

which is more than double the high rate capacity (35 mAh/g) of the control rutile TiO₂ as shown in FIG. 7b.

The voltage-capacity profile of anatase TiO₂-FGS (2.5 wt % FGS) at C/5 rate shows plateaus around 1.8 V (discharge process) and 1.9 V (charge process) is shown in FIG. 7d, which is similar to that of control anatase TiO₂ and nanostructured anatase. The plateaus are related to the phase transition between the tetragonal and orthorhombic phases with Li insertion into anatase TiO₂. Similar to rutile TiO₂-FGS, the specific capacity of the anatase TiO₂-FGS hybrid is enhanced at all charge-discharge rates as shown in FIG. 7e. The specific capacity of the anatase TiO₂-FGS at the rate of 30 C is as high as 96 mAh/g compared with 25 mAh/g of control anatase TiO₂. Furthermore, the coulombic efficiencies of TiO₂-FGS hybrids at various charge/discharge rates are greater than 98% as shown in FIG. 8. Both rutile and anatase TiO₂-FGS hybrids show good capacity retention of the Li-ion insertion/extraction with over 90% capacity retention after 100 cycles at a 1 C rate, as shown in FIGS. 7c and 7f.

To identify the capacity contribution from FGSs, the Li-ion insertion/extraction behavior of the FGSs was also studied. The initial capacity of FGS of 100 mAh/g with 50% irreversible loss is observed between 1-3 V potential window applied, which is consistent with a recent study of Li-ion storage in graphene described in Yoo, E.; Kim, J.; Hosono, E.; Zhou, H.-s.; Kudo, T.; Honma, I. Large Reversible Li Storage of Graphene Nanosheet Families for Use in Rechargeable Lithium Ion Batteries. *Nano Lett.* 2008, 8, 2277-2282. However, the specific capacity of FGS rapidly decreases to 25 mAh/g within 10 cycles. At higher charge/discharge rates, FGS has almost negligible Li-ion insertion as shown in FIG. 9. For 1 wt % FGS hybrids, the capacity contribution from FGS itself after 2 cycles can be a maximum value of 0.4 mAh/g. Thus, the increase of the specific capacity at high rate is not attributed to the capacity of the graphene additive itself in the hybrid materials.

To further understand the improved high-rate performance, electrochemical impedance spectroscopy measurements on rutile TiO₂-FGS hybrid materials were performed after cycles. The Nyquist plots of the rutile TiO₂-FGS electrode materials with different percentage of graphene cycled in electrolyte, as shown in FIG. 10(a), all show depressed semicircles at high frequencies. As electrolyte and electrode fabrication are similar between each electrode, the high frequency semicircle should relate to the internal resistance of the electrode. We estimate that the resistivity of the cells decreased from 93Ω for the pure TiO₂ to 73 Ω with the addition of only 0.5 wt % graphene.

By increasing the graphene percentage in the hybrid materials further, the specific capacity is slightly increased, e.g., to 93 mAh/g in the hybrid material with 5 wt % FGS, indicating that a kinetic capacity limitation may be reached by only improving the electrode conductivity with the incorporation of FGSs as shown in FIG. 10(b). Rutile TiO₂-CNT hybrids prepared and tested under similar conditions showed poorer performance at identical carbon loadings than the rutile TiO₂-FGS hybrid anodes, as shown in the yellow bar in FIG. 10(b). Similarly, hybrid nanostructures prepared using solution reduced graphene oxides also showed even poorer performance, indicating the importance of the highly conductive graphene phase of FGSs.

To study the properties of electrode materials without any Super P carbon, Li-ion insertion/extraction properties of the rutile TiO₂-FGS (10 wt % graphene) were compared with control rutile TiO₂ with 10 wt % Super P at high charge-discharge rates. The hybrid material showed a much higher capacity at all charge-discharge rate, as shown in FIG. 11.

This result indeed confirms that the graphene in the self-assembled hybrid materials is more effective than the commonly used Super P carbon materials in improving high rate performance of the electrode materials.

The high rate performance is important for applications where fast charge and discharge is needed, such as in load leveling utility applications. The simple self-assembly approach, and the potential low manufacturing cost of graphene of the present invention, thus provide a new pathway for large scale applications of novel hybrid nanocomposite materials for energy storage.

While the invention has been illustrated and described in detail in the drawings and foregoing description, the same is to be considered as illustrative and not restrictive in character. Only certain embodiments have been shown and described, and all changes, equivalents, and modifications that come within the spirit of the invention described herein are desired to be protected. Any experiments, experimental examples, or experimental results provided herein are intended to be illustrative of the present invention and should not be considered limiting or restrictive with regard to the invention scope. Further, any theory, mechanism of operation, proof, or finding stated herein is meant to further enhance understanding of the present invention and is not intended to limit the present invention in any way to such theory, mechanism of operation, proof, or finding.

Thus, the specifics of this description and the attached drawings should not be interpreted to limit the scope of this invention to the specifics thereof. Rather, the scope of this invention should be evaluated with reference to the claims appended hereto. In reading the claims it is intended that when words such as "a", "an", "at least one", and "at least a portion" are used there is no intention to limit the claims to only one item unless specifically stated to the contrary in the claims. Further, when the language "at least a portion" and/or "a portion" is used, the claims may include a portion and/or the entire items unless specifically stated to the contrary. Likewise, where the term "input" or "output" is used in connection with an electric device or fluid processing unit, it should be understood to comprehend singular or plural and one or more signal channels or fluid lines as appropriate in the context. Finally, all publications, patents, and patent applications cited in this specification are herein incorporated by reference to the extent not inconsistent with the present disclosure as if each were specifically and individually indicated to be incorporated by reference and set forth in its entirety herein.

The invention claimed is:

1. A nanocomposite material comprising a metal oxide bonded directly to a graphene layer, wherein the graphene layer consists essentially of 1 to 147 graphene sheets, the nanocomposite material having a specific capacity at least twice that of the metal oxide without the graphene layer at a charge/discharge rate greater than about 10 C.

2. The nanocomposite material of claim 1 wherein the graphene layer has a carbon to oxygen ratio of 10-500:1.

3. The nanocomposite material of claim 1 wherein the metal oxide is M_xO_y, and where M is Ti, Sn, Ni, Mn, V, Si, or Co, or is a combination thereof.

4. The nanocomposite material of claim 1 wherein the metal oxide is titania.

5. The nanocomposite material of claim 1 wherein the metal oxide is tin oxide.

6. The nanocomposite material of claim 1 including a plurality of graphene layers having metal oxide bonded directly thereto, the plurality of graphene layers forming a nanoarchi-