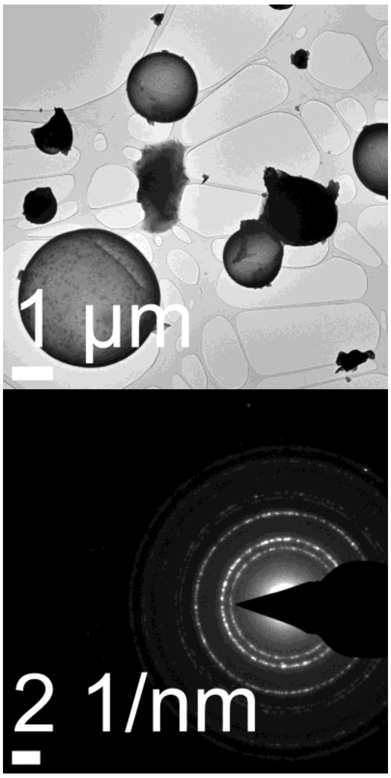
Properties of novel graphene oxide/ lithium manganese oxide nanocomposites annealed in high vacuum

Dominika A. Ziolkowska[1], Jacek B. Jasinski[2], Monika Michalska[3], Krzysztof P. Korona[1], Ludwika Lipinska[3], Maria Kaminska[1]

[1] Faculty of Physiscs, University of Warsaw, Hoza 69, 00-681 Warsaw, Poland
[2] Conn Center for Renewable Energy Research, University of Louisville, 40292 Louisville, KY, USA
[3] Institute of Electronic Materials Technology, Wólczyńska 133, 01-919 Warsaw, Poland



A new method of nanocomposites synthesis, consisting of lithium manganese oxides nanoparticles confined in graphene oxide spherical matrix, is reported [1]. The obtained materials are chemically identical with materials used for Li-ion batteries, however they has very attractive form of hollow nanospheres. The production method is based on thermal processing of xerogel precursor consisting of lithium and manganese organic salts mixed with citric and acetic acids made by a simple and low cost sol-gel method. The nanocomposites grow as hollow spheres during the annealing process. The micro- and nanospheres morphology is formed by heating the precursor grains in a vacuum condition at temperatures about 350°C. Depending on the ambient pressure during heating above the crystallization temperature (ca. 450°C), the forming nanocomposite will consist of either MnO (Fig.1) or $LiMn_2O_4$ nanoparticles. Both compounds are important materials for lithium-ion battery applications as anodes or cathodes, respectively. Finally, modifying the temperature of the synthesis, the structure of the carbonaceous matrix can be controlled. For example, heating in the temperature above 800°C can lead to the formation of graphene-related structures, such as reduced graphene oxide.

We will present in -situ TEM investigations of growing of these nano-objects. For, our studies we prepared few samples of different compositions: managanese salt/organic precursor, lithium salt/organic precursor and pure organic precursors. We used in situ TEM annealing to produce example nanocomposites, performed their detailed characterization (HRTEM, SAED, EELS, EDX and Raman spectroscopy) and proposed a mechanism to explain their formation. We observed that the gaseous decomposition products of lithium organic precursor are responsible for the hollow spheres formation and the citric acid takes part of the carbonaceous framework formation. The carbon structure was examined during the synthesis by HRTEM and EELS spectroscopy and we indicate that carbonaceous structure changes from amorphous to graphene-like structure depending on annealing temperatures. The final products were also investigated by Raman spectroscopy and shows that in certain synthesis conditions reduced graphene oxide can be produced using a simple sol-gel method.

[1] J.Jasinski, D. Ziolkowska, M. Michalska, L. Lipinska, K.P. Korona, M. Kaminska, *RSC Adv.* **3,** 22857 – 22862 (2013)