



Properties of a granulated nitrogen-doped graphene oxide aerogel

S.A. Baskakov^a, R.A. Manzhos^a, A.S. Lobach^a, Y.V. Baskakova^a, A.V. Kulikov^a, V.M. Martynenko^a, F.O. Milovich^b, Yogesh Kumar^c, A. Michtchenko^{d,*}, E.N. Kabachkov^{a,e}, A.G. Krivenko^a, Y.M. Shulga^{a,b}

^a Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka 142432, Moscow Region, Russian Federation

^b National University of Science and Technology MISIS, Leninsky pr. 4, Moscow 119049, Russian Federation

^c Department of Physics, ARSD College, University of Delhi, Delhi 110021, India

^d Instituto Politécnico Nacional, SEPI-ESIME-Zacatenco, Av. IPN S/N, Ed.5, 3-r piso, Ciudad de Mexico, C.P. 07738, Mexico

^e Chernogolovka Scientific Center, Russian Academy of Sciences, Chernogolovka 142432, Moscow Region, Russian Federation

ARTICLE INFO

Keywords:

Aerogel from graphene oxide
Heating in the air
Hydrazine reduction
Element analysis
X-ray photoelectron spectroscopy
Oxygen reduction reaction

ABSTRACT

At first, a granulated aerogel of graphene oxide was obtained, which was later reduced by hydrazine vapour. The reduced aerogel was characterized through elemental analysis, infrared (IR) and Raman spectroscopy, electron paramagnetic resonance (EPR), thermogravimetric analyses (TGA), voltammetry, and X-ray photoelectron spectroscopy (XPS). Furthermore, the reduced sample was found to contain approximately 3 wt.% of nitrogen, which was present in the aerogel in three states corresponding to the photoelectron peaks N1s with binding energies of 399.5, 401.3, and 403.6 eV. In the electroreduction of oxygen, an appreciable catalytic effect was observed for the sample under study, which resulted from reducing the overvoltage of the reaction by ~90 mV and changing the mechanism of reduction.

1. Introduction

Researchers have been paying close attention to carbon materials doped with nitrogen [1, 2]. Graphene is a two-dimensional carbon material that is only one-atom thick; it displays outstanding thermal stability and excellent mechanical properties. Recently, much effort has been made with respect to improving graphene-based materials for diverse applications. Furthermore, 2D free-standing graphene films have paved the way for promising applications, including high strength concerning electrical conductivity, enhanced thermal performance of energy-saving materials (higher-energy density batteries), sustainable and lightweight materials for buildings, additives for coatings, corrosion, insulation (flame-resistant heat shields for aircraft), thermal breaks, optical and imaging devices, condensation control, architectural lighting panels, outdoor/sports gear, and clothing (super-elastic composites).

Keeping the different focus areas of the research in the mind, graphene-based materials are being modified for developing their task-specific desirable properties. In this context, researchers have introduced dopant in the carbon structure or at the surface of the graphene. It is known that the reduction of graphene oxide with ammonia or hydrazine results in the formation of nitrogen-containing functional groups and/or nitrogen atoms embedded in the carbon lattice [3–8].

Nitrogen modification of the reduced graphene oxide has a positive aspect, since such samples can, in principle, be utilised as catalysts for the oxygen reduction reaction (ORR) [9–12] or as a carrier for metal-containing catalysts. In the latter case, the coordination between the metal particles and the nitrogen atom of the substrate prevents the aggregation of the metallic particles during catalysis [13].

On the other hand, nanomaterials qualify as graphene too, but the properties of these composites are found to be different than the ones expected. The poor dispersion of graphene is the primary reason for failure in this regard. Agglomeration owing to π - π stacking interactions between graphene sheets leads to bulk formation. In order to fully exploit the properties of graphene, different methodologies must be devised to convert 2D materials into 3D structures. The preparation and characterisation of graphene materials with 3D-structures, such as aerogels, hydrogels, and macroporous films, are extremely significant from the perspective of application. Aerogels depict great potential and have been investigated extensively among the aforementioned structures [14–24].

A variety of chemical compounds can be converted into aerogels, which denote a diverse class of materials with unique properties. Furthermore, aerogels are synthesised by combining a polymer with a solvent to form a gel. Subsequently, the liquid from the gel is removed and replaced with air. Air content of up to 99.9% makes it the lightest

* Corresponding author.

E-mail address: almichtchenko@ipn.mx (A. Michtchenko).

solid (lighter than air). Graphene aerogels (3D scaffold) exhibit higher electrical conductivity compared to those that have been prepared through dispersion of graphene sheets [25–27]. Furthermore, at present, they have attracted a lot of interest owing to their designed lattice structures, high porosity (ability to absorb up to 900 times their own weight), excellent insulation properties, superhydrophobic attributes, low thermal conductivity, high mechanical strength (capable of recovering completely after more than 90% compression), and massive adsorption capacity. These aerogels can be synthesised by employing hydrothermal reduction/self-assembly, chemical reduction, template-directed reduction, cross-linking, dry freezing, and sol-gel processes.

These synthesised aerogels have recently found application as advanced energy materials. Several parameters influence the performance of energy storage and conversion systems. Overall efficiency in this regard depends on the specific structure and properties of the incorporated functional materials. Furthermore, 3D network/aerogel structures are one of the innovative structures that have larger active sites for reactions; their porous hierarchical structure facilitates rapid electron/ion transport, superior chemical and physical stability, and good cycle performance. Recently, synergetic hybrid aerogels of vanadia and graphene have been successfully employed as electrode materials of supercapacitors [28].

Another useful feature of these aerogels is that they can function as fire-retardant material. Fire-resistant, as well as heat-resistant, materials are required for fire-retardant suits, shoes (boots), helmets, and tents. Washable (water resistant, not susceptible to leaching with water, and durable), lightweight flame-retardant films, with long shelf lives (immune to the effects of ageing), are required for manufacturing goods and appliances. These materials must be resistant to abrasion and fracture. However, the fibre-based materials, such as glass and aramid filaments or textile ceramics, have been playing an increasingly important role pertaining to fire protection at construction sites. New high-quality thermal insulation materials possess great potential with respect to energy-efficient building design, transportation, and the aircraft industry. Hence, the heat-resistant coating of graphene-based materials is also extremely useful for fire protection applications. The coating of graphene, which is one-atom thick, creates a physical barrier that provides resistance to heat and gases. The composite of organic molecules with GO sheets enhances thermal stability owing to strong inter- and intra-molecular interactions [29]. Graphene is observed to be a good catalyst in the 3D form, for instance, in aerogels [30]. Considered to be one of the highly innovative uses of graphene-based 3D sponge, the modulated light that shines on a 3D graphene sponge has been incorporated into the construction of loudspeakers [31]. Graphene aerogels with aramid honeycombs are known for their application in the field of insulation [32]. The researchers of this study prepared compressible and reusable absorbents from graphene aerogel [33]. Along with this, a report concerning nitrogen-doped aerogels for water purification has also been published [34]. Furthermore, hydrophobic GAs have recently been reported for filtration [35, 36].

In this paper, we have set ourselves the goal of obtaining a nitrogen-doped graphene oxide aerogel (GOA), in addition to processing and validating it through elemental analysis, IR spectroscopy, voltammetry, and X-ray photoelectron spectroscopy. More importantly, we aim to study the composition of the thermal decomposition products of such aerogels through mass spectrometry. To the best of our knowledge, the latter task has not been previously described in the literature. Furthermore, attention has also been paid to the electrochemical behaviour of nitrogen-doped GOA (N-dGOA) in the ORR.

2. Experiment

Graphite oxide was obtained through the modified Hummers' method [37]. Subsequently, a water suspension of graphene oxide was obtained through micromechanical exfoliation of graphite oxide in an ultrasonic field.

The granulated aerogel was prepared as follows: a gelled suspension of graphene oxide with a concentration of 15 mg/ml was slowly dripped through a syringe to a Dewar vessel filled with liquid nitrogen. After freezing, drops in the form of granules fell to the bottom of the vessel. Subsequently, frozen granules were dried at a temperature of liquid nitrogen for three days in a Martin Christ ALPHA 1–2 LD freeze-dryer. The specific mass of dry GO granules was determined to be 20 mg/cm³.

The GOA granules were reduced in hydrazine vapour. For this purpose, two petri dishes were placed at the bottom of a hermetically sealed polypropylene container with a volume of one litre. In the first dish, a sample of GOA (0.5 g) was placed, whereas hydrazine hydrate (1 ml) was poured into the second. Subsequently, the container was closed and placed in an oven at 60 °C for 24 h. A day later, the granules were removed from the container and dried in the air for three to four hours at 60–70 °C. It was observed that the granules changed their colour from grey-brown to black following the process of reduction.

Furthermore, elemental analysis of the samples was conducted on the CHNS analyser “Vario MICRO cube” Elementar Analysensysteme GmbH. In addition, IR spectra were obtained by employing a Perkin Elmer Spectrum 100 Fourier spectrometer with a UATR attachment in the range 675–4000 cm⁻¹. Excitation of the Raman spectra was conducted using an Ar laser ($\lambda = 514.5$ nm) and recorded with a Horiba Jobin Yvon T64000 spectrometer. The power of the laser radiation on the sample did not exceed 0.1 mW to prevent the effect of local heating of the sample. Electron micrographs of the samples were obtained on a scanning electron microscope – Zeiss SUPRA 25 (electron energy 3.4 kV, chamber pressure 2×10^{-5} Pa). The EPR spectra were recorded on an Elexys II E 500 EPR spectrometer at room temperature. Moreover, the content of the paramagnetic centres in the sample and the g-factor were determined in accordance with the Xep software package. Thermogravimetric (TG) curves were obtained on a STA 409 LUX X Netzsch instrument in an airflow-programmed heating mode of 5 K/min.

The XPS spectra were obtained by utilising a Specs PHOIBOS 150 MCD electron spectrometer and X-ray tube with a magnesium anode ($h\nu = 1253.6$ eV). It must be noted that the vacuum in the spectrometer chamber did not exceed 4×10^{-8} Pa. The spectra were registered in the regime of constant transmission energy (40 eV for wide spectra and 10 eV for individual lines). In addition, the survey spectrum was recorded in steps of 1.00 eV, whereas the spectra of individual lines were recorded in steps of 0.03 eV.

Electrochemical measurements were determined in a conventional three-electrode cell by employing a VED-06 rotating disk electrode setup (Volta, Russia) with an IPC Pro-L potentiostat (A.N. Frumkin Institute of Physical Chemistry and Electrochemistry of RAS, Russia). A glassy carbon (GC) disk, which was 3 mm in diameter and had been pressed into the Teflon, served as a working electrode. It was polished with 1 μ m Al₂O₃ powder prior to each experiment. A platinum foil functioned as a counter electrode. An Ag/AgCl (sat. KCl) electrode was used as a reference electrode. All potential values (*E*) have been inferred with reference to this electrode. The working solution was prepared on the basis of the chemical grade KOH and double distilled water. The suspension of the GOA reduced with hydrazine N-dGOA (3% N) was obtained through ultrasonic dispersing of 1 mg of N-dGOA granules in 5 ml of water, with the addition of 0.1 ml of 10% Nafion[®] solution. Subsequently, the GC electrode was modified through 10 μ l of suspension and was dried in an ambient environment for 12 h.

3. Results and discussion

3.1. Elemental analysis

Data pertaining to the elemental composition of GOA, before and after reduction, have been presented in Table 1. It can be observed that the reduction of GOA with hydrazine was accompanied by an increase in the carbon content and a decrease in the oxygen content.

Download English Version:

<https://daneshyari.com/en/article/7899676>

Download Persian Version:

<https://daneshyari.com/article/7899676>

[Daneshyari.com](https://daneshyari.com)