Carbon-Coated Mesoporous TiO$_2$ Nanocrystals Grown on Graphene for Lithium-Ion Batteries

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Supporting Information

ABSTRACT: Graphene-based hybrids have been well studied as advanced catalysts and high-performance electrode materials. In this Article, we have fabricated a novel graphene@mesoporous TiO$_2$ nanocrystals@carbon nanosheet by a simple one-step solvothermal method. We have found that titanocene dichloride can act as an extraordinary source with multiple roles for forming TiO$_2$ nanocrystals, ultrathin carbon outer shells, and cross-linkers to binding TiO$_2$ nanocrystals on graphene surface. Moreover, it also serves as a controlling agent to produce mesoporous structure on TiO$_2$ nanocrystals. The loading-concentration of mesoporous TiO$_2$ nanocrystals on graphene sheets can be well controlled by adjusting the initial content of titanocene dichloride. The as-obtained graphene@mTiO$_2$@carbon nanosheets possess a uniform sandwich-like structure, highly crystalline mesoporous TiO$_2$ nanocrystals, a high surface area of $\sim$209 m$^2$/g, and a large pore volume of $\sim$0.68 cm$^3$/g. When used as anodes for LIBs, the resultant nanosheets show a high reversible capacity ($\sim$145 mAh/g), good rate capability, and long cycling life (capacity remains 110 mAh/g after 100 cycles at a current density of 0.2 A/g). We believe that our method represents a new path way to synthesize novel nanostructured graphene-based hybrids for future applications.

KEYWORDS: mesoporous, TiO$_2$ nanocrystals, graphene, carbon, lithium-ion batteries

1. INTRODUCTION

Graphene, a single layer of honeycomb-like network of carbon atoms, has exceptionally electrical, thermal, mechanical, and optical surface properties and is thought to be one of most promising and striking materials in the 21st century.1,2 Especially, it has been used as an ideal substrate for fabricating a large number of functional nanohybrids.3–8 To date, various metal oxides nanoparticles, such as Co$_3$O$_4$,9,10 SnO$_2$,11–13 FeO$_x$,14–18 TiO$_2$,19–26 and MnO$_x$,27,28 have been integrated with graphene to overcome their intrinsic shortcomings such as low electrical conductivity, low surface area, and large structural change associated with their applications. As a result, these graphene-based hybrids show improved performances in numerous promising areas including sensor, photocatalysis, solar energy conversion, capacitor, lithium ion batteries (LIBs), and so on.

Several methods have been developed to fabricate graphene-based hybrid materials such as two-step solution process, gas-phase synthesis pathway, and sol–gel method.29–32 However, a big challenge is the weak interaction between nanoparticles and graphene during the synthetic process, which may hinder the transfer of electrons and Li ions between them, thus impeding applications in catalysis and energy storage.33,34 Recently, TiO$_2$ nanomaterials have attracted extensive research interests because of their unique properties and wide applications in catalysis and energy storage.35–38 It has been found that additives like glucose and polyaniline can be used as the linker and/or face-controlling agent to achieve in situ growth of ultradispersed TiO$_2$ nanocrystals on the surface of graphene aerogels, but the loading-concentration of TiO$_2$ nanoparticles is low and cannot be controllable.39,40 Moreover, during multiple-cycle lithium insertion/extraction processes, TiO$_2$ nanoparticles would fall off from graphene surface. Recently, a carbon outer shell has been shown to be a valuable protocol to solve the problem; however, it requires additional synthetic processes for coating.41–46 Therefore, it is still a great challenge and highly desired to accomplish in situ one-pot growth of carbon-coated TiO$_2$ nanocrystals on graphene with strong binding interactions and controllable loading-concentrations.

Herein, we develop a simple one-step solvothermal method for controllable synthesis of graphene@mesoporous TiO$_2$ nanocrystals@carbon nanosheets (denoted as graphene@
mTiO2@carbon). In this case, GO was first prepared by a modified Hummers method.47 Titanocene dichloride acts not only as titanium source but also as a carbon precursor for ultrathin carbon outer shells and a cross-linker to binding TiO2 nanocrystals on graphene surface. Moreover, it also serves as a controlling agent to produce mesopores on TiO2 nanocrystals. The loading-concentration of mesoporous TiO2 nanocrystals on graphene sheets can be well controlled by tuning the initial content of titanocene dichloride. The resultant graphene@mTiO2@carbon nanosheets possess a uniform sandwich-like structure, highly crystalline mesoporous TiO2 nanocrystals, a high surface area of ∼209 m2/g, and a large pore volume of ∼0.68 cm3 g−1. When used as anodes for LIBs, the as-obtained nanosheets show a high reversible capacity, good rate capability, and excellent cycling stability.

2. RESULTS AND DISCUSSION

Characterizations of Graphene@mTiO2@carbon Nanosheets. The formation process of the graphene@mTiO2@carbon nanosheets is illustrated in Scheme 1.18 Detailed experimental steps are described in the Supporting Information. A field emission scanning electron microscopy (FESEM) image of the graphene@mTiO2@carbon nanosheets (Figure 1a, Supporting Information Figure S1) shows that the product is composed of many free-standing and ultrathin sheets with morphology similar to that of initial GO sheets with no naked graphene sheets or free TiO2 nanoparticles, suggesting the uniform TiO2 nanocrystals deposited on graphene sheets. The magnified FESEM images (Figure 1b and Supporting Information Figure S2) clearly disclose a rough surface of the graphene@mTiO2@carbon nanosheets, which results from the loosely packed TiO2 nanocrystals. The magnified FESEM image of nanosheet cross sections (Figure 1c) shows the uniform loading of carbon-coated mesoporous TiO2 nanocrystals on both sides of graphene sheets. TEM images of the nanosheets (Figure 1d) notably show the typical single or overlapping sheetlike morphology but uniformly loading plenty of small nanoparticles, which is consistent with the FESEM results. Figure 1e shows that a large number of TiO2 nanocrystals are densely packed on graphene sheets (Supporting Information Figure S3). The selected area electron diffraction (SAED) pattern (Figure 1e, inset) obviously presents well-resolved diffraction rings, which can be well indexed as the planes of anatase TiO2, indicating the existence of TiO2 nanoparticles on graphene sheets.48 X-ray spectroscopy (EDS) analysis (Supporting Information Figure S4) further confirms the presence of C, Ti, and O elements in the graphene@mTiO2@carbon nanosheets, while the Cu peak originates from the copper grid supporting the sample. HRTEM images (Figure 1f, Supporting Information Figure S5) show that TiO2 nanoparticles are highly crystalline with well-defined crystalline lattices (a d spacing of 0.35 nm corresponding to the (101) plane of anatase TiO2) and an average size of ∼9 nm on graphene sheets. Additionally, TiO2 nanoparticles are uniformly coated by ultrathin carbon layers. More importantly, one can clearly see mesopores centered in TiO2 nanoparticles (the light-colored part in the center of TiO2).

The uniformly dispersed TiO2 nanoparticles on graphene sheets are further elucidated by the scanning TEM (STEM) image and the corresponding element mapping images (Figure 2) of C, Ti, and O in the graphene@mTiO2@carbon nanosheets. Atomic force microscopy (AFM) analyses (Figure 3) further confirm the 2D features of graphene@mTiO2@carbon nanosheets with a thickness of ∼50 nm and a rough surface, which is well consistent with the FESEM and TEM results. As the thickness of the nanosheets is much thicker than the size of TiO2 nanoparticles, we can confirm that TiO2 nanoparticles form a multilayered nanostructure on graphene sheets. XPS spectra confirm that simple pyrolysis of GO sheets in our approach can effectively reduce graphene oxide to graphene (Supporting Information Figure S6).

In the absence of GO sheets, mesoporous TiO2@carbon nanoparticles can be obtained. Transmission electron micros-
reveal the resultant graphene@mTiO2@carbon nanoparticles is calculated to be ~69 and 73 wt %, respectively. Assuming the consistent transformation of titanocene dichloride into TiO2 and carbon, the weight fraction of graphene in the resultant graphene@mTiO2@carbon nanosheets is possibly estimated to be ~6 wt %.

The pore structures of the resultant graphene@mTiO2@carbon nanosheets and mTiO2@carbon nanoparticles were studied by measuring N2 adsorption/desorption isotherms at 77 K. The BET surface area and pore volume of graphene@mTiO2@carbon nanosheets are calculated to be 209 m2 g⁻¹ and 0.68 cm³ g⁻¹, higher than that of mTiO2@carbon nanoparticles (181 m2 g⁻¹, 0.19 cm³ g⁻¹) (Figure 4c), respectively. The corresponding size distribution curves of graphene@mTiO2@carbon nanosheets and mTiO2@carbon nanoparticles are shown in Figure 4d. The pore size of the nanosheets is mainly 11.3 nm with a wide distribution, which may be originated from the aggregation of TiO2 nanocrystals on graphene and nanosheet itself, respectively. In contrast, mTiO2@carbon nanoparticles have a relatively narrow pore size of ~7.5 nm.

The influence of the initial titanocene dichloride concentration on the resultant structures of nanosheets was investigated. At a low dosage, aggregated TiO2 nanoparticles are uniformly dispersed on GO sheets (Supporting Information Figure S8a, b). The HRTEM image (Supporting Information Figure S8c) shows that the edge of GO sheets (~2 layers) can be clearly observed, and the TiO2 nanocrystals (~9 nm) are mesoporous structure and highly crystalline. Additionally, an ultrathin carbon layer is formed on the surface of TiO2 nanocrystals. With the rise of titanocene dichloride dosage (0.1 g), the density of TiO2 nanoparticles loaded on GO sheets is obviously increased (Supporting Information Figure S8d–f), but the particle size of TiO2 nanocrystals is still ~9 nm. When the dosage of titanocene dichloride is higher than 0.3 g, graphene@mTiO2@carbon nanosheets would be obtained; however, mTiO2@carbon nanoparticles are concurrently formed and aggregated (Supporting Information Figure S8g, h) due to the excess of titanocene dichloride compared with graphene backbones. These results can also be confirmed by the corresponding FESEM results (Supporting Information Figure S9). Therefore, by rationally controlling the concentration of initial titanocene dichloride, uniform graphene@mTiO2@carbon nanosheets could be obtained, and the density of TiO2 nanoparticles can be facilely tuned.

**Electrochemical Performances.** The electrochemical performance of graphene@mTiO2@carbon nanosheets and mTiO2@carbon nanoparticles as anode materials for LIBs were evaluated by galvanostatic charge/discharge measurements. Figure 5a shows voltage profiles at the first cycle and the second cyclic performances at a current density of 0.2 A g⁻¹ in a voltage window of 1.0–3.0 V, which clearly exhibits two distinct domains. The horizontal discharge plateau is at 1.74 V, and the horizontal charge plateau is at 1.95 V, which are characteristic of intercalation and deintercalation between TiO2 nanoparticles and Li₂TiO₃. An obvious slope below 1.7 V is also observed which is characteristic of capacitive behavior and results from the improved storage of lithium ions owing to mesoporous structures of TiO2, and the multileveled packed porous structure of nanosheets. As a result, a high capacity of 195 mAh g⁻¹ can be delivered in the first discharge with a corresponding charge capacity of 145 mAh g⁻¹. In a control experiment, mTiO2@carbon nanoparticles have a lower capacity of ~178 mAh g⁻¹ in the first discharge with a
corresponding charge capacity of 76 mAh g$^{-1}$ (Figure 5b). The fast capacity decays of both the graphene@mTiO$_2$@carbon nanosheet and mTiO$_2$@carbon nanoparticle electrodes in the first cycle may be attributed to irreversible reactions with the electrolyte and/or the formation of a solid electrolyte interphase (SEI) layer$^{52,53}$. Figure 5c displays the comparison of cycling performance of the nanosheets at current rates of 0.2 and 2 A g$^{-1}$ in the voltage range of 1.0–3.0 V (vs Li$^+$/Li) up to 100 cycles. Also, it shows a good cyclic retention of 100 cycles at each current rate and a Coulombic efficiency approaching almost 100% (Supporting Information Figure S10). To investigate the rate capability, the graphene@mTiO$_2$@carbon nanosheets and mTiO$_2$@carbon nanoparticles were discharged and charged at various current rates from 0.2 to 10 A g$^{-1}$ as shown in Figure 5d. Clearly, graphene@mTiO$_2$@carbon nanosheets show better cyclic capacity retention at each
current density than that of mTiO2@C nanoparticles, which degrade very quickly due to the low content of conductivity agent (carbon black, Super P, 5%). The Nyquist plots show that the charge transfer resistance ($R_{ct}$) of the graphene@mTiO2@carbon nanosheet electrode is much smaller than that of the mTiO2@carbon nanoparticle electrode (Supporting Information Figure S11). It suggests that the highly conductive graphene and carbon shell could greatly facilitate the charge carrier transfer from TiO2 nanocrystals to the current collector. It clearly indicates the advantage of such unique nanostructures of nanosheets as anodes for LIBs. Additionally, after the high-current density cyclic, the capacity of graphene@mTiO2@carbon nanosheets at 0.2 A g$^{-1}$ can recover to the initial capacity which indicates its high reversibility. The good electrochemical performances of the graphene@mTiO2@carbon nanosheets may be attributed to synergistic effects in the nanosheets (Supporting Information Figure S12): (1) The ultrathin carbon shell can greatly enhance the internal electrical conductivity and suppress the aggregation of TiO2 nanocrystals, which thus eventually ensure the stability of the graphene@mTiO2@carbon nanosheet electrode. (2) The small size of primary mesoporous TiO2 nanocrystal can greatly increase the lithium storage capacity and lithium solid solubility. (3) The graphene nanosheets serve as the conductive medium between the TiO2 nanocrystals and current collector. As a result, the electrons could be effectively and rapidly conducted back and forth from the TiO2 nanocrystals to the current collector through the highly conductive graphene nanosheets with the assistant of carbon shell, resulting in good rate capability. (4) The relatively large interface area not only provides more Li$^+$ insertion/extraction sites but also facilitates fast Li$^+$ ion transfer between electrode and electrolyte, thus leading to a large reversible specific capacity of the nanosheet electrode.

3. CONCLUSION

In conclusion, we report a one-step solvothermal method for synthesis of graphene@mTiO2@carbon nanosheets. Titancene dichloride is used as Ti, C source, and the cross-linker to achieve in situ growth of carbon-coated mesoporous TiO2 nanocrystals on graphene sheets. The as-obtained graphene@mTiO2@carbon nanosheets possess high surface area (~209 m$^2$/g) and large pore volume (~0.68 cm$^3$/g). The loading-density of TiO2 nanoparticles dispersed on graphene sheets can be facilely controlled by adjusting the concentration of titancene dichloride. The resultant graphene@mTiO2@carbon nanosheets show a high reverse capacity (145 mAh/g), good cycling stability (capacity remains 110 mAh/g after 100 cycles at a current density of 0.2 A/g), and excellent rate performances. This synthetic route describes the blueprint of in situ growth of metal oxide/carbon hybrid materials to extend their functions and achieve specific applications in lithium-ion batteries, sensor, and photocatalysis.

ASSOCIATED CONTENT

Supporting Information
Experimental details, FESEM and TEM images; EDX spectra; Coulombic efficiency. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b01450.

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Notes
The authors declare no competing financial interest.

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REFERENCES


