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Effect of chemical heterogeneity on photoluminescence of graphite oxide treated with S-/N-containing modifiers

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ABSTRACT

Graphite oxide (GO) obtained using Hummers method was modified by hydrothermal treatment either with sulfanilic acid or polystyrene (3-ammonium) sulfonate at 100 °C or 85 °C, respectively. Both modifiers contain sulfur in the oxidized forms and nitrogen in the reduced forms. The materials were characterized using FTIR, XPS, thermal analysis, potentiometric titration and SEM. Their photoluminescent properties and their alteration with an addition of Ag^+ were also measured. As a result of these modifications nitrogen was introduced to the graphene layers as amines, imides, amides, and sulfur as sulfones and sulfonic acids. Moreover, the presence of polyaniline was detected. This significantly affected the polarity, acid–base character, and conductivity of the materials. Apparently carboxylic groups of GO were involved in the surface reactions. The modified GOs lost their layered structure and the modifications resulted in the high degree of structural and chemical heterogeneity. Photoluminescence in visible light was recorded and linked to the presence of heteroatoms. For the polystyrene (3-ammonium) sulfonate modified sample addition of Ag^+ quenched the photoluminescence at low wavelength showing sensitivity as a possible optical detector. No apparent effect was found for the sulfanilic acid modified sample.

1. Introduction

Graphite oxide, a richly oxygenated derivative of graphene, has been of recent interest of materials scientists due to its unique surface features and easiness of modifications. Its chemical composition is dependent on an oxygen content and synthesis route. The incorporation of covalently bound oxygen groups such as epoxy, carboxylic and phenolic [1] to the graphitic layers results in surface defects. The chemically active nature of graphite oxide (due to the presence of highly unstable epoxy groups) encourages researchers to further study this material and its behavior upon various modifications or treatments. As a result of these, the fabrication of chemically modified graphite oxides that can be used for electrochemical process (capacitors) and energy storage [2,3], sensing [4], composites [5–7] and adsorbents [8] have been demonstrated.

Generally, the modification of graphite oxides (GO) can either be carried out via an introduction of organic functional groups depending on the application and desired properties. Teng and coworkers reported the tuning of the electronic structure of GO using a steady stream of NH_3, which resulted in an n-type conductivity enhancing water splitting [9]. In another approach graphite oxide was treated with octadecylamine to produce amido graphites with decreased hydrophilic properties [10]. A chemical reduction of graphite oxide with amino acids and subsequent heat treatment lead to the formation of highly ordered graphitic carbon that are stable in organic solvents [11]. Lee and coworkers used ammonium carbonate, $(NH_4)_2CO_3$, as a precursor for the introduction of amine groups and the in situ dissipation of ammonia played an important role in the functionalization process [12]. The potential usage of graphite oxide and its aminoazobenzene derived composites in energy storage electrodes was investigated [13].

Another heteroatom widely introduced to GO is sulfur. Krueger and coworkers functionalized graphite oxide with thiol groups using phosphorus pentasulfide (P_4S_{10}). The thiolated graphite oxide was further used for transition metals decoration with high nanoparticle loading [14]. Treatment of GO with poly-sodium polystyrene sulfone increased the interlayer spacing and improved the thermal and electrical properties of the material [15]. A sulfur

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reduced graphene oxide was obtained using a sodium thiosulfate precursor and further used as Hg^{+2} adsorbent [16]. In another approach graphite oxide was modified with aromatic thiol groups and was further investigated as a potential low cost purification material [17]. Thermal treatment of GO in sulfur dioxide atmosphere resulted in an incorporation of sulfur containing functional groups [18]. A simple exfoliation of graphite oxide in the presence of carbon disulfide led to formation of graphene–sulfur nanocrystals with a high performance in lithium–sulfur batteries [19]. Exploring the thio-ene photo polymerization of graphite oxide led to a simple method for the fabrication of UV-curable nanocomposite coatings with higher glass transition (T_g) temperatures than thio-enes nanocomposites. The enhancement in the thermal properties of those composites was primarily attributed to the strong dispersive and interfacial adhesion phenomenon between functionalized graphene and thio-enes [20].

Since modified GO can be used as a composite component [8,21–24] and an increase in GO chemical heterogeneity was shown as a positive factor affecting the final properties of the materials as separation media [25], the functionalization of graphite oxide leading to heterogeneous structures desires further exploration. Thus the objective of this paper is to evaluate the surface chemistry of the GOs modified using a simple hydrothermal treatment in the presence of chemicals containing reduced nitrogen groups and oxidized sulfur groups. The emphasis is on the chemical nature of S- and N-compounds incorporated to GO and on their acid-base properties. Even though the sulfur and nitrogen co-doped GO have been recently synthesized using either two different precursors such as NH_3 and H_2S [26], pyrimidine and thiophene [27], or one precursor such as thiourea [28] or sulfide reducing bacteria [29] the novelty of our approach is in usage of simple organic compounds containing specific chemical configurations of sulfur (oxidized) and nitrogen (reduced) as a source of heteroatoms. The changes in the GO chemistry are expected to originate not only as a result of the precursor-graphene matrix interactions but also from transformation within the precursor molecule. The analysis of the surface properties is of paramount importance for the possible application of these materials as components of more complex nano-composites for a wide range of applications [30,31]. Moreover, the luminescence properties of the resulting materials were tested and the effect of the GO surface and the presence of heteroatom-based polar species on these phenomena was evaluated. This test could be an indirect indication of the suitability of a graphene-based phase for application as optical sensors.

2. Materials and methods

2.1. Materials

Graphite oxide was synthesized by the oxidation of graphite following a well known Hummers methods [32] and it was used as a precursor for sulfur- and nitrogen-modified GOs. Briefly, graphite powder was oxidized using sulfuric acid, potassium permanganate and hydrogen peroxide at room temperature. The mixture was left overnight for a particle settlement. GO particles were separated from the excess liquid by decantation followed by centrifugation, and washed excessively with water. The wet form of graphite oxide "slurry" was then centrifuged and freeze-dried. A fine brown powder of the initial graphite oxide was obtained. The resulting material is referred to as GO.

A super saturated solution of sulfanilic acid was prepared, sonicated for 0.5 h (8.66 g in 70 mL H_2O) and then transferred to a beaker containing 0.249 g of GO and sonicated for an additional 1 h. The dispersion was stirred for 24 h. The GO/SA mixture was transferred to an autoclave and heated at 100 °C in the oven for 48 h. The product was filtered with excess water and dried in air. The air-dried product is referred to as GO-SA. The conditions of the experiment were chosen not to reduce GO but to use its surface chemistry for further modifications.

Poly (4-styrenesulfonic acid) ammonium salt modified GO, GO-PSN, was prepared by mixing 70 mL of 30 wt.% aqueous polymer solution (polystyrene (3-ammonium) sulfonate), Mw ~ 200,000; Aldrich) with 1.20 g of GO followed by stirring of the suspension for 24 h. The suspension was then transferred to an autoclave and heated at 85 °C for 98 h. The product was then filtered, rinsed with water and dried in air. The air-dried product is referred to as GO-PSN.

3. Methods

3.1. Potentiometric titration

Potentiometric titration experiments were performed with a Metrohm 888 Titrando automatic titrator. The instrument was set at the mode when the equilibrium pH was collected. The initial pH of the samples was recorded. Subsamples of the materials studied of about 0.100 g in 50 mL 0.01 M $NaNO_3$ were placed in a container thermostatted at 298 K and equilibrated overnight with the electrolyte solution. To eliminate the influence of atmospheric CO_2, the suspension was continuously saturated with N_2. The sample suspension was stirred throughout the measurements. Volumetric standard NaOH (0.1 M) was used as the titrant. The experiments were done in the pH range of 3–10. Each sample was titrated with base after acidifying the sample suspension. The experimental data were transformed into a proton binding curves, Q, representing the total amount of protonated sites [33].

By solving integral equation representing total number of acidic groups pK_a using the numerical SAIEUS procedure [33,34] information about a detailed surface chemistry was obtained.

3.2. SEM/EDX

Scanning electron microscopy (SEM), was performed on Zeiss Supra 55 instrument with a resolution of 5 nm at 30 kV. Analyses were performed on a sample powder previously dried. For some samples, a sputter coating of a thin layer of gold was performed to avoid specimen charging. Electron-dispersive X-ray spectroscopy (EDX) analysis was done at a magnification of 15K× with an accelerating voltage of 15.00 kV.

High magnification SEM and EDX studies were performed in a Helios Nanolab 650 Dual Beam from FEI company. This is a microscope with a Schottky field emission source for SEM (FESEM) and a Tomohawk focused ion beam (FIB). The microscope is equipped with energy dispersive X-ray detector (EDS) and electron backscatter diffraction detector (EBSD) from Oxford.

3.3. XRD

To obtain information on the crystallographic structure of the materials XRD was employed. Using standard powder diffraction procedures, the adsorbents (fresh and exhausted) were placed in a mount and inserted in the machine; the X-ray diffraction was measured on a Philips X'Pert X-ray diffractometer using $Cu_{K\alpha}$ radiation with a routine power of 1600 W (40 kV, 40 mA)

3.4. Nitrogen sorption

Nitrogen adsorption isotherms were measured at −196 °C using an ASAP 2020 (Micromeritics, Surface Area and Porosity Analyzer). Prior to each measurement, initial and exhausted samples were outgassed at 120 °C. The specific surface area, S_{BET} (calculated by