Centre for Clean Energy Technology & School of Chemistry and Forensic Science

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Graphene-based Nanocomposite Materials for High-performance Supercapacitors and Lithium Rechargeable Batteries

A Thesis Presented in Fulfillment of the Requirements for the Degree of

Doctor of Philosophy

By

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Certificate of Authorship/Originality

I certify that the work in this thesis has not previously been submitted for a degree nor has been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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Abstract

Human activity and energy supplies mainly rely on the consumption of non-regenerative fossil fuels. With the gradual decrease of these carbon-based energy sources and the increase in environmental pollution, finding alternative green and sustainable energies has become critical. Therefore, innovative and renewable energy technologies must be developed to combat global warming and climate change.[1, 2] Extensive research has been performed on the development of solar cells,[3, 4] fuel cells,[5] lithium-ion batteries[6, 7] and supercapacitors[8, 9] to replace carbon-based energy.

Graphene has been considered a promising electrode material for energy storage applications due to its ultrahigh surface area (2600 m^2 g^{-1}),[10] excellent electric conductivity,[11] and one-atom thick two-dimensional sp^2 carbon arrangement.[12] However, the surface area of graphene nanosheets (GNS) is often dramatically reduced because monolayer GNS always stack to multilayer in the dry state. The stacking of GNS leads to unexposed surface area, which hinders the ion diffusion from the electrolyte to the electrode, resulting in a low electrochemical performance.

To prevent the re-stacking of GNS, and thus maintain well-exposed surface area, nanocrystals can be inserted between graphene layers to form nanocomposite materials. With the above motivation, graphene-based nanocomposite materials have been intensively studied in this thesis. All the materials examined were prepared via different synthesis techniques and well characterized. Their electrochemical properties were evaluated for supercapacitors and/or lithium rechargeable batteries. Sn/GNS is shown to have a very high reversible specific capacity of 785 mAh g^{-1}. Mn_3O_4/GNS shows a specific capacitance of 256 F g^{-1}, almost double that of pure GNS. Of the examined materials, Co_3O_4/GNS presents the highest supercapacitance of 478 F g^{-1} and a rechargeable specific capacity of 722 mAh g^{-1}. S/GNS generates ultra-high specific capacity of up to 1580 mAh g^{-1} and excellent rate capability. SnO_2 nanoparticles supported by GNS deliver a specific capacity of 830 mAh g^{-1} with well maintained cycling stability. CoS_2/GNS yields high capacitances of 314 F g^{-1} in an aqueous electrolyte and 141 F g^{-1} in an organic electrolyte. The enhanced overall electrochemical performances of these nanocomposite materials can be attributed to the dual contributions of the decorating materials, creating enlarged interlayer spacing, and graphene itself, with its facility for flexible nanolayered structure. The results of this study of these graphene-based nanocomposite materials indicate their great potential for application to practical energy storage devices.