SELF ASSEMBLED MULTI-LAYER NANOCOMPOSITE OF GRAPHENE AND METAL OXIDE MATERIALS

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 bonded to metal oxides, devices using such materials, methods for forming nanocomposite materials of graphene bonded to metal oxides, and devices using those materials. More specifically, this invention relates to self-assembling multi-layer nanocomposite materials of graphene bonded to metal oxides, devices using such materials, methods for forming self-assembling multi-layer nanocomposite materials of graphene bonded to metal oxides and devices using those materials.

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. One such energy storage application is Lithium ion (Li-ion) batteries.

Currently, Li-ion batteries are used in a variety of portable electronic devices. As a result of their excellent weight to power ratio, they are also 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.

For Li-ion batteries, SnO_2, Sn and Si are promising high capacity anode materials, but have large volume expansions upon lithiation, causing degradation and rapid fading during charge/discharge cycling. Efforts have been made to prepare composite materials to mix metal oxides and conductive materials such as amorphous carbon, carbon nanotubes and graphene, as discussed in Moriguchi, I.; Hidaka, R.; Yamada, H.; Kudo, T.; Murakami, H.; Nakashima, N. *Advanced Materials* 2006, 18, 69-73; Zhang, W. M.; Hu, J. S.; Guo, Y. G.; Zheng, S. F.; Zhong, L. S.; Song, W. G.; Wan, L. J. *Advanced Materials* 2008, 20, 1160; and Huang, H.; Yin, S. C.; Nazar, L. F. *Electrochemical and Solid State Letters* 2001, 4, A170-A172.

Recently pre-synthesized metal oxide nanoparticles (e.g., TiO_2 and SnO_2) were deposited on graphene surfaces to form nanocomposites as described in Williams, G.; Seger, B.; Kamat, P. V. *ACS Nano* 2008, 2, 1487-1491; and Paek, S.-M.; Yoo, E.; Honma, I. *Nano Letters* 2009, 9, 72-75. Other stud-