

Graphene-based materials for energy storage: synthesis and properties

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Applications of graphene require large scale technologies of its synthesis. Here graphite oxide (GO) plays an important role. Methods of conversion of GO into graphene include microwave exfoliation of GO¹ and a chemical reduction of GO using various strong reducing agents, such as hydrazine hydrate, sodium borohydride, dimethylhydrazine². The present paper gives a review of our recent work focused on synthesis and studies of structure-properties relationship in graphene and GO-based materials aimed for use in energy storage applications.

Microwave exfoliated graphite oxide (MEGO) was synthesized and studied by various techniques including X-ray photoelectron spectroscopy, mass-spectroscopy, infrared and Raman spectroscopy, scanning electron microscopy and broadband dielectric spectroscopy. Specific surface area and volume of microwave exfoliated graphite oxide reached 600 m²/g (20 m²/g for the initial GO) and 6 cm³/g, respectively. Utilized in the work explosive reduction process results in emission of CO₂, CO and H₂O and, in some cases, SO₂ gases. The resulting reduced graphene-related product shows similar to graphite IR spectra and has a dc-conductivity of 0.12 S cm⁻¹ [1].

Chemical reduction of GO normally results in its incomplete reduction yielding, materials containing various amounts of residual oxygen, as related to the type of the reducing agent used. Comparison of the efficiency of various reducing agents showed that the best reduction degree yields C/O ratios of 16:1 and 10:1. Extent of reduction of graphene-related materials can be increased by heating them to 900 °C in inert gas. Thermal reduction of GO yields less contaminated by oxygen graphene-related materials with high degree of reduction (the ratio C/O becomes 43:1). However, 60 % of the material is lost during the high temperature processing [2].

Simultaneous reduction of GO and Pt(IV) used as H₂PtCl₆ takes place when sodium borohydride and hydrazine have been used as reducing agents. This allowed to prepare catalysts useful for the various

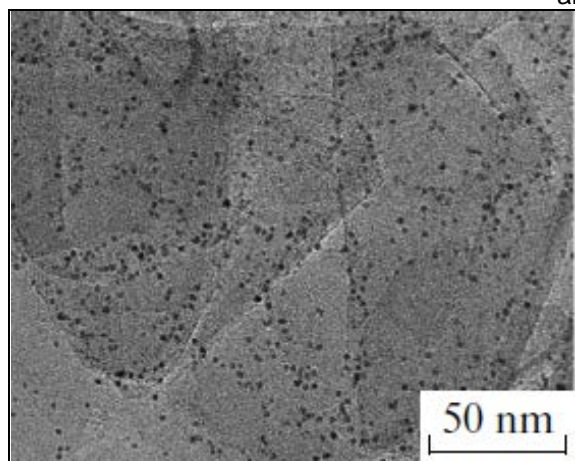


Figure 1. TEM Image of the Pt-rGO composite reduced by sodium borohydride.

hydrogenation processes where Pt nanoparticles were deposited on a carbon surface of the rGO (see Figure 1). Particles of platinum are probably fixed on the defects, vacancies, and functional groups that form as a result of the reduction process. The obtained Pt/C nanocomposites catalyzed the hydrogenation of 1-decene yielding propanol-2 and showed a good catalytic activity [3].

A self-reduction of graphene oxide (GO) film deposited on a copper substrate takes place at room temperature after a prolonged storage and is evidenced by a decrease in oxygen content and a dramatic, 6 orders in magnitude, increase in dc conductivity. Experiments revealed that the stored GO into the reduced GO structure [4].

The 200-500 nm thick GO films become conductive (Ω increases from 10⁻⁶ to 10⁻² S/cm when the humidity increases from 30 to 100 %). The conductivity of the GO films increases in the vapors of polar solvents (alcohols, acetone, pyridine), while the vapors of nonpolar (toluene and hexane) and chlorinated (CCl₄, CHCl₃) solvents do not show such an effect. Studies of the diffusion processes in a GO film showed that a drastic isotopic effect [$\sigma\text{H}/\sigma\text{D} = 1.4 \pm 0.1$] confirming a suggestion of the proton character of conductivity [5].

A film of deeply oxidized graphene oxide was used for the first time as a separator in a supercapacitor. The supercapacitor contain a layer structure PANi/GO/PANi (PANi – polyaniline; GO - graphene oxide). The capacity of this supercapacitor is around 150 F/g for the total weight of the electrode, separator, and electrolyte (1 M H₂SO₄). The supercapacitor capacity has decreased only by 10% after 1500 charge/discharge cycles (Figure 2). Change of the current through a GO membrane in experiments using H₂O or D₂O-containing electrolytes unambiguously indicated the proton type of conductivity of the GO membranes [6].

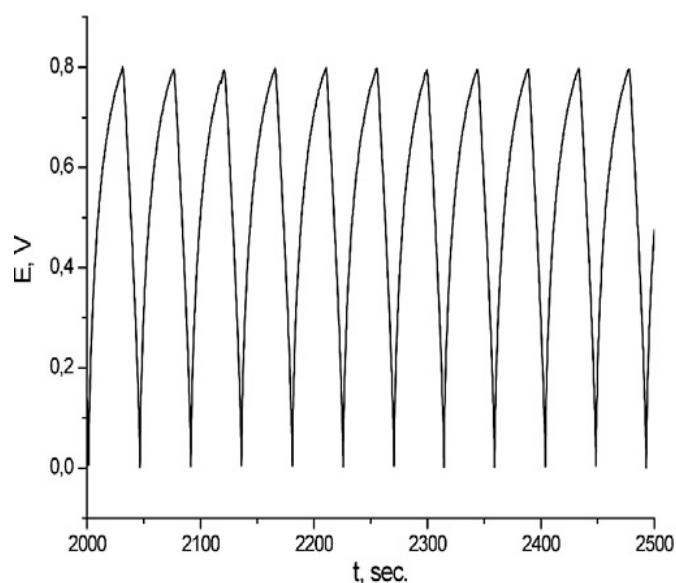


Figure 2. A part of the GCD curve obtained for the PANi/GO/PANi supercapacitor in a 1 M H₂SO₄ electrolyte.

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