Redox processes in graphene oxide for storing and converting energy

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Abstract. In this paper for the first time, a comparison was made of the electrochemical activity of graphene oxides synthesized by modified Hummer's, Brodie and electrochemical methods in aprotic media. Electrodes based on these GOs exhibit electrochemical activity in an aprotic solvent of propylene carbonate with 0.1 M $(C_4H_9)_4NClO_4$ electrolytes in the potential range from -3 to 1 V rel. Ag^+/Ag in 0.01M $AgNO_3$ 0.1M $(C_4H_9)_4NClO_4$ in acetonitrile. These redox processes are irreversible. Despite the fact that the types of oxygen groups in GO synthesized by different methods are the same, the ratio of these groups is different. The specific capacity of electrodes based on GO during redox processes in aprotic media correlates with the C:O ratio determined from elemental analysis. The use of new active electrode materials based on graphene in electrochemical processes will allow the creation of electrochemical energy storage devices with a higher energy density and capacity.

INTRODUCTION

The demand for compact electronic and electrochemical devices with increased functionality requires development of new systems with increased specific characteristics. As recently shown electrochemical energy storage and memory devices [1] with 2D materials demonstrate excellent performance. Using graphene based materials dramatically reduces the size and weight of the devices, as well as significantly improve the dynamics of electrochemical processes. Graphene oxide (GO) is considered as one of the promising derivatives of graphene, in which the ratio of the number of oxidized areas of graphene (sp^3) and regions where carbon has sp^2-hybridization can be controlled by varying the conditions of the material synthesis. GO is considered as promising material for ultra-high density of storage and computational elements production [1-4], highly selective membranes for gas dehumidification [5-6] as well as a an effective conductive additive for positive electrodes of $Li\text{-}V_2O_5$ [7] and or Li-S [8]. A number of synthetic approaches to the production of GO have been demonstrated using both chemical [2] and electrochemical [8] methods for the exfoliation and oxidation of graphite, and the oxidation of CVD graphene by atomic oxygen [9] and photocatalytic oxidation [4]. The control of the degree of oxidation opens up the possibility of obtaining both highly conductive and dielectric materials based on graphene, meanwhile, they can be both hydrophilic and hydrophobic. Numerous studies were focused on the methods of graphene oxidation and types of oxygen groups as well as its stability during thermal treatment under inert atmosphere and water based solutions. At the same time, only a few studies of redox processes in materials based on graphene in aprotic media have been carried out, and there is no information about the electrochemical activity of GO synthesized by various methods. The purpose of this work is to study the redox reactions of functional groups of chemically and electrochemically synthesized graphene oxide in aprotic media. This approach allows us to reveal the role of new active graphene-based electrode materials in electrochemical processes. The use of new active electrode materials based on graphene in electrochemical processes will allow the creation of electrochemical energy storage devices with a higher energy density and capacity.

EXPERIMENTAL

In our experiments, we studied the electrochemical properties of graphene oxides obtained by the modified Hummers method (HGO) [2], Brodie method (BGO) [10] and electrochemically graphite exfoliation (ECGO) [11]. Electrochemical testing of electrodes based on GO was performed in a cell with three electrodes. Silver served as reference electrode, Pt as counter electrode and airbrushed GO film on Al foil as working electrode. To increase the electronic conductivity of the HGO working electrode, carbon nanotubes (0.5 wt.%) were used as a conductive additive. Electrochemical activity of graphene oxide was investigated in aprotic solvents of propylene carbonate with 0.1M $(C_4H_9)_4NClO_4$ in the potential range from -3 to 1 V rel. Ag^+/Ag 0.01M $AgNO_3$ и 0.1M $(C_4H_9)_4NClO_4$ in acetonitrile.

RESULTS

The efficiency of the degree of oxidation of the synthesized graphene oxides was controlled using X-ray photoelectron spectroscopy and transmission infrared spectroscopy. From C 1s photoemission spectra, we found that the types of oxygen groups in HGO, BGO and ECGO are the same, but the ratio of groups is different. The number of carbonyl and carboxyl groups in ECGO is higher than in HGO and BGO (Table 1). The C:O ratio in electrochemically synthesized GO samples is lower than in chemically synthesized ones (Table 1).

Table 1. Summary of C 1s binding energies (eV) and the specific capacities during electrochemical reduction of chemically and electrochemically synthesized GOs at different voltages

Sample	**Type of oxygen group**	**Binding Energy, eV**	**At. %**	**C:O**	**Specific capacity (mA*h/g) of GO after reduction at**	
					-1,6 V	**-2,5 V**
HGO	C=C (sp^2)	284,6	38,7	1,7:1	100	112
	C-O	286,7	52,5			
	C=O	288,2	8,8			
BGO	C=C (sp^2)	284,5	50,5	2,9:1	97	105
	C-O	286,51	45,1			
	C=O	288,35	4,4			
ECGO	C=C (sp^2)	284,6	62,7	4,8:1	67	76

	C-O	286,32	24,5
	C=O	288,3	12,8

FTIR spectroscopy further confirmed that chemical oxidation and exfoliation of graphite results in stronger oxidation of graphite comparing with electrochemical synthesis. Fig.1 shows the IR spectra of the different GOs. A number of vibrations from oxygen-containing functionalities are clearly seen: C=O stretching (≈ 1674–1776 cm^{-1}), COOH/O–H stretching (≈ 3600–2800 cm^{-1}), H–O–H deformation (1620 cm^{-1}), O–H deformation (1408 cm^{-1}) and C-O stretching (number of peaks in the range of 1332-1039 cm^{-1}). The contribution of line ascribed to adsorbed water (1620 cm^{-1}) is significantly smaller relatively carbonyl stretching vibrations in comparison with chemical GOs. Also, in contrast to HGO, the IR spectrum of ECGO and BGO clearly reveals the mode of valence vibrations of C=C bonds, its intensity is higher relative to the mode of adsorbed water (1620 cm^{-1}), which indicates partial preservation of the π-conjugated system in these samples compared to HGO. According Raman spectroscopy, the degree of structural damage of HGO is higher than of BGO and ECGO.

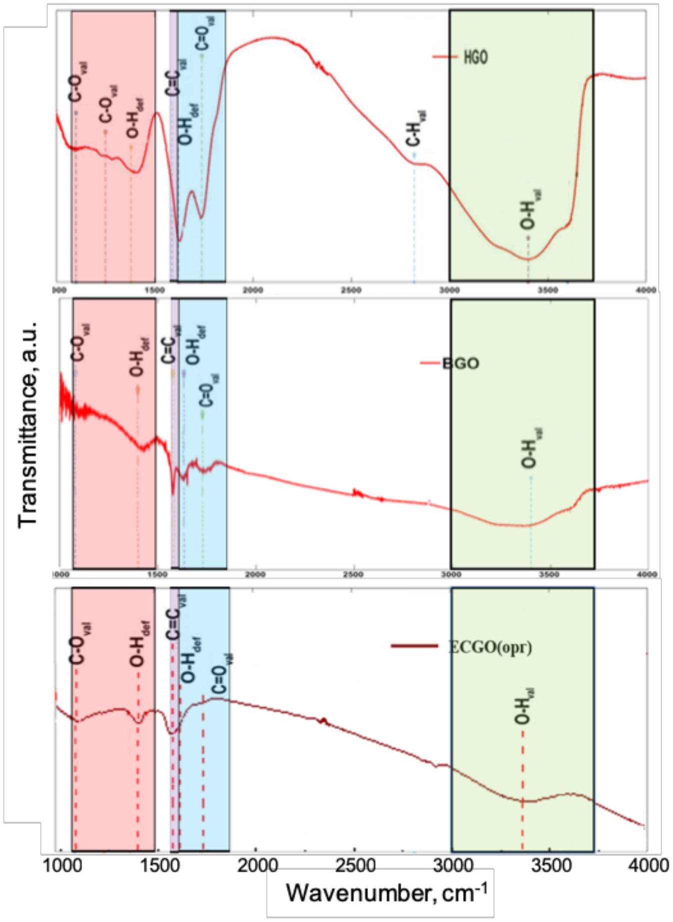

FIGURE 1. FTIR spectra of HGO, BGO and ECGO.

Graphene oxide exhibits electrochemical activity in an aprotic solvent of propylene carbonate with 0.1 M $(C_4H_9)_4NClO_4$ electrolyte in the potential range from -3 to 1 V rel. Ag^+/Ag in 0.01M $AgNO_3$ и 0.1M $(C_4H_9)_4NClO_4$ in acetonitrile. These redox processes are irreversible. The analysis of IR data clearly indicated that the composition of functional groups during electrochemical reduction of graphene oxide differs from the reduction in an aqueous medium. Electrochemical reduction led to the almost complete elimination of carboxyl and hydroxyl groups, as well as intercalated and adsorbed water. Lines ascribed to carbonyl, ether stretching vibrations intensity significantly decreased. C-O vibrations in range 1332–1039 cm^{-1}, which were easily distinguishable before reduction, cannot be resolved after hydrothermal treatment due to broadening and decreased intensity. The appearance of a peak corresponding to the aromatic system (stretching $C{=}C_{val}$ 1588 cm^{-1}) in the HGO indicates a partial regeneration of the π-system after its reduction. According IR spectroscopy this reduction is partial and some stable oxygen groups still remain during cycling.

In summary, it was found that the type of graphene oxide used significantly affects the behavior of redox processes of GO-based electrodes. The specific capacity of electrodes based on GO during processes redox in aprotic media correlates with the C:O ratio determined from elemental analysis. The differences in reduction efficiency may be due to the better electrical conductivity of the ECGO sample compared to HGO and BGO. It is shown that the cathode current passing through the ECGO electrode at -1.6 V is almost 2 times lower than for chemically synthesized GO (Table 1). At the same time, for ECGO, the charge passed through the cathode during reduction at -1.6 V is 33% less than the charge at -2.5 V. For HGO and BGO, the difference in charge at -1.6 and -2.5 V differs by no more than 11-12%. This is consistent with XPS spectroscopy data. According XPS data for ECGO, the contribution of the most stable to the reduction carbonyl and carboxyl groups was higher than for chemically synthesized GOs. It is possible that due to the elimination of the most stable oxygen containing groups in ECGO, the value of the specific capacity in the sample varies significantly at a more negative potential. Further quantitative elemental analysis is required to confirm these assumptions. Our previous work [9] demonstrated that the contribution of the redox of HGO in the capacity of sulfur-GO based cathode is negligible (<1%). However, it is important to note that the electrochemical studies of graphene oxide in aprotic solvents revealed that when using graphene oxide as an additive or active component in the potential range below -1.6 V Rel. Ag^+/Ag (more negative than the working potentials of Li-S batteries), it is necessary to pay attention to the irreversible reduction of graphene oxide, in which the oxygen groups are partially eliminated, the electrical conductivity increases, the specific surface and polarity of the material decreases, and hence its role in the electrochemical process varies significantly.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (RFBR No. 19-29-03050, No. 17-03-01067 and No. 18-29-06036). This work was performed using equipment purchased within the Program of Development of the Lomonosov Moscow State University.

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