PCCP



PAPER



Cite this: Phys. Chem. Chem. Phys., 2023, **25**, 9648

Received 26th January 2023, Accepted 22nd February 2023

DOI: 10.1039/d3cp00426k

rsc.li/pccp

Introduction

Graphite oxide (GO) is a layered material formed from graphene planes decorated with oxygen-containing groups – hydroxyl, carbonyl, carboxyl, *etc.*^{1,2} There are two main synthetic methods used for GO preparation which are the procedures reported by Brodie^{3,4} and Hummers;⁵ the materials prepared are called B-GO and H-GO, respectively. Both materials are obtained in the form of powders. B-GO and H-GO differ in several physicochemical parameters. The oxidation levels and interplanar distances are quantitatively different, which are measured by XPS and XRD methods, respectively. Qualitative differences may be found in IR, SEM and HRTEM images.⁶

B-GO and H-GO swell easily in polar liquids with an increase in interplanar distances and simultaneous liquid intercalation into the interplanar space. The swollen structures formed were regarded as equilibrium binary phases with temperaturedependent composition and interplanar distances.⁷ In the case

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Phase transformation in the "Brodie graphite oxide-acetonitrile" system – influence of the oxidizing level of the material

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Reversible phase transformation in the Brodie graphite oxide–acetonitrile system, which is intercalation or release of part of the sorbed liquid from the interplanar space accompanied by an increase or a decrease in interplanar distances, is commonly observed in twice-oxidized materials. We observed this phenomenon for once-, twice- and thrice-oxidized materials using the EPR spin probe technique, DSC, and temperature programmed XRD. It was shown that all materials under study formed similar low temperature (LT) and high temperature (HT) swollen structures with acetonitrile. The phase transformation of these structures is observed for materials with different oxidation levels in the same temperature range (\sim 20 K). The twice- and thrice-oxidized material sorbs less acetonitrile at lower temperatures, but shows the same interplanar distances as those in twice- and thrice-oxidized materials. The spin probe technique has proven its sensitivity to the appearance of small amounts of the new forming swollen structures, which makes this method useful in studies of phase transformations.

of H-GO, the latter two parameters changed gradually, which allowed the swollen structures of H-GO to be regarded as solid solutions. For better ordered B-GO,⁶ these parameters are temperature independent in certain temperature intervals, which makes these swollen structures appear as binary solid compounds.

It was recently revealed that B-GO-polar liquid binary systems demonstrated reversible transformations of low-temperature (LT) swollen structures into high-temperature (HT) ones with the release of part of the sorbed liquid.^{8-11,12} Such transformations were observed for acetonitrile, methanol, DMFA, n-octanol, and n-nonanol using XRD and DSC methods. During heating, the process occurred with the adsorption of heat and with a decrease in the interplanar distance. In the case of acetonitrile, the thermal effect is ~ 12 J per 1 g of B-GO; the interplanar distance changes from 12 Å to 9 Å.¹⁰ This process resembles incongruent melting, the phase transformation typical for many inorganic hydrates, e.g. transformation of CaCl₂·6H₂O into CaCl₂·4H₂O with the release of 2 molecules of H₂O. Electron paramagnetic resonance (EPR) combined with the spin probe technique proved to be a new rather sensitive method to monitor phase transformations in the swollen structures of B-GO-polar liquid systems. Using EPR, it was shown that the phase transformation in the B-GO-acetonitrile system proceeds in a wide temperature range ($\sim 20^{\circ}$).¹³ It has been suggested that this wide range reflects the inhomogeneity of the material.¹⁴ At present, there are no reports of theoretical

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calculations that could shed light on the molecular mechanism of particular transformations. However, the application of molecular dynamics methods¹⁵ and *ab initio* methods¹⁶ to similar systems has proved to be rather effective.

The main objective of the present study was to get a clearer understanding of the nature of phase transformations in B-GO swollen structures in the B-GO-acetonitrile system for example. Using EPR and temperature programmed XRD, both of which are rather sensitive to such transformations, we examined the dependence of the transition parameters on the degree of oxidation of B-GO. It is known that Brodie's synthetic procedure can be repeated several times to produce differently oxidized materials. According to the original observation of Brodie, there will be no changes in the composition and properties of B-GO after four repeated oxidation steps.⁴ In the present study, it has been demonstrated that the phase transformation in the swollen structures of B-GO with acetonitrile can be detected for B-GO oxidized one, two and three times (B-GO-1, B-GO-2, and B-GO-3, respectively) in the same temperature interval; however, the amount of acetonitrile intercalated into the LT swollen structure of B-GO-1 is less than those in B-GO-2 and B-GO-3. The results obtained could be useful for preparation of B-GO membranes and prediction of their temperature behavior since sorption/swelling could be a key factor determining transport through such membranes.

Experiment

Substances

Graphite oxide was obtained by oxidizing graphite according to the Brodie method.⁴ Natural graphite flakes (200–300 μ m, Zavalyevskoye field) were used as the starting material. Oxidation was performed using a mixture of potassium chlorate (KClO₃; TetraChem, >99.95%) and fuming nitric acid (HNO₃). Distilled water and hydrochloric acid (HCl; 10 w%, TetraChem) were used for graphite oxide purification.

Acetonitrile for HPLC was purchased from RCI Labscan.

The stable nitroxide radical TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl) was used as a spin probe. The radical was purchased from Sigma-Aldrich.

Synthesis

At the first oxidation step, graphite (5 g) was mixed with potassium chloride (49.3 g) and fuming nitric acid (35 mL) was added dropwise to this mixture with further stirring for 6 hours at room temperature. The next day, an excess amount of fuming nitric acid (15 mL) was added to the resulting mixture and the mixture was heated to 330 K with stirring for 8 hours. After that, the mixture was cooled to room temperature and placed in 1 L of distilled water. The obtained graphite oxide (B-GO-1) was decanted and washed with hydrochloric acid solution and distilled water until the pH of the solution reached 7. Then the B-GO-1 sample was dried by the freezedrying method. The mass of dried B-GO-1 was 4.8 g; the reaction product yield was 70%. B-GO-1 was re-oxidized according the same method; the twice-oxidized material is named B-GO-2. The product obtained from re-oxidation of B-GO-2 is named B-GO-3. The reaction product yields for B-GO-2 and B-GO-3 were 95% and 93%, respectively.

EPR spectroscopy

Sample preparation. The radicals were dissolved in acetonitrile to form a solution with a concentration of $\sim 1 \text{ mmol L}^{-1}$ and then 3–5 mg of B-GO was mixed with the excess of the solution. The resulting samples were heterogeneous equilibrium mixtures of swollen B-GO and the bulk liquid. It was shown earlier that, in such a mixture, TEMPOL radicals penetrated into the interplanar space of B-GO together with acetonitrile and equilibrated between the inner surfaces of the material, intercalated acetonitrile and bulk acetonitrile.¹³ The amount of radicals in the swollen samples reached \sim (2–5) × 10¹⁵ spins per 1 mg of graphite oxide.

EPR spectroscopy. EPR spectra were recorded using a Bruker EMX-500 spectrometer in the temperature range of 210–350 K. A Bruker temperature control unit (accuracy: ± 1 K) and a highsensitivity Bruker ER 4119 HS resonator were also used. The spectra of the solutions were recorded at room temperature in glass tubes with an inner diameter of 1 mm. The spectra of the B-GO–acetonitrile–TEMPO samples were recorded in quartz ampoules with an inner diameter of 2 mm. The microwave power was chosen in such a way to avoid saturation of the EPR signals of the probe molecules.

XRD. The X-ray diffraction (XRD) spectra of the initial dry powders of B-GO-1, B-GO-2 and B-GO-3 at T = 298 K were recorded on a Rigaku D/MAX 2500 instrument with CuK α radiation ($\lambda = 1.5418$ Å).

The temperature dependences of the XRD spectra were obtained using a Synergy-DW HyPix-Arc 150° (Rigaku Oxford Diffraction) instrument with MoK α radiation ($\lambda = 0.7090$ Å). The instrument was equipped with a Cobra Plus cryosystem (Oxford Cryosystems). The measurements were carried out in the 2θ range of up to 60° in the temperature interval of 220–300 K. The temperature of the system studied was equilibrated for 15 minutes before each measurement.

DSC. The measurements were carried out with a DSC-30 TA instrument from Mettler. DSC heating traces in the B-GO-CH₃CN systems were used to determine the sorption of acetonitrile (g g⁻¹) at its melting temperature ($T_{\rm m}$ = 228 ± 1 K, ref. 17). Samples for DSC measurements were prepared by saturation/swelling of B-GO in the excess of CH₃CN. The method of determining sorption is based on an experimental observation^{7,18} that liquids sorbed into the interlayer space of GO do not take part in the melting/freezing process at $T_{\rm m}$. The mass of free liquid in direct contact with B-GO was determined from the area of the melting peak at $T_{\rm m}$. Subtracting this mass from the total mass of CH₃CN in the system provides the amount of CH₃CN sorbed by B-GO. The peak corresponding to the phase transformation of the LT to HT swollen structure was detected on the same DSC heating traces. The temperature of the transition was additionally checked using the melting temperature of CH₃CN as an internal standard. The cooling DSC traces showed the supercooling of ~ 20 K for both freezing of acetonitrile and HT \rightarrow LT transformation.

Isopiestic measurements

The values of equilibrium sorption of acetonitrile into B-GO samples at 298 K were determined by the isopiestic method. Equilibration of B-GO with acetonitrile vapor in a thermostatic desiccator continued until the mass of the swollen GO saturated with the solvent became constant.

XPS. XPS analyses were carried out using a Kratos Axis Ultra DLD instrument. The samples were evacuated at a pressure of 10^{-9} torr for 2 hours. An aluminum anode (AlK α) was used as the radiation source. Survey and high resolution spectra were recorded at transmission energies of 160 eV and 40 eV, respectively. The spectra were calibrated to an O1s binding energy of 532.5 eV.

Results and discussion

Parameters of dry B-GO powders

The interplanar distances and C: O ratios for the B-GO samples prepared are presented in Table 1 and Fig. 1 along with the sorption data for CH₃CN into the same materials. For comparison, Table 1 shows also the characteristics of B-GO-2 reported in the literature. Taking into account the uncertainties of measurements, it may be stated that the parameters of B-GO-1, B-GO-2, and B-GO-3 differ only slightly. However, the increase in the C:O ratio and the decrease in the d(001)interplanar distance of B-GO-1 are visible. The XRD spectrum of B-GO-1 even indicates the presence of unoxidized areas of graphite (see the peak at $2\theta = \sim 28^{\circ}$ in Fig. 1); d(001) = 3.4 Å.¹⁹ An attempt to separate B-GO-1 from graphite by suspending the former in water failed. It was found that B-GO-1 cannot be suspended. This indicates that the oxidized and unoxidized areas are located on the same flakes of the material. Apparently, B-GO-1 flakes were oxidized at the edges, but retained the structure of unoxidized graphite in the middle. Similar H-GO materials with low oxidation levels are described in detail in ref. 20. Sorption of CH₃CN at 295 K is equal for all three materials. However, it can be noted that sorption into B-GO-1 at 229 K is lower compared to the other samples.

Phase transformation of swelled graphite oxide as revealed by EPR spectroscopy

The EPR spectra of the spin probe TEMPOL in the B-GO-2acetonitrile system recorded at two different temperatures are





7.0 Å

Fig. 1 XRD ($\lambda = 1.5418$ Å) spectra of B-GO-1 (black line) and B-GO-3 (red line) dry powders. The XRD patterns were normalized to make the intensity at the maxima equal.

shown in Fig. 2a. Each spectrum is a superposition of three signals, namely, the native signal of B-GO and the signals of the radicals characterized by fast and slow rotational mobility. The detailed interpretation of these spectra including computer simulations is given in ref. 13. Fast rotation is typical for radicals dissolved in liquid acetonitrile, both bulk and intercalated into the interplanar space of B-GO, while slow rotation can be attributed to radicals sorbed on the inner surface of the material. It is well known that the distance between the low-field and high-field lines of the spectra of the low mobility (slowly rotated) nitroxide radicals (ΔB) correlates with the rotational mobility of these paramagnetic species.²¹ A decrease in ΔB reflects an increase in the rotational mobility of radicals.

Fig. 3a presents the temperature dependences of ΔB for the B-GO-1–acetonitrile–TEMPOL, B-GO-2–acetonitrile–TEM-POL, and B-GO-3–acetonitrile–TEMPOL systems. It is known that the Brodie graphite oxide is chemically stable up to 420 K;⁶ hence, all observed effects reflect the changes in the swollen structures. It can be seen that above 275 K and below 255 K the values of ΔB increase (the rotational mobility of the spin probes decreases) with decreasing temperature. Such dependence is quite common. However, in the range of 275–255 K, the values of ΔB decrease (the rotational mobility of the spin probes increases) with decreasing temperature. In the same temperature interval, the HT swollen structure of B-GO-2 with CH₃CN transforms into the corresponding LT structure.^{10,13} The phase transformation is accompanied by an increase in interplanar distances (see Fig. 2c). The increase in the distances between

Table 1 Parameters of the B-GO samples				
	Interplanar distance <i>d</i> (001), Å	Oxidation level C:O	Equilibrium sorption at 229 K g g^{-1} (GO)	Equilibrium sorption at 295 K g g^{-1} (GO)
B-GO-1	6.0 ± 0.2	3.3 ± 0.3	0.46 ± 0.07	0.21 ± 0.03
B-GO-2	6.6 ± 0.2	2.8 ± 0.3	0.54 ± 0.09	0.20 ± 0.03
B-GO-3	7.0 ± 0.2	2.5 ± 0.3	0.53 ± 0.05	0.25 ± 0.03
B-GO-2 ⁷	6.7 ± 0.2	2.6 ± 0.3	0.53 ± 0.04	0.25 ± 0.02



Fig. 2 (a) EPR spectra of the B-GO-2-acetonitrile-TEMPOL system recorded at 210 K (blue line) and 245 K (black line). (b) Determination of ΔB for the low mobility nitroxide radicals. The intensive native signal of graphite oxide is clipped. (c) Phase transformations between the high-temperature and low-temperature swollen structures.



Fig. 3 (a) Temperature dependences of ΔB for the "B-GO-1-acetonitrile-TEMPOL" (black), "B-GO-2-acetonitrile-TEMPOL" (red), and "B-GO-3-acetonitrile-TEMPOL" (blue) systems. The dependences were recorded with decreasing temperature. (b) Semilogarithmic temperature dependences of the rotational diffusion coefficients (s⁻¹) of the spin probes in the systems under study (the color representation is the same as that in (a)). All lines are a guide to the eye.

the oxidized graphene layers, presumably, causes an increase in the mobility of the sorbed radicals. Hence, EPR is able to detect the appearance of even a small amount of the new structure, in the case under consideration – the LT structure, and to capture the beginning of the phase transformation. The end of the inverse temperature dependence means that the LT structure has been formed. The data presented in Fig. 3a show that the swollen structures of B-GO-1 and B-GO-3 with CH₃CN also undergo phase transformations, and the temperature intervals of the transformation coincide with those for the B-GO-2–acetonitrile system.

Fig. 3b shows the temperature dependences of the rotational diffusion coefficients D_{rot} of the spin probes in all systems

under study; the dependences are presented in Arrhenius coordinates. The $D_{\rm rot}$ values were calculated from the values of ΔB on the basis of spectral simulations performed in our earlier work.¹³ It can be seen that the slope of the dependences presented in Fig. 3b in the regions before and after the phase transition (above 275 K and below 255 K, respectively) is close for all systems. This means that the mechanism of rotational mobility of the radicals sorbed on the oxidized graphene planes is the same; the characteristic activation energies of rotation reach ~(8–18) kJ mol⁻¹.

The dependences presented in Fig. 3a show that the increase in the rotational mobility of the spin probes during the phase transformation in the case of B-GO-1 is much less than that in the cases of B-GO-2 and B-GO-3. The sorption data presented in Table 1 indicate that the amount of acetonitrile intercalated into B-GO-1 during the phase transformation is less in comparison with B-GO-2 and B-GO-3. An indirect proof of this fact is the absence of DSC heating traces reflecting the phase transformation in the B-GO-1–acetonitrile system. Apparently, in this case, the sensitivity of DSC is insufficient to detect the phase transition. Based on the above, it can be assumed that the mobility of sorbed radicals in the area of the phase transformation correlates with the amount of intercalated liquid: the more the liquid in the interplanar space, the higher the mobility of the radicals on the surface (T = const.).

Phase transformation of swollen B-GO as revealed by temperature programmed XRD

The phase transformations in all systems under study were also observed using temperature programmed XRD. The temperature dependence of XRD spectra for the B-GO-2–acetonitrile system recorded on cooling is shown in Fig. 4a. Fig. 4b allows examining in detail the shape of the spectra.

One can see that above 285 and below 265 K there are two different spectra with the same position of the peak maximum $(2\theta = 9.0 \text{ and } 2\theta = 12.5, \text{ respectively})$. They correspond to HT and LT swollen structures. It is worth noting that such wide temperature intervals with constant XRD patterns were not

Fig. 4 (a) Temperature dependences of the XRD (λ = 0.7090 Å) spectrum for the B-GO-2-acetonitrile system. The experiment was carried out on cooling. Arrows show the interval of the phase transformation in the peak intensities. (b) XRD spectra for the B-GO-1-acetonitrile and B-GO-2-acetonitrile systems at temperatures of 220 K and 300 K.



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reported for H-GO swollen structures. HT and LT structures may be viewed as phases, and the sorption at 295 K and 229 K (see Table 1) determines the compositions of the HT and LT phases, respectively. The HT \rightarrow LT phase transformation occurred gradually in the temperature interval of 285–255 K on cooling. A similar temperature interval of the transformation was indicated by the EPR experiments (see Fig. 3).

The temperature dependence of XRD spectra for the B-GO-1– acetonitrile and B-GO-3–acetonitrile systems was found to be similar to the dependence for the B-GO-2–acetonitrile system. Phase transformations were observed for all three systems. In Fig. 4c the XRD spectra for the B-GO-1–acetonitrile and B-GO-2–acetonitrile systems at 220 K and 300 K are compared. It should be noted that the interplanar distances in the LT and HT phases of the low-oxidized B-GO-1 are similar to those in the corresponding swollen structures of B-GO-2. At the same time, the amount of intercalated acetonitrile in the B-GO-1 LT phase is less than that in the B-GO-2 LT phase (see Table 1). It can be assumed that the LT phase of the B-GO-1–acetonitrile system is a "pillared structure" similar to that described in ref. 22. In such a case, acetonitrile is located only in the oxidized regions of the material, "maintaining" certain interplanar distances in the non-oxidized regions. This hypothesis can be proved by the fact that in the XRD spectra of swollen B-GO-1 there is no reflex of unoxidized graphite, similar to the reflex observed for the dry material (see Fig. 1).

The transformation of the LT structure into the HT structure on heating, as revealed by EPR, XRD and DSC

Fig. 5a–c presents the transformation of the swollen structures of B-GO-2 on heating; the process was observed by three different methods. XRD detected a decrease in the interplanar



Fig. 5 The LT-to-HT transformation of the swollen structure. Black arrows limit the interval of phase transformation. (a) XRD (λ = 0.7090 Å) spectra of the B-GO-2–CH₃CN system recorded on heating, (b) ΔB vs. T^{-1} for B-GO-2–CH₃CN recorded on heating through EPR measurements, and (c) DSC heating trace for the B-GO-2–CH₃CN system.

distance in the temperature interval from 280 K to 295 K (Fig. 5a). EPR pointed to almost the same interval (275–300 K) of transition (Fig. 5b). The broad endothermic DSC peak of transition extended from 280 K to 295 K (Fig. 5c). The DSC peak extremum appeared at ~60 degrees above the equilibrium melting temperature of acetonitrile. The latter temperature value was observed on the same DSC trace and served as the internal standard. Compared to the other two methods, DSC is better suited for detecting the discontinuity in the phase transformation. The three methods showed that the phase transformation occurred in the temperature interval of $\Delta T_{\rm trr}$ ~ 20 K. Similar data were obtained for the swollen structures of B-GO-3. For B-GO-1, the DSC peak was not detected. A comparison of heating and cooling XRD data (see, *e.g.*, Fig. 4a and 5a) showed that overcooling in the system amounted to approximately 20 K.

Three phases, namely, LT, HT, and liquid acetonitrile, can coexist in equilibrium only at one temperature. By simple equilibrium approximation, the transformation of the LT swollen structure into the corresponding HT structure should occur at only one temperature where the LT and HT structures coexist in equilibrium with the liquid (the peritectic temperature). One has to assume that this temperature is located within $\Delta T_{\rm tr}$. The reason for the occurrence of the temperature interval of transition could be the inhomogeneity of the composition of the LT and HT swollen structures and/or the formation of the solid solutions of LT and HT.

Conclusions

Brodie graphite oxide materials produced by repeated oxidation form similar low temperature (LT) and high temperature (HT) swollen structures with acetonitrile. These structures were characterized by a spin probe method, temperature-programmed XRD and sorption measurements. For materials made through twoand three-oxidation steps, the interplanar distances and compositions of B-GO/acetonitrile were very close and reproducible. In the one-time oxidized material B-GO-1, the degree of oxidation was lower which led to a reduction of sorption at low temperature (229 K). The LT structure in this case contains less acetonitrile, while the HT structure shows the same composition as the HT structure for B-GO-2 and B-GO-3. The transformation from the LT to HT swollen structure was detected in a certain temperature interval (~ 20 K) for all materials under study. The upper and lower limits of the transition interval were detected by spin probe and XRD methods. The former method, which has recently begun to be used to study graphene oxide based materials, proved to be a sensitive tool for detecting phase transformations in B-GO swollen structures. The method revealed the phase transformation of B-GO-1 swollen structures that could not be detected by DSC.

Author contributions

Conceptualization – N. A. Ch., M. V. K., and E. A. E.; methodology – N. A. Ch. and M. V. K.; investigation – D. S. P., A. V. K., O. N. Kh., and A. T. R.; funding acquisition – A. T. R.; writing – original draft – N. A. Ch.; and writing – review and editing – N. A. Ch. and M. V. K.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

This research was funded by Russian Scientific Foundation (RSF) (grant no. 21-73-00124) and partially by the Program of Fundamental Research of the Russian Federation (reg. no. 122040500068-0) and the Ministry of Science and Higher Education within the State assignment FSRC 'Crystallography and Photonics' RAS. The temperature dependences of XRD spectra were obtained using the equipment of the Shared Research Center FSRC 'Crystallography and Photonics' RAS. We thank Dr S. Savilov and his group at the Scientific Centre of NanoChemistry and NanoMaterials in the Department of Chemistry of MSU for making XPS measurements.

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