DOCTORAL (PH.D.) THESES

Chemical and nanostructure of graphite oxide

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2006

1. INTRODUCTION

Since the advent of nanotechnology, the diverse forms of carbon materials have attracted a great attention. The recently discovered fullerenes, single and multiwalled nanotubes as well as carbon nanosrolls and graphite polyhedral crystals are materials with nanometric dimensions, thus, their sizes are comparable with those of nano-objects and nano-devices. Fabrication of such systems, mainly motivated by the microelectronic engineering, is the ultimate goal of miniaturization trends in the modern materials science. In addition, carbon materials possess excellent and, in many cases, unique physicochemical properties like rectifying, high temperature superconductivity or exceptionally high specific surface area.

The enhanced interest towards these novel carbon nanostructures resulted in a simultaneous effacement concerning the research of "bulky" graphite and its compounds. For example, graphite bears an insignificant role in electric engineering because its application for the preparation of ordered, conductive thin layers is not straightforward. The main reason for this is that the cleavage of its coarse crystallites into elementary graphenes or at least into nanometric graphene aggregates is impossible utilizing conventional physical methods, therefore, it is also not possible to obtain highly stable dispersions of colloidal graphite either in aqueous or in organic media. On the other hand, graphite oxide (GO), which features the main topic of the present dissertation, is a graphite based material offering solution for the problem pointed out above.

The fundamental goal of my doctoral research was to reveal the chemical and supramolecular structure of graphite oxide via the detailed investigation of its physicochemical and colloid chemical properties. The potential technological application of this graphite compound was also issued. According to the extensive perusal of the literature, the exact chemical structure of GO is still ambigous, and the models proposed so far contradict each other as well as the observed properties of the material in many respect. The better understanding of the GO structure is not solely motivated by the fundamental research of carbon materials: it is obviously important for many practical purposes, e.g. for its improved application in materials science (adsorption, surface functionalization that is, linking molecules, macromolecules through specific functional groups or binding nanoparticles to graphite oxide for making novel derived carbon composites, chemical or biosensors, etc.).

Realization of the above challenges prompted me to contribute to the sustained effort to unravel the real chemical structure of graphite oxide. A number of structure analytical techniques were available in the Department of Colloid Chemistry (University of Szeged) and in the laboratories of the collaborating research groups, the results of which, by consistent consideration of the properties of the substance observed earlier, enabled me to propose a new structure model for GO.

The second aim was to characterize the colloid chemical properties and the nanostructure of solid GOs and their aqueous suspensions. Small angle X-ray scattering provided valuable information on the specific surface area, porosity, fractal dimension, and the mean distances of inhomogenities in the disperse system, while the acidity and the pH and ionic strength dependent surface charge of graphite oxide dispersed in aqueous electrolyte solutions were characterized by means of potentiometric acid-base titration. The study of this issue is highly relevant in a practical point of view because the surface charge state of colloids in electrolyte media governs the colloid stability and adsorption behaviour of the solid GO particles dispersed in water.

The knowledge of structural features and colloid properties of the material has prompted my next effort to prepare a conductive graphitic film of nanometric thickness on glass support. The technique of the so-called layer-by-layer self-assembly developed in the past few decades was applied for this purpose which offers a viable approach for the deposition and organization of most of the charged colloids by use of a proper polyelectrolyte on surfaces of practically arbitrary shape and chemical entity.

The final aim of my doctoral research was the magnetic derivatization of the GO surfaces and the characterization of the as-obtained nanocomposites. These experiments featured to be a relevant part of the collaboration between the Department of Colloid Chemistry and the Institute of Materials Science, NCSR “Demokritos” which was realized in two international research projects (“NATO Science Program” and “Greek-Hungarian Intergovernmental Scientific and Technological Cooperation”).

2. MATERIALS AND METHODS

A series of progressively oxidized graphite oxides (consisting of four specimens) were synthesized from natural, size fractionated graphite flakes according to the conventional Brodie method using $NaClO_3$ and fuming nitric acid.

Ultrathin films of graphite oxide were deposited on glass slide via layer-by-layer self-assembly by means of a cationic polyelectrolite poly(diallyldimethylammonium) chloride (PDDA).

The magnetically modified carbon composite was obtained via an exchange reaction between the tris(2,2’-bypiridine) complex of Fe(II) and the cation exchange sites of graphite oxide followed by calcination.

The atomic composition of the graphite oxides was determined by a Perkin-Elmer 2400 Series II. CHNS/O Analyzer (Institute of Pharmaceutical Chemistry).

The basal distances of graphite, GOs and the self-assembled nanofilms were measured by a Philips X-ray diffractometer (PW1830 generator, PW 1820 goniometer and a Cu anode) in the 2Θ range of 1-30°. The wavelength of the CuKα radiation is 0.1542 nm (CuKβ photons were absorbed by a Ni filter). The small angle X-ray scattering measurements were carried out in vacuum by a compact Kratky camera (KCEC/3).

The thermal behaviour of the GO series was investigated by a MOM Derivatograph Q-1500 D thermobalance (25-1000 °C temperature range) in air and N_2 atmosphere against Al_2O_3 as a reference.

For ^{13}C magic angle spinning (MAS) NMR measurements, a Bruker Avance DRX500 spectrometer was used operating in a 11.7 T magnetic field equipped with a 4 mm diameter solid-state probe head (Department of Organic Chemistry).

Infrared spectra were collected by using a Biorad FTS-60A FT-IR device equipped with a diffuse reflectance unit (Department of Physical Chemistry). The DRIFT spectra were recorded by a DTGS detector from 256 scans in a digital resolution of 2 cm^{-1}.

X-ray photoelectron spectra of GOs were recorded on an XR3E2 (VG Microtech) twin anode X-ray source and a Clam2 hemispherical electron energy analyzer (Department of Atomic Physics, Budapest University of Technology and Economics).

Electron spin resonance measurements were perfomed at room temperature by a Bruker ER200D instrument equipped with and Anristsu microwave fequency counter (Institute of Materials Science, NCSR "Demokritos", Athens).

Optical characterization of the GO/polymer nanofilms were carried out by a Uvikon 930 double-beam spectrophotometer (Kontron Instruments).

The electric conductivity of the self-supporting GO films and the GO/PDDA ultrathin multilayers were measured by a Keithley 2400 Series Source Meter.

Specific surface areas were determined by N_2 adsorption using a Micromeritics Gemini 2375 automated gas adsorption apparatus.

Electron microscopic examinations were performed on a Philips CM-10 electron microscope operating at 100 kV acceleration voltage (EM laboratory of the Department of Anatomy and Pathology).

The topography of the self-assembled PDDA/GO nanofilms were scanned by means of a Digital Instruments Nanoscope III Multimode AFM apparaus in the so-called tapping (non-contact) mode.

pH-potentiometric titrations were performed on a home-built, computer-controlled titration system.

The magnetization curve of the iron-oxide/carbon nanocomposite was recorded on a VSM02 (Hirst Magnetic Instruments) vibrating sample magnetometer (Institute of Materials Science, NCSR "Demokritos", Athens).

3. NOVEL SCIENTIFIC RESULTS

T.1 *Evolution of the surface functional groups and the physicochemical properties of graphite oxide upon successive oxidation treatments*

1.a According to the atomic compositions of anhydrous graphite oxides, the molar ratio of heteroatoms (O and H) increases with the repetition of the oxidation steps, resulting in a concomitant decrease of the amount of carbon atoms in the compound. A strong correlation was found between the water content and the amount of heteroatoms suggesting that the incorporation of more and more oxygen containing species increases the hydrophilicity of the lamellar GO surfaces. Adsorption of the ambient humidity as well as the intercalation of the H_2O molecules were found to be rapid, during which a discontinuous increment in the layer distances of graphite oxides takes place.

1.b Deuterium exchange was applied for the first time in the infrared spectroscopic research on graphite oxide, which enabled for clear distinction between the OH stretching vibrations of structural hydroxyl groups and adsorbed water molecules. By using deuteration experiments a previously obscured, hidden band has also been revealed (which can be assigned to organic carbonates) and it has been evidenced as well that phenolic OH groups, besides terminating the edges of the GO layers, may exist along the basal planes of the carbon sheets.

1.c XPS measurements showed (in agreement with the results of infrared spectroscopy) that the compound included a significant amount of carbonyl groups. Thus these species cannot be exclusively attributed to the presence of the COOH groups at the edge sites. Moreover, their amount greatly increases after the subsequent oxidation steps which refers to the evolution of the surface speciation, that is, OH groups and ethers progressively transform to moieties of higher oxidation number such as ketones, quinones or carboxylic groups.

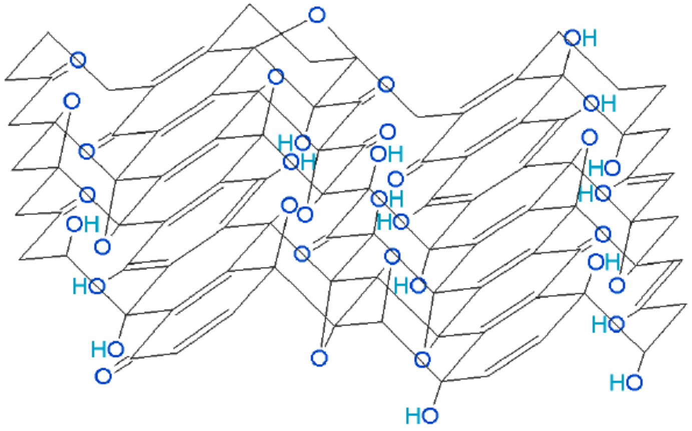
1.d Graphite oxide has never been examined by ESR-spectroscopy by far. It was pointed out for the first time that the moderately oxidized graphite oxides possessed microwave absorption, while the well oxidized solids showed no spin resonance. The origins of the spin species in the former materials are not localized free radicals or graphite-like conduction electrons. Instead, they are mobile π electrons of condensed aromatic ring systems confined to small (nanometric or sub-mamobetric) areas which remained over the lamellae due to incomplete oxidation.

1.e Self-supporting thin films could be prepared from graphite oxides via casting/evaporation of suspensions containing finely dispersed particles. The as-obtained, 15 µm thick membrane is flexible, exhibits fair mechanic stability and, it can be cut into arbitrary shapes. It was established (in good correlation with the ESR and XPS investigations) that the conductivity of GOs could be tuned from the semi-conductive to the insulating state by simple repetition of the oxidative treatments.

T.2 *A new structure model of graphite oxide*

The above results clearly pointed out that the previous structure models of graphite oxide could not be upheld; therefore, a new one was proposed.

According to this model, the chemical structure of graphite oxide is based on a corrugated carbon skeleton consisting of flat carbon hexagons and trans linked cyclohexane chairs. In the case of moderate oxidation state, nanometric domains of condensed aromatic ring systems may remain unoxidized, which are randomly distributed over the lamellae. The oxygen-containing species featuring the model (tertiary alcohols, phenols, ketones, quinones and 1,2- and 1,3-ethers) are linked to the carbon network by covalent bonds and can be orientated either above or below the layer planes, while the edges of the GO slabs are terminated by COOH and OH groups.



The structure model of GO proposed

In contrast to the previous ones, the present model proposed can be reconciled with all the observed properties (chemical formula, oxidative and acidic character, NMR, ESR, IR and XPS spectra) of graphite oxide without the necessity to assume highly instable structure elements.

T.3 *Nanostructure and colloid chemical properties of graphite oxides*

3.a By means of small angle X-ray scattering (investigated for the first time for solid state GO) it was established that, in contrast to the totally flat surface of graphite lamellae, the GO particles turned to be more and more folded and crumpled upon oxidation. The highly oxidized samples exhibit surface fractal dimensions of 3, which is consistent with the TEM observations showing the presence of wrinkled membranes. The correlation lengths of the GOs showed a decreasing tendency: partial exfoliation occurs in the course of oxidation. The specific surface areas, although do not approach the geometrical surface area, were found to be one magnitude higher that the BET-surfaces, indicating that (i) the solids contain closed pores and (ii) the stacked lamellar aggregates are the primary, homogeneous scattering centers.

3.b Geometrical considerations enabled me to calculate the specific surface area of the ultimately exfoliated graphite oxide lamellae. The obtained geometrical surfaces ranged from 1650 to 1800 m^2/g dependig on the extent of oxidation, which are in excellent agreement with those experimentally determined earlier from adsorption from binary mixtures.

3.c It has been proven that the potentiometric acid-base titration is applicable for the quantitative characterization of the surface charge developed on the GO lamellae dispersed in electrolyte media. Proton binding isotherms were found to be greatly influenced by the solution conditions, that is, the pH and the electrolyte concentration. The results of the titrations also pointed out that the cation exchange capacity of the graphite oxides could not be characterized by a single value because it was strongly affected by the above parameters. The surface density of dissociated functional groups could be also calculated in terms of the surface charging curves and the specific surface areas of GOs. BET surface areas determined by N_2 adsorption provided irrationally high site densities, while the geometrical surface areas provided acceptable values. Finally, it could be concluded that the subsequent oxidative treatments resulted in the enhanced acidity of graphite oxides.

T.4 *Fabrication of conductive carbon nanofilms from ultrathin self-assembled GO/polymer multilayers*

Graphite oxide was successfully deposited on glass slides with a cationic polyelectrolyte (PDDA) by means of layer-by-layer self-assembly. The optical thickness of the alternating PDDA/GO multilayers was proportional with the number of deposition steps (bilayer numbers). X-ray diffraction revealed that the GO layers were present in hydrated state in the ultrathin films. Hydrazine reduction of the nanofilm did not restore the graphitic structure; instead, the XRD patterns and AFM images showed the presence of turbostratic carbon involving paralelly aligned graphenes without a real three-dimensional ordering. However, this carbon/PDDA film can be transformed to a partially graphitized thin layer by calcination at 400 °C, via which its electric conductivity increases by at least four magnitudes.

T.5 *Preparation of a carbon nanocomposite with superparamagnetic behaviour*

Graphite oxide offers a novel preparative route towards magnetically modified turbostratic carbons. The synthesis involves two steps: (i) subjection of GO to ion-exchange reaction with $[Fe(bipy)_3]^{2+}$-ions, and (ii) calcination of the as-prepared product at temperatures higher than the deflagration point of GO (e.g. 400 °C). The success of the experiment depends crucially on the pH of the suspension used for ion-exchange: an insignificant amount of iron precursors adsorbs on GO at the original, slightly acidic pH. On the other hand, the amount of iron complex immobilized on GO surfaces and in the intergallery space can be greatly increased at alkaline pHs due to the enhanced acidity and the peptization of the aggregated lamellae. The high surface area turbostratic carbon nanocomposite obtained after calcination contains (besides haematite) highly dispersed maghemite nanocrystals exhibiting superparamagnetic behaviour, being responsible for the magnetization observable in macroscopic dimensions too.

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