical performance owing to their synergistic effects.<sup>17–25</sup> When TiO<sub>2</sub> and MoS<sub>2</sub> are combined in a smart system, TiO<sub>2</sub> with excellent chemical stability and low volume variation (<4%) is obtained,<sup>26</sup> acting as a skeleton to effectively accommodate the strain of volume changes. Moreover, the high capacity of MoS<sub>2</sub> can compensate the low specific capacity of TiO<sub>2</sub>. However, the MoS<sub>2</sub> sheets present on the surface of TiO<sub>2</sub> are still prone to strong restacking, and the intermediate polysulfides dissolve during repeated charge/discharge processes.<sup>27,28</sup> Thus, the rational design of advanced hybrid materials of MoS<sub>2</sub> and other functional components with complementary electrochemical properties is significantly desired to overcome these inherent obstacles.

To date, significant efforts have been made to integrate MoS<sub>2</sub> with carbonaceous materials (such as graphene, carbon nanotubes, amorphous carbon, carbon nanosheets, etc.),<sup>14,29–44</sup> and all these composites exhibit better electrochemical performances as anode materials for LIBs due to the fully synergistic

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c9na00019d



effect of nanostructured MoS<sub>2</sub> and superior conductivity of highly flexible carbon materials. The carbon component could effectively accommodate the strain of volume change during cycling, prevent the aggregation and improve the electric conductivity.<sup>45,46</sup> Despite the abovementioned success, there are still obstacles that hinder the further development of MoS<sub>2</sub> because of the polysulfide shuttling effect causing capacity loss due to the lack of a top conductive protection layer. Therefore, it is highly required to develop an ideal hierarchical architecture with enhanced electrical conductivity and better electrode stability in which the synergistic effects of every component are manifested.

Herein, we designed template-assisted fabrication of hierarchical MoS<sub>2</sub> nanosheet hollow spheres sandwiched between a graphite-coated TiO<sub>2</sub> core and an amorphous carbon shell. Compared with the case of the simple core-shell TiO<sub>2</sub>@MoS<sub>2</sub> nanostructure, the introduction of a graphite inter-layer and a carbon shell has two advantages: on the one hand, graphitic coating the mesoporous TiO<sub>2</sub> hollow spheres provided a rapid pathway for lithium and electron transfer between the abundant interfaces of the sandwich-like MoS<sub>2</sub>/G/TiO<sub>2</sub>, accommodated the volume change and maintained the integrity of the hollow structure; on the other hand, the deposited carbon coating on the surface of the MoS<sub>2</sub> nanosheets could prevent MoS<sub>2</sub> from aggregation and the diffusion of sulfur while improving the electron conductivity and modifying the interface between the electrode/electrolyte. The synergistic effect of these three components and the hierarchical nanostructure endowed the carbon-coated TiO<sub>2</sub>@G@MoS<sub>2</sub> hollow sphere with improved electrochemical properties for application in LIBs.

## Results and discussion

The overall synthesis procedure of the triple-layer TiO<sub>2</sub>@G@MoS<sub>2</sub> hollow nanosphere is illustrated in Fig. 1a, which involves four steps. First, SiO<sub>2</sub> nanospheres were prefabricated as a core template based on the Stöber method.<sup>47</sup> Fig. 1b shows the scanning electron microscopy (SEM) image of the SiO<sub>2</sub> nanosphere with the diameter of *ca.* 290 nm, and the spheres are significantly monodisperse, smooth and uniform. In the

second step, amorphous TiO<sub>2</sub> shells were deposited on the SiO<sub>2</sub> nanospheres *via* a versatile kinetics-controlled coating method. Then, the as-prepared SiO<sub>2</sub>@TiO<sub>2</sub> spheres were placed in a glucose solution and hydrothermally treated. In this step, the surface of the mesoporous TiO<sub>2</sub> network was covered with decomposed glucose. Due to the catalytic effect of TiO<sub>2</sub> nanoparticles, the glucose-coated SiO<sub>2</sub>@TiO<sub>2</sub> spheres were transformed into SiO<sub>2</sub>@TiO<sub>2</sub>@graphitic carbon (SiO<sub>2</sub>@TiO<sub>2</sub>@G) core-shell nanospheres *via* calcination at 800 °C for 5 hours. The SEM images of the SiO<sub>2</sub>@TiO<sub>2</sub>@G samples show larger monodisperse spheres with the uniform diameter of 500 nm (Fig. 1c). The high-magnification SEM image clearly revealed that the surface consisted of primary small nanoparticles. Finally, the vertically oriented MoS<sub>2</sub> nanosheets grew on the surface of SiO<sub>2</sub>@TiO<sub>2</sub>@G by an L-cysteine-assisted hydrothermal method. During the hydrothermal process, the MoO<sub>4</sub><sup>2-</sup> anions were reduced to MoS<sub>2</sub> by S<sup>2-</sup> released from L-cysteine. Moreover, multifunctional groups (SH, NH<sub>2</sub>, and COO) of L-cysteine could guide the self-assembly growth of the MoS<sub>2</sub> nanosheets on the surface of the carbon intermediate layer.<sup>29</sup> The sample was further treated at 500 °C for 2 hours under a vacuum condition to obtain highly crystalline MoS<sub>2</sub>. Fig. 1d shows the typical SEM images of the as-synthesized SiO<sub>2</sub>@TiO<sub>2</sub>@G@MoS<sub>2</sub> nanosphere structures, which indicates that the SiO<sub>2</sub>@TiO<sub>2</sub>@G spheres are uniformly coated with the MoS<sub>2</sub> shell, and the diameter of these multi-layer core-shell spheres increases to *ca.* 600 nm. The high-magnification images revealed that the MoS<sub>2</sub> shell was composed of interconnected vertically oriented ultrathin nanosheets. After the selective removal of SiO<sub>2</sub> template by HF immersion, triple-layer TiO<sub>2</sub>@G@MoS<sub>2</sub> hollow nanospheres were obtained (Fig. 1e).

As shown in Fig. 2a, the interior space is revealed from an incomplete hollow sphere. The FESEM image of partly peeled TiO<sub>2</sub>@G@MoS<sub>2</sub> hollow nanospheres clearly discloses that the hierarchical nanospheres consist of a mesoporous TiO<sub>2</sub> core and a MoS<sub>2</sub> nanosheet shell (Fig. 2b). The detailed core-shell hollow structure was further characterized by a transmission electron microscope (TEM). From a single core-shell nanosphere, it can be observed that the MoS<sub>2</sub> nanosheet shell was uniformly attached to the surface of TiO<sub>2</sub> (Fig. 2c). All the hollow

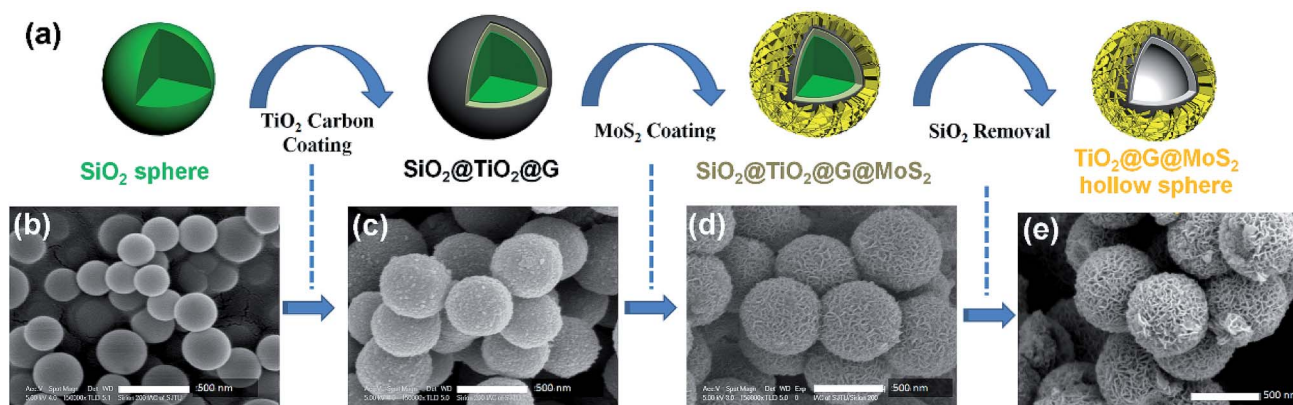


Fig. 1 (a–e) Schematic of the synthesis of hierarchical TiO<sub>2</sub>@G@MoS<sub>2</sub> hollow nanospheres.



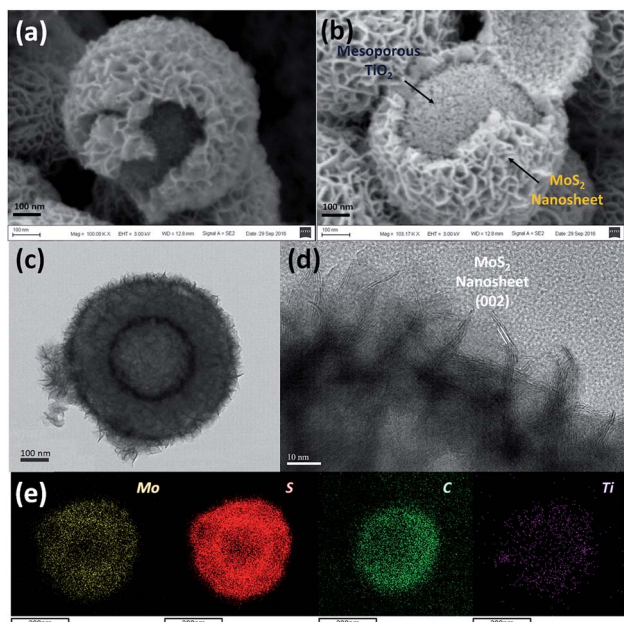


Fig. 2 (a and b) SEM, (c) TEM and (d) HRTEM images of the  $\text{TiO}_2\text{-G@MoS}_2$  hollow nanospheres. (e) EDX-elemental mapping images of Mo, S, C and Ti.

spheres showed the uniform shell thickness of about 150 nm and an inner cavity of  $\sim 300$  nm, which was consistent with the diameter of the  $\text{SiO}_2$  templates. The HRTEM images show the lattice fringes of the  $\text{MoS}_2$  nanosheet structures. The thickness of the nanosheets was about several nanometers. The distance of the parallel lattice planes at the edge of the  $\text{MoS}_2$  nanosheet was about  $6.5 \text{ \AA}$ , which corresponded to the  $d$  spacing of the (002) planes of  $\text{MoS}_2$  (Fig. 2d). To investigate the element distribution of  $\text{MoS}_2$ , carbon and  $\text{TiO}_2$  in the  $\text{TiO}_2\text{-G@MoS}_2$  hollow nanospheres, energy dispersive X-ray (EDX) spectroscopy was carried out (Fig. 2e). The elemental mapping images show that the Mo and S elements formed the shell and the core consisted of C and Ti with smaller diameter. These results directly demonstrated the hierarchical surface modification of the  $\text{MoS}_2$  nanosheet on graphite-coated  $\text{TiO}_2$  hollow spheres.

The XRD patterns (Fig. 3a) were acquired for the  $\text{TiO}_2\text{-G@MoS}_2$  hollow nanospheres to obtain their crystallographic

structure information. The diffraction peaks at  $2\theta = 14.3, 32.5, 36.0$  and  $58.5$  correspond to the (002), (100), (102) and (110) planes of  $2\text{H-MoS}_2$  (JCPDS no. 37-1492).<sup>48</sup> In addition, the characteristic diffraction peaks assigned to (101), (200), (105), (111) and (204) of hexagonal  $\text{TiO}_2$  (JCPDS no. 21-1272) were present. Further insight into the nanostructure of  $\text{TiO}_2\text{-G@MoS}_2$  was achieved by examination of its Raman spectrum (Fig. 3b). The characteristic Raman shifts at about  $377$  and  $400 \text{ cm}^{-1}$  expected for the  $\text{E}_{2g}^1$  and  $\text{A}_{1g}$  vibrational modes of hexagonal  $\text{MoS}_2$  were clearly observed.<sup>49</sup> Moreover, the presence of the  $\text{TiO}_2$  core was confirmed by the Raman peaks emerging at  $150, 282, 333$  and  $639 \text{ cm}^{-1}$ , which corresponded to the vibrational modes of the Ti-O bonds.<sup>50</sup> The bands at  $1357$  and  $1580 \text{ cm}^{-1}$  were the typical D and G lines of graphitic carbon.<sup>51</sup> Note that two strong bands emerging at  $817$  and  $990 \text{ cm}^{-1}$  can be assigned to SiC. In the annealing process, we predicted that the amorphous carbon would evaporate into the mesoporous  $\text{TiO}_2$  shell under a high vacuum condition; this would induce the formation of SiC. The existence of SiC would be beneficial for the improvement of stability because of its high mechanical strength.

X-ray photoelectron spectroscopy (XPS) was employed to characterize the chemical nature and bonding state of the  $\text{TiO}_2\text{-G@MoS}_2$  hollow spheres. Fig. 4a displays the detailed XPS scans of the Mo, S and Ti binding energies. All the spectra were calibrated by a carbon 1s peak located at  $284.50 \text{ eV}$ . Moreover, two peaks at  $229.3$  and  $228.4 \text{ eV}$  were assigned to Mo 3d<sub>5/2</sub> and Mo 3d<sub>3/2</sub>, respectively (Fig. 4b).<sup>33,52,53</sup> Fig. 4c shows the XPS spectrum of the S 2p region. In the high-resolution spectrum of Ti 2p (Fig. 4d), two peaks at  $464.5$  and  $458.8 \text{ eV}$  were attributed to Ti 2p<sub>1/2</sub> and Ti 2p<sub>3/2</sub>, respectively. However, the Ti 2p peaks were relatively weak, indicating the full coverage of the  $\text{MoS}_2$  shell. The XPS results further confirmed the coexistence of  $\text{MoS}_2$  and  $\text{TiO}_2$  in the  $\text{TiO}_2\text{-G@MoS}_2$  hierarchical structure, which agreed well with the XRD and Raman results.

The electrochemical performance of the  $\text{TiO}_2\text{-G@MoS}_2$  hollow structures as lithium-ion battery anodes was examined by assembling them into Li half-cells. Electrodes made up of the pure  $\text{TiO}_2$  hollow spheres and  $\text{MoS}_2$  nanoparticles were also prepared for comparison. Fig. 5a shows the cyclic voltammograms (CVs) of the initial three discharge/charge cycles at the scan rate of  $0.1 \text{ mV s}^{-1}$  within the potential window of  $0.0\text{-}3.0 \text{ V}$  (versus  $\text{Li}^+/\text{Li}$ ). In the first cycle, the two irreversible peaks at

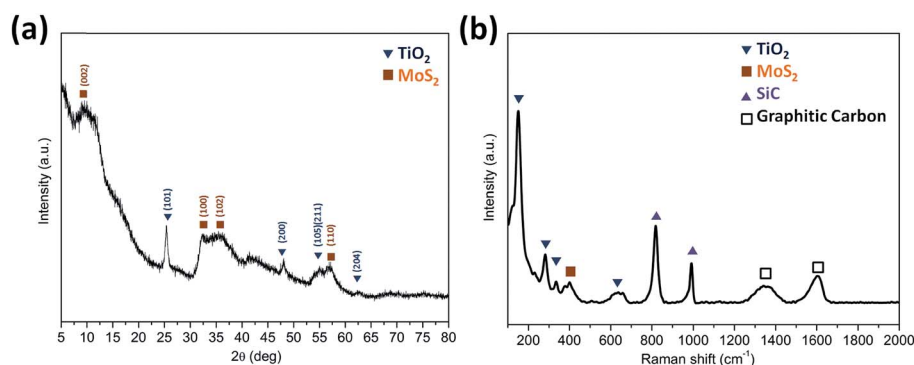


Fig. 3 (a) An XRD pattern and (b) the Raman spectrum of the  $\text{TiO}_2\text{-G@MoS}_2$  hollow nanosphere.



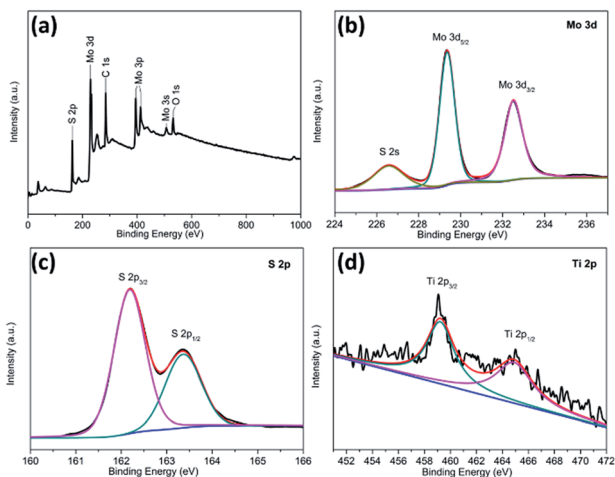
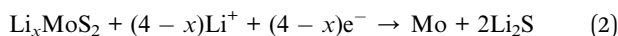


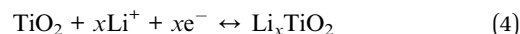
Fig. 4 XPS spectra for the  $\text{TiO}_2@\text{G}@\text{MoS}_2$  hollow nanospheres: (a) the survey spectrum and high-resolution (b) Mo 3d, (c) S 2p, and (d) Ti 2p spectra.

1.127 and 0.473 correspond to the phase transition of  $\text{MoS}_2$ , resulting from the intercalation of  $\text{Li}^+$  ions and the decomposition of  $\text{MoS}_2$  into Mo NPs, respectively.<sup>54–57</sup>



These peaks disappeared in the second and third discharge processes because few amorphous  $\text{MoS}_2$  lattices were reformed

after the first charge process (lithium extraction). After the first cycle, the electrode was mainly composed of Mo and S instead of initial  $\text{MoS}_2$ .<sup>33</sup> In the successive second and third discharge processes, a new broad peak appeared at 1.917 V, corresponding to the presence of a multistep lithium insertion mechanism, which involved the lithiation of  $\text{TiO}_2$  and S to form  $\text{Li}_x\text{TiO}_2$  and  $\text{Li}_2\text{S}$ , respectively.<sup>29,58</sup>



In the charging process, there was an oxidation peak at 2.37 V with few changes in the subsequent sweeps, corresponding to the lithium extraction process.<sup>30,59</sup> Moreover, a broad peak at 1.75 V could be attributed to the partial oxidation of Mo to  $\text{Mo}^{4+}$ .<sup>56</sup> These results illustrate that both  $\text{MoS}_2$  and  $\text{TiO}_2$  made a contribution to the charge–discharge capacity.

Fig. 5b shows the discharge–charge potential profiles of the  $\text{TiO}_2@\text{G}@\text{MoS}_2$  hollow spheres in the 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> cycle at the current density of  $0.1 \text{ A g}^{-1}$  between 0.01 V and 3 V. In agreement with the CV results, two potential plateaus at 1.12 V and 0.47 V were observed in the first discharge process, which respectively corresponded to the phase transition of  $\text{MoS}_2$  and the conversion reaction process. In the subsequent discharge curves, the plateaus obtained in the first discharge disappeared, whereas a new plateau appeared at 1.8 V, which was attributed to a multi-step lithium insertion process. During the charging process, a conspicuous potential plateau at about 2.3 V was observed, which was also in accordance with the CV study.

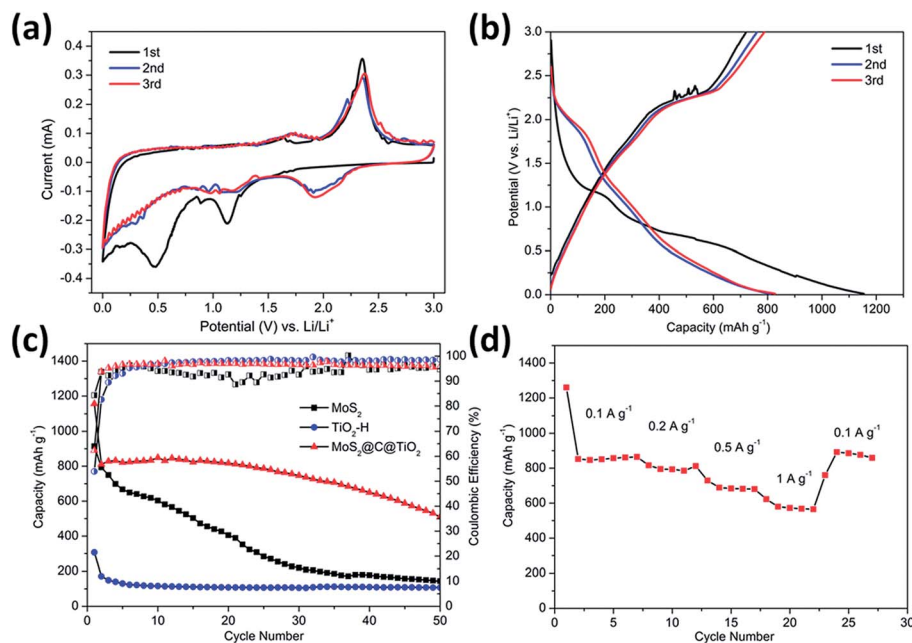


Fig. 5 (a) Cyclic voltammograms of the  $\text{TiO}_2@\text{G}@\text{MoS}_2$  hollow nanospheres at the scan rate of  $0.5 \text{ mV s}^{-1}$  in the voltage range of 0.01–3 V (vs.  $\text{Li}/\text{Li}^+$ ). (b) Charge–discharge voltage profiles at the current density of  $0.1 \text{ A g}^{-1}$  of the  $\text{TiO}_2@\text{G}@\text{MoS}_2$  hollow nanospheres. (c) Comparative cycling performance of the pure  $\text{MoS}_2$  particle,  $\text{TiO}_2$  hollow sphere and  $\text{TiO}_2@\text{G}@\text{MoS}_2$  hollow sphere electrodes, and the corresponding coulombic efficiency. (d) Rate capability of the  $\text{TiO}_2@\text{G}@\text{MoS}_2$  electrode.



The cycling performances of the  $\text{TiO}_2@\text{G}@\text{MoS}_2$  hollow spheres as well as pure  $\text{MoS}_2$  and  $\text{TiO}_2$  hollow spheres were evaluated at the discharge current density of  $0.1 \text{ A g}^{-1}$ , as shown in Fig. 5c.  $\text{MoS}_2$  delivered capacity fading from  $914 \text{ mA h g}^{-1}$  at the initial cycle to  $143 \text{ mA h g}^{-1}$  at the 50<sup>th</sup> cycle during discharge/charge cycles due to aggregation and pulverization. Moreover, the  $\text{TiO}_2$  hollow spheres exhibited excellent cycling stability; however, the capacity was only  $105 \text{ mA h g}^{-1}$  after 50 cycles. The lower charge capacities were mainly attributed to the lower theoretical capacity of  $\text{TiO}_2$ . In contrast, the hierarchical hollow spheres showed significantly enhanced capacity and cycling stability. The initial discharge and charge specific capacities were  $1330$  and  $908 \text{ mA h g}^{-1}$ , respectively, leading to the coulombic efficiency (CE) of 62%, which quickly stabilized at approximately 96% from the second cycle, being close to the coulombic efficiency of the  $\text{TiO}_2$  hollow spheres. Compared to the case of the  $\text{MoS}_2$  particles, the increased coulombic efficiency of the  $\text{TiO}_2@\text{G}@\text{MoS}_2$  spheres was mainly attributed to their hollow structure since the hollow sphere architecture could provide large surface area and shorten the lithium ion diffusion path; moreover, the  $\text{TiO}_2@\text{G}@\text{MoS}_2$  electrodes displayed an extraordinary capacity of  $860 \text{ mA h g}^{-1}$  in the first 20 cycles, which significantly exceeded that of either individual components. We suggest that the high theoretical capacity of the  $\text{MoS}_2$  shell, the superior cycling stability performance of the  $\text{TiO}_2$  hollow core and the excellent electric conductivity of the graphitic carbon interlayer are synergistically combined in the hierarchical  $\text{TiO}_2@\text{G}@\text{MoS}_2$  composite electrode. Fig. 5d shows the rate capacity of triple-layer  $\text{TiO}_2@\text{G}@\text{MoS}_2$  hollow sphere electrode at various current densities ranging from  $0.1$  to  $1 \text{ A g}^{-1}$ . The specific discharge capacities of the composite were about  $860$ ,  $780$ ,  $680$ , and  $570 \text{ mA h g}^{-1}$  upon cycling at  $0.1$ ,  $0.2$ ,  $0.5$ , and  $1 \text{ A g}^{-1}$ , respectively. When back to  $0.1 \text{ A g}^{-1}$ , the capacity returned to  $860 \text{ mA h g}^{-1}$ , indicating good rate performance of the  $\text{TiO}_2@\text{G}@\text{MoS}_2$  composite.

However, upon long-term discharge/charge processes, the cycling performance of the  $\text{TiO}_2@\text{G}@\text{MoS}_2$  electrodes was still poor owing to the aggregation and pulverization of the  $\text{MoS}_2$  nanosheet shell, which contributed to most of the capacity as well as the highly conductive laminated layers to offer high interfacial contact areas and shorten the lithium ion diffusion paths.<sup>60,61</sup> Therefore, the carbon thin shell was chosen as the top conductive protective layer to alleviate the volume changes, prevent the aggregation and pulverization of  $\text{MoS}_2$  and enhance the overall electronic conductivity of the electrode.<sup>62</sup> The resorcinol-formaldehyde resin polymer shell was first deposited on the  $\text{TiO}_2@\text{G}@\text{MoS}_2$  sphere. After carbonization of the polymer shell precursors under an ultrahigh vacuum at  $600 \text{ }^\circ\text{C}$  for 2 hours, the core-shell carbon-coated  $\text{TiO}_2@\text{G}@\text{MoS}_2$  hollow sphere electrode was obtained. It was observed that the nanospheres retained their spherical shape; moreover, after coating, their surface became smooth (instead of showing vertically orientated  $\text{MoS}_2$  nanosheets); this confirmed the uniform carbon coating (Fig. 6a and b). The TEM images demonstrate that the multiple-layer carbon coating  $\text{TiO}_2@\text{G}@\text{MoS}_2$  sphere shows a similar hollow structure as  $\text{TiO}_2@\text{G}@\text{MoS}_2$ , but with a thin carbon shell coated on the surface of

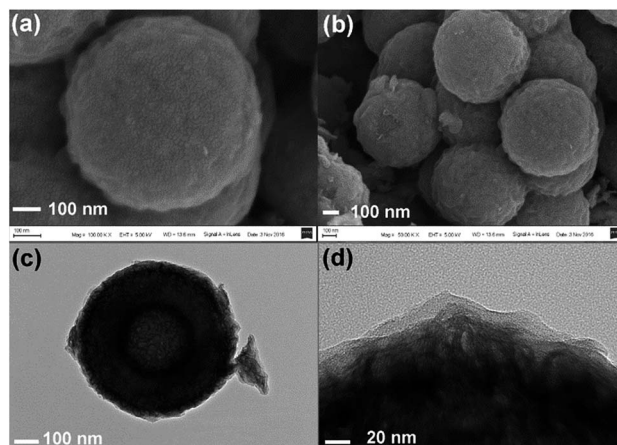


Fig. 6 (a and b) SEM, (c) TEM and (d) HRTEM images of carbon-coated  $\text{TiO}_2@\text{G}@\text{MoS}_2$  hollow nanosphere.

$\text{MoS}_2$  (Fig. 6c). The curved  $\text{MoS}_2$  nanosheets were encapsulated into an amorphous carbon layer with a thickness of  $20 \text{ nm}$  (Fig. 6d). To determine the pore structure and surface area of the as-prepared  $\text{TiO}_2@\text{G}@\text{MoS}_2@\text{C}$ , the  $\text{N}_2$  adsorption/desorption test was conducted, as shown in Fig. S1.† The specific surface area was about  $15.179 \text{ m}^2 \text{ g}^{-1}$ , and the main pore size was about  $3.063 \text{ nm}$  in diameter. To verify the content of the prepared sample, ICP-AES was used to determine the contents of Mo and Ti. The Mo and Ti contents in  $\text{TiO}_2@\text{G}@\text{MoS}_2@\text{C}$  were found to be 29.66% and 0.43%, respectively. The  $\text{MoS}_2$  and  $\text{TiO}_2$  contents were calculated to be 49.5% and 0.72%, respectively. The sulfur and carbon contents were analyzed by TGA. As shown in Fig. S2,† the weight loss occurring between  $298$  and  $451 \text{ }^\circ\text{C}$  was mainly due to the oxidation of  $\text{MoS}_2$  to  $\text{MoO}_3$  and the removal of carbon. The remaining product after  $500 \text{ }^\circ\text{C}$  was pure  $\text{MoO}_3$  with the weight percentage of 46.7%. The content of  $\text{MoS}_2$  was calculated to be 51.9%, which was approximately consistent with the ICP-AES result.

Fig. 7a shows the CV curves of carbon-coated  $\text{TiO}_2@\text{G}@\text{MoS}_2$  electrode compared with those of the uncoated sample. The carbon-coated core-shell  $\text{TiO}_2@\text{G}@\text{MoS}_2$  electrode had a lower anodic peak potential ( $2.31 \text{ V}$ ) and a higher cathodic peak potential ( $0.56 \text{ V}$ ), suggesting its better electrochemical reactivity and reversibility. The charge-discharge voltage profiles were obtained at the current density of  $0.1 \text{ A g}^{-1}$ , indicating the initial discharge and charge capacities of  $1208$  and  $933 \text{ mA h g}^{-1}$ , respectively, and the coulombic efficiency of 76.6% (Fig. 7b).

Fig. 7c shows the cycling performance of the carbon-coated  $\text{TiO}_2@\text{G}@\text{MoS}_2$  hollow spheres at the current density of  $0.1 \text{ A g}^{-1}$  between  $0.01$  and  $3.0 \text{ V}$ . It exhibits enhanced capacity retention stability and high reversible capacity of  $823 \text{ mA h g}^{-1}$  even after 100 cycles, which is 88% of the capacity retention of the initial charge capacity. Moreover, the coulombic efficiency quickly stabilized at around 99% from the 4<sup>th</sup> cycle and was maintained in the following cycles. Compared to other  $\text{TiO}_2/\text{MoS}_2$  composites, the carbon-coated  $\text{TiO}_2@\text{G}@\text{MoS}_2$  hollow spheres showed higher electrochemical energy storage



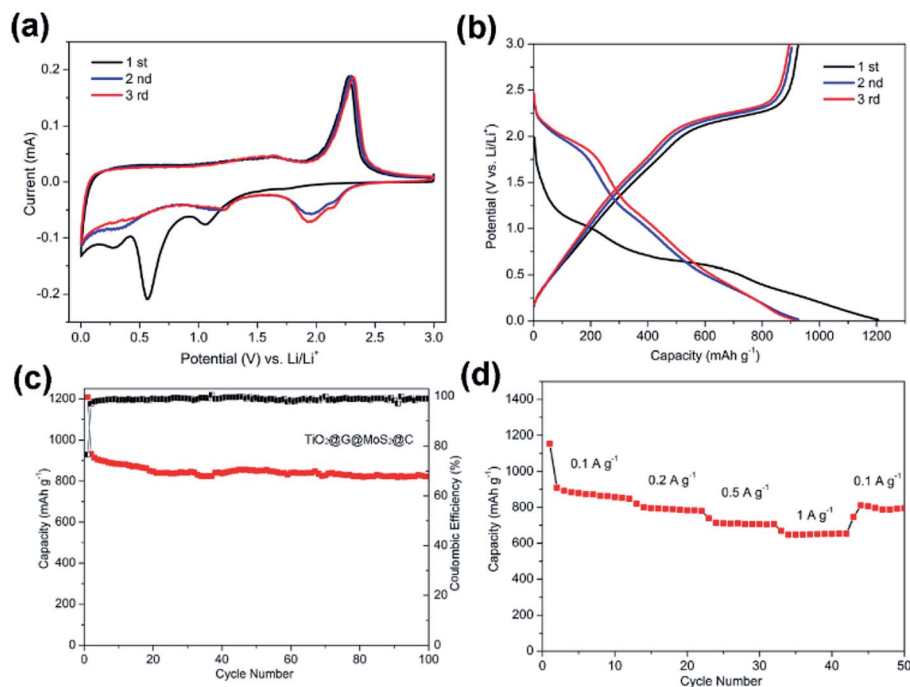


Fig. 7 (a) Cyclic voltammograms of the  $\text{TiO}_2@\text{G}@\text{MoS}_2@\text{C}$  hollow nanospheres at the scan rate of  $0.5 \text{ mV s}^{-1}$  in the voltage range of  $0.01\text{--}3 \text{ V}$  (vs.  $\text{Li}/\text{Li}^+$ ). (b) Charge–discharge voltage profiles at the 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> cycle at the current density of  $0.1 \text{ A g}^{-1}$  of the  $\text{TiO}_2@\text{G}@\text{MoS}_2@\text{C}$  hollow nanospheres. (c) Cycling performance of  $\text{TiO}_2@\text{G}@\text{MoS}_2@\text{C}$  hollow sphere electrodes, and corresponding coulombic efficiency. (d) Rate capability of the  $\text{TiO}_2@\text{G}@\text{MoS}_2@\text{C}$  electrode.

performances,<sup>17–25</sup> especially high reversible capacity, which was attributed to the synergistic effects of all the components. The rate performance test was carried out for the carbon-coated  $\text{TiO}_2@\text{G}@\text{MoS}_2$  hollow spheres to investigate their stability. The specific capacities of the composite were 850, 783, 700 and  $650 \text{ mA h g}^{-1}$  upon cycling at 0.1, 0.2, 0.5 and  $1 \text{ A g}^{-1}$ , respectively. When the current density was reset to  $0.1 \text{ A g}^{-1}$ , the capacity could still return to  $850 \text{ mA h g}^{-1}$ ; this confirmed the outstanding rate capability. We carried out the SEM and TEM characterization for the as-prepared electrodes of  $\text{TiO}_2@\text{G}@\text{MoS}_2@\text{C}$  and  $\text{TiO}_2@\text{G}@\text{MoS}_2$  hollow spheres after cycling. As shown in Fig. S3,† the SEI films of the  $\text{TiO}_2@\text{G}@\text{MoS}_2$  electrode were clearly thicker than those of the carbon-coated electrode (Fig. S3c and d†). Fig. S4† exhibits the TEM image of the as-prepared electrodes; the carbon hollow nanostructure was well preserved after 50 cycles, whereas the  $\text{MoS}_2$  particle was not observed on the carbon sphere surface for the  $\text{TiO}_2@\text{G}@\text{MoS}_2$  hollow spheres sample; this was due to the detachment and diffusion of  $\text{MoS}_2$ . Fig. S4c and d† show the TEM images of  $\text{TiO}_2@\text{G}@\text{MoS}_2@\text{C}$ , in which the hollow structure is well maintained, and the  $\text{MoS}_2$  particles distributed in the carbon coating shells can be still seen; this indicates the superior structural stability of  $\text{TiO}_2@\text{G}@\text{MoS}_2@\text{C}$  during long-term cycling.

The excellent cycling stability and remarkable rate capability of the hierarchical multiple-layer carbon-coated  $\text{TiO}_2@\text{G}@\text{MoS}_2$  hollow spheres could be attributed to their unique structural advantages and synergistic effect. First, the graphitic carbon-coated mesoporous  $\text{TiO}_2$  hollow structure could

effectively buffer the mechanical strain accompanying the lithium intercalation/exfoliation, alleviate huge volume variation of  $\text{MoS}_2$ , and enhance the internal electronic conductivity of the hierarchical electrode.<sup>63</sup> Second, the vertically oriented  $\text{MoS}_2$  laminated layers with high surface area provided a large electrode/electrolyte interface and shortened the diffusion paths for  $\text{Li}^+$  ions, thus improving the dynamic performance of  $\text{Li}^+$  storage.<sup>64,65</sup> Third, the carbon-coated top layer prevented  $\text{MoS}_2$  from aggregation and pulverization, enhancing the electronic conductivity and contributing to the obvious improvement of long-term cycling stability.<sup>66,67</sup> Based on the synergistic effect of all the aforementioned merits, the rationally designed carbon-coated  $\text{TiO}_2@\text{G}@\text{MoS}_2$  core-shell hollow sphere exhibited remarkable electrochemical performance for lithium-ion storage.

## Experimental

### Synthesis of carbon-coated $\text{TiO}_2@\text{G}@\text{MoS}_2$ hollow nanospheres

Colloidal  $\text{SiO}_2$  nanospheres with a uniform diameter of 300 nm were fabricated by the Stöber method. For  $\text{TiO}_2$  coating, 0.2 g of the as-obtained  $\text{SiO}_2$  nanospheres was homogeneously dispersed in ethanol (150 mL). After this, ammonia solution (0.7 mL) was added to the suspension, and the mixture was stirred by a magnetic bar for 1 h. Then, tetrabutoxide titanate (TBOT, 2.0 mL) was added, and the reaction was proceeded at  $45 \text{ }^\circ\text{C}$  for 24 h under continuous stirring. To produce the graphitic carbon-coated  $\text{SiO}_2@\text{TiO}_2$  spheres, the  $\text{SiO}_2@\text{TiO}_2$  core-shell



structured spheres were homogeneously dispersed in a glucose solution (0.1 M, 15 mL) and hydrothermally treated at 180 °C for 2 h; this yielded the SiO<sub>2</sub>@TiO<sub>2</sub>@C spheres. Then, the amorphous TiO<sub>2</sub>/C shells could be converted to crystalline TiO<sub>2</sub>/graphitic carbon hybrid structures after annealing at 800 °C.

To grow the hierarchical MoS<sub>2</sub> shell on the graphitic carbon intermediate layer, 0.2 g of SiO<sub>2</sub>@TiO<sub>2</sub>@G sphere templates were dispersed in 60 mL of de-ionized water and 20 mL ethanol solution. Then, 0.6 g of sodium molybdate (Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O) and 2.5 g of L-cysteine were added to the abovementioned solution. After ultrasonication, the reaction solution was then transferred to a Teflon-lined stainless steel autoclave and hydrothermally treated at 180 °C for 24 h. After etching of SiO<sub>2</sub> by a 5% HF solution, 0.08 g of the as-obtained hollow nanospheres were dispersed in 2.82 mL of ethanol and 7.04 mL of deionized water, followed by the addition of 0.23 g cetyltrimethylammonium bromide (CTAB), 0.035 g resorcinol and 0.01 mL ammonia. After stirring at 35 °C for 30 min, 0.05 mL formalin was added to the dispersion. Then, the reaction was proceeded at 35 °C for 6 h under continuous stirring. The obtained polymer-coated TiO<sub>2</sub>@G@MoS<sub>2</sub> was annealed at 600 °C for 2 h under a high vacuum atmosphere, and then, the carbon-coated TiO<sub>2</sub>@G@MoS<sub>2</sub> hollow nanospheres were obtained.

### Material characterization

The morphology information was determined by the FEI Sirion 200 scanning electron microscope (SEM) and the JEOL 2100F transmission electron microscope (TEM). Samples were characterized by X-ray diffraction (XRD, Rigaku Ultima IV X-ray Diffractometer) equipped with Cu K $\alpha$  radiation. Surface composition of the sample was analyzed by X-ray photoelectron spectroscopy (XPS, AXIS ULTRA DLD, Kratos, Japan). Raman spectroscopy was conducted using the Renishaw inVia-reflex system at room temperature. A laser with the wavelength of 532 nm was used as the excitation source. Inductively coupled plasma-atomic emission spectrometry (ICP-AES, Thermo, iCAP7600) was used for detecting the concentrations of Mo and Ti ions. Thermogravimetric analysis (TGA) was carried out using a thermogravimetric analysis instrument (TGA, SDT Q600 V8.2 Build 100).

### Electrochemical measurements

The electrochemical tests were carried out in coin cells. The working electrode consisted of 80 wt% of active material, 10 wt% of conductive carbon black, and 10 wt% of polymer binder (polyvinylidene fluoride, PVDF). The electrolyte was 1 M LiPF<sub>6</sub> in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) (1 : 1 : 1 by volume). The typical mass loading of the active materials was about 1 mg cm<sup>-2</sup>. Lithium disc was used as both the counter electrode and the reference electrode. Cell assembly was carried out in an Ar-filled glove box with moisture and oxygen concentrations below 1.0 ppm. The charge–discharge tests were performed using the Land CT2001A battery test system. Cyclic voltammograms (CVs) were obtained using the CHI 660D electrochemical workstation.

## Conclusions

In summary, a hybrid architecture of carbon-coated TiO<sub>2</sub>@G@MoS<sub>2</sub> has been successfully synthesized. The hierarchical MoS<sub>2</sub> hollow spheres with high theoretical capacity were sandwiched by graphite and microporous carbon. The role of the carbon layer in the electrochemical energy storage performance was systematically investigated, and the key factors that controlled the capacity and cycling stability were identified. Due to the unique hierarchical core–shell nanostructure and the synergistic effect of every component, the rationally designed carbon-coated TiO<sub>2</sub>@G@MoS<sub>2</sub> hollow sphere electrode exhibited high charge capacity and the cycling stability of 823 mA h g<sup>-1</sup> at the current density of 100 mA g<sup>-1</sup> after 100 cycles, retaining almost 88% of the initial reversible capacity with the high coulombic efficiency of 99%. Our study suggests a new mean for the synthesis of high-performance core/shell structure electrodes by the introduction of a carbon shell or interlayer for energy storage, which is expected to be widely extended to metal oxides or metal sulfides.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work was supported by the Natural Science Foundation of China (Grant no. 11174197 and 11574203).

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