LITHIUM ION BATTERIES WITH TITANIA/GRAPHENE ANODES

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation in part of U.S. Ser. No. 12/460,993 filed Jul. 27, 2009, now U.S. Pat. No. 8,257,867 which claims priority to U.S. Provisional Application No. 61/084,140 filed Jul. 28, 2008, entitled Metal Oxide-Graphene Hybrid Nanostructures and Method of Making.

The invention was made with Government support under Contract DE-AC0676RLO 1830, awarded by the U.S. Department of Energy. The Government has certain rights in the invention.

TECHNICAL FIELD

This invention relates to nanocomposite materials of graphene in electrical communication with metal oxides and methods for forming nanocomposite materials of graphene in electrical communication with metal oxides.

BACKGROUND OF THE INVENTION

Graphene is generally described as a one-atom-thick planar sheet of sp2-bonded carbon atoms that are densely packed in a honeycomb crystal lattice. The carbon-carbon bond length in graphene is approximately 0.142 nm. Graphene is the basic structural element of some carbon allotropes including graphite, carbon nanotubes and fullerenes. Graphene exhibits unique properties, such as very high strength and very high conductivity. Those having ordinary skill in the art recognize that many types of materials and devices may be improved if graphene is successfully incorporated into those materials and devices, thereby allowing them to take advantage of graphene's unique properties. Thus, those having ordinary skill in the art recognize the need for new methods of fabricating graphene and composite materials that incorporated graphene.

Graphene has been produced by a variety of techniques. For example, graphene is produced by the chemical reduction of graphene oxide, as shown in Gomez-Navarro, C.; Weitz, R. T.; Bittner, A. M.; Scolari, M.; Mews, A.; Burghard, M.; Kern, K. Electronic Transport Properties of Individual Chemically Reduced Graphene Oxide Sheets. and *Nano Lett.* 2007, 7, 3499-3503. Si, Y.; Samulski, E. T. Synthesis of Water Soluble Graphene. *Nano Lett.* 2008, 8, 1679-1682.

While the resultant product shown in the forgoing methods is generally described as graphene, it is clear from the specific capacity of these materials that complete reduction is not achieved, because the resultant materials do not approach the theoretical specific capacity of neat graphene. Accordingly, at least a portion of the graphene is not reduced, and the resultant material contains at least some graphene oxide. As used herein, the term "graphene" should be understood to encompass materials such as these, that contain both graphene and small amounts of graphene oxide.

For example, functionalized graphene sheets (FGSs) prepared through the thermal expansion of graphite oxide as shown in McAllister, M. J.; LiO, J. L.; Adamson, D. H.; Schniepp, H. C.; Abdala, A. A.; Liu, J.; Herrera-Alonso, M.; Milius, D. L.; CarO, R.; Prud'homme, R. K.; Aksay, I. A. Single Sheet Functionalized Graphene by Oxidation and Thermal Expansion of Graphite. *Chem. Mater.* 2007, 19, 4396-4404 and Schniepp, H. C.; Li, J. L.; McAllister, M. J.; Sai, H.; Herrera-Alonso, M.; Adamson, D. H.; Prud'homme, R. K.; Car, R.; Saville, D. A.; Aksay, I. A. Functionalized Single Graphene Sheets Derived from Splitting Graphite Oxide. *J. Phys. Chem. B* 2006, 110, 8535-8539 have been shown to have tunable C/O ratios ranging from 10 to 500. The term "graphene" as used herein should be understood to include both pure graphene and graphene with small amounts of graphene oxide, as is the case with these materials.

Further, while graphene is generally described as a one-atom-thick planar sheet densely packed in a honeycomb crystal lattice, these one-atom-thick planar sheets are typically produced as part of an amalgamation of materials, often including materials with defects in the crystal lattice. For example, pentagonal and heptagonal cells constitute defects. If an isolated pentagonal cell is present, then the plane warps into a cone shape. Likewise, an isolated heptagon causes the sheet to become saddle-shaped. When producing graphene by known methods, these and other defects are typically present.

The IUPAC compendium of technology states: "previously, descriptions such as graphite layers, carbon layers, or carbon sheets have been used for the term graphene . . . it is not correct to use for a single layer a term which includes the term graphite, which would imply a three-dimensional structure. The term graphene should be used only when the reactions, structural relations or other properties of individual layers are discussed". Accordingly, while it should be understood that while the terms "graphene" and "graphene layer" as used in the present invention refers only to materials that contain at least some individual layers of single layer sheets, the terms "graphene" and "graphene layer" as used herein should therefore be understood to also include materials where these single layer sheets are present as a part of materials that may additionally include graphite layers, carbon layers, and carbon sheets.

The unique electrical and mechanical properties of graphene have led to interest in its use in a variety of applications. For example, electrochemical energy storage has received great attention for potential applications in electric vehicles and renewable energy systems from intermittent wind and solar sources. Currently, Li-ion batteries are being considered as the leading candidates for hybrid, plug-in hybrid and all electrical vehicles, and possibly for utility applications as well. However, many potential electrode materials (e.g., oxide materials) in Li-ion batteries are limited by slow Li-ion diffusion, poor electron transport in electrodes, and increased resistance at the interface of electrode/electrolyte at high charging-discharging rates.

To improve the charge-discharge rate performance of Li-ion batteries, extensive work has focused on improving Li-ion and/or electron transport in electrodes. The use of nanostructures (e.g., nanoscale size or nanoporous structures) has been widely investigated to improve the Li-ion transport in electrodes by shortening Li-ion insertion/extraction pathway. In addition, a variety of approaches have also been developed to increase electron transport in the electrode materials, such as conductive coating (e.g., carbon), and uses of conductive additives (e.g., conductive oxide wires or networks, and conductive polymers). Recently, TiO_2 has been extensively studied to demonstrate the effectiveness of nanostructures and conductive coating in these devices.

TiO_2 is particularly interesting because it is an abundant, low cost, and environmentally benign material. TiO_2 is also structurally stable during Li-insertion/extraction and is intrinsically safe by avoiding Li electrochemical deposition. These properties make TiO_2 particularly attractive for large scale energy storage.

Another way to improve the Li-ion insertion properties is to introduce hybrid nanostructured electrodes that intercon-