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Graphite oxide swelling in molten sugar alcohols and their aqueous solutions.

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ABSTRACT

Graphite oxides (GO) are intercalated rapidly by one to several layers of solvent when immersed in liquid but the GO solvates are typically unstable on air due to solvent evaporation. Here we study swelling of GO in solvents (sugar alcohols) with melting temperature point above ambient. Using *in situ* synchrotron radiation XRD experiments we demonstrated GO swelling in molten xylitol and sorbitol. The expanded GO structure intercalated with one layer of xylitol or sorbitol is preserved upon solidification of melt and cooling back to ambient conditions. The structure of solid solvates of GO with xylitol and sorbitol is based on non-covalent interaction and pristine GO can be recovered by washing in water. Intercalation of xylitol and sorbitol into GO structure in aqueous solutions yields similar but less ordered structure of GO/sugar alcohol solid solvates. Very similar inter-layer distance was observed for GO intercalated by sugar alcohols in melt and for GO immersed in sugar solutions. This result shows that sugar alcohols penetrate into GO inter-layer space without hydration shell forming 2D layers with orientation parallel to graphene oxide sheets. Therefore, hydration diameter of molecules should not be considered as decisive factor for permeation through graphene oxide inter-layers in multilayered membranes.

1. Introduction

Graphite oxides (GO) are materials with 150 years old history which recently attracted enormous attention as precursors for preparation of graphene.[1] The easiest method to produce graphene discovered already in 1960-s is to disperse GO in water using mild sonication and then to reduce single layered graphene oxide sheets.[1-2] These dispersions can be then deposited as multilayered graphene oxide papers[3] and membranes.[4-5]

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GO preserves layered structure inherited from precursor graphite but the interlayer distance increases up to $\sim 6\text{-}7$ Å due to oxidation [4, 6]. The exact structure of graphite oxide was debated in hundreds of studies over past years, see e.g.[7-14]. A number of functional groups was experimentally identified as a part of GO already in 60-s (e.g. carboxyl, hydroxyl, enol, ether, double bonded oxygen [15]). However, early attempts to identify exact periodic structure of GO were not successful. Starting from the end of 90-s the structural model of Lerf-Klinowski become the most widely cited. The model suggested non-periodic and non-stoichiometric structure which cannot be determined e.g. by X-ray diffraction (XRD) methods.[16-17] The Lerf-Klinowski model suggests functionalization of graphene sheets by epoxy and hydroxyl groups on the planes [8-9, 18] Other functional groups are known to terminate edges around graphene oxide flakes, edges of holes in the flakes and be attached to vacancies or point defects.[9, 13, 19] Among them carboxylic groups are most important since they are responsible for the acidic character of GO in solution. In recent years many studies with detailed analysis specific types of functionalization of graphene oxide on planes and edges were published - see for example recent reviews in refs.[18, 20] However, very often the new models describe properties of specific material synthesized (in almost all models) by Hummers oxidation, very often using “modified” procedures and specific oxidation degree. The importance of structural defects produced in graphene oxide in Hummers oxidation was emphasized in some recent studies aimed on reduction of graphene oxide to produce less defected graphene.[21-23] More exotic model which suggested “two-component” structure of graphene oxide[24] proved to be highly controversial. The “cleaning” method proposed to reveal true graphene oxide in this study (washing with NaOH) is known to cause chemical modification of GO. [25-26]

In fact, graphite oxides are many materials, not just one. It can be synthesized by different methods (most common are Brodie (BGO)[27] and Hummers (HGO) [28] oxidation procedures) and with rather strong variation in oxidation degree, defect state, amount of specific synthesis-related impurities (e.g. sulfur), relative amount of functional groups and distribution of functional groups over the graphene surface. Therefore, we argued in our earlier studies that discussion of precise structural model general for any kind of “graphite oxide” has little meaning. Properties of different types of GO very likely demand somewhat different structural models and might be specific for certain types of materials and their preparation methods. It should be noted here structural models of GO were proposed over past 20 years were mostly proposed based on studies of materials produced by Hummers oxidation, e.g. [9, 14] However, BGO and HGO are different materials in respect to some key properties which include e.g. swelling [29-30], exfoliation [30-32] and mechanical properties[33]. The difference between solvation/hydration properties of BGO and HGO was subject of several recent studies but remains to be poorly understood.[32]

Swelling in polar solvents is one of the most remarkable properties of graphite oxides and multi-layered graphene oxide membranes/papers.[4, 29, 34-36] Swelling is of key importance for almost all applications of GO, e.g. dispersion of GO in solutions, solution based chemical functionalization of GO, preparation of pillared porous GO materials,[32, 37-39] preparation of graphene oxide membranes and their permeation in filtration experiments. Swelling can be considered as intercalation of GO with formation of solid solvates or less ordered solid solutions.[40] The solvent molecules inserted between graphene oxide layers are disordered as evidenced by absence of reflections in XRD additional to those which originate from GO structure.

Distinctly different phases which correspond to the structures intercalated with one and two layers of solvent were reported in our earlier studies for BGO in liquid methanol,[41] ethanol,[42] DMF,[42] acetone,[43] acetonitrile, [44] and several others.[44] Multilayered intercalation of octanol was reported in our most recent study.[45] Transitions between the phases with different number of intercalated solvent layers were found under variation of temperature or pressure.[40, 42, 45] Moreover, selective intercalation of methanol from water/methanol mixtures was observed for BGO.[46-47]

In contrast, HGO shows no selectivity in sorption from binary mixtures, no phase transitions and absence of clearly distinct phases with certain amount of intercalated solvent. The gradual changes in the “inter-layer distance” provided by position of (001) reflection in XRD are likely to be explained by the effects of interstratification[48] and intrastratification.[48-49] Interstratification corresponds to random stacking of differently spaced GO layers while intrastratification is related to inhomogeneous hydration/intercalation within one inter-layer of GO structure.

Most of the modern time studies of GO swelling were performed using the same types of solvents which were reported already in 60-s: e.g. short and long chain alcohols,[50-51] glycols,[52] various kind of amines,[53-54] amides,[54] ketones.[52, 54] The common feature of all these solvents is that they are liquid at ambient conditions. Swelling occurs rather rapidly when GO is immersed into liquid solvent, but solvents evaporate at least partly once the GO is exposed to ambient air conditions. The GO/solvent can be frozen to make solid solvates[55] but they are anyway unstable when heated back to room temperature.

Here we present new strategy to prepare materials with expanded GO structure stable at ambient conditions (solid solvates of GO). Sugar alcohols (sorbitol and xylitol) are solids at ambient temperature but become polar solvents above the melting point. Swelling of BGO and HGO in molten sugar alcohols results in the lattice expansion, which corresponds to insertion of one and two molecular layers. The expanded GO structure is preserved at temperatures below the melting point thus allowing to prepare solid solvates stable at room temperatures. Intercalation/sorption of sugar alcohols from aqueous solutions is also demonstrated.

2. Experimental

GO powder was purchased from ACS Materials. It was synthesized using Hummers method and according to X-ray photoelectron spectroscopy (XPS) showed C/O = 2.47. Brodie GO was synthesized using the original procedure using two oxidation steps which resulted in yellow coloured powder. Samples from two different batches were used, first one showed C/O = 2.55 and in later experiments second batch with C/O = 2.7 as determined by XPS. Detailed characterization of these materials using XRD, FTIR, TGA and some other methods were presented in our previous publications.[30, 40, 44, 48, 56] The ref [56] provides characterization of the same materials as those which are used here for study of sugar alcohol intercalation. XRD data were recorded using in house diffractometers Siemens D5000 and PANalytical X'pert using CuK α radiation. Part of the data was recorded using synchrotron radiation at MAX-Lab, beamline, Lund. 2D XRD images were recorded in glass capillaries filled with powders of GO/Xylitol and GO/xylitol mixed in different proportions and heated above melting point (110°C) for 30 minutes. The radiation wavelength was calibrated using a LaB₆ standard ($\lambda = 0.98987 \text{ \AA}$). Fit2D software was used to integrate the diffraction images into diffraction patterns. *In situ* heating experiments were recorded at ID22 beamline, $\lambda = 0.46794 \text{ \AA}$. For these experiment powders of GO and sugar alcohols (xylitol or sorbitol) were pre-mixed with strong excess of sugar to ensure saturated intercalation (~1:2 GO/sugar g/g), loaded into glass capillary with diameter of 0.7 mm. Note that intense grinding of GO/xylitol powders in agate mortar was observed to result in particle intercalation already at room temperature. Therefore, the powders were accurately mixed without grinding. Heating/cooling of samples in sealed capillaries was performed using Oxford Cryosystems CryoStream system. The temperature was changed by steps of ~10 degrees. XRD scans were recorded using short exposure time of ~30 sec, new spot was selected for every scan to avoid degradation of samples under X-ray beam.

3. Results and discussion

First set of experiments was performed using powder of BGO mixed with sorbitol or xylitol in different proportions and annealing for 30 minutes at 110 °C. This temperature is above melting point of sugar alcohols (92 °C and 95 °C for xylitol and sorbitol respectively) but below the temperature limit of GO degradation (~140 °C).

The XRD patterns recorded from these samples after cooling at room temperature are shown in Figure 1. Typical XRD pattern of BGO is known to show rather few and relatively broad diffraction peaks reflecting complete disorder of functional groups. Intercalation of GO is known to result in expansion of interlayer distance of GO structure (provided by (001) reflection) and does not affect in plane lattice of graphene oxide.[41, 57] Therefore, our experiments were mostly focused on the diffraction angle

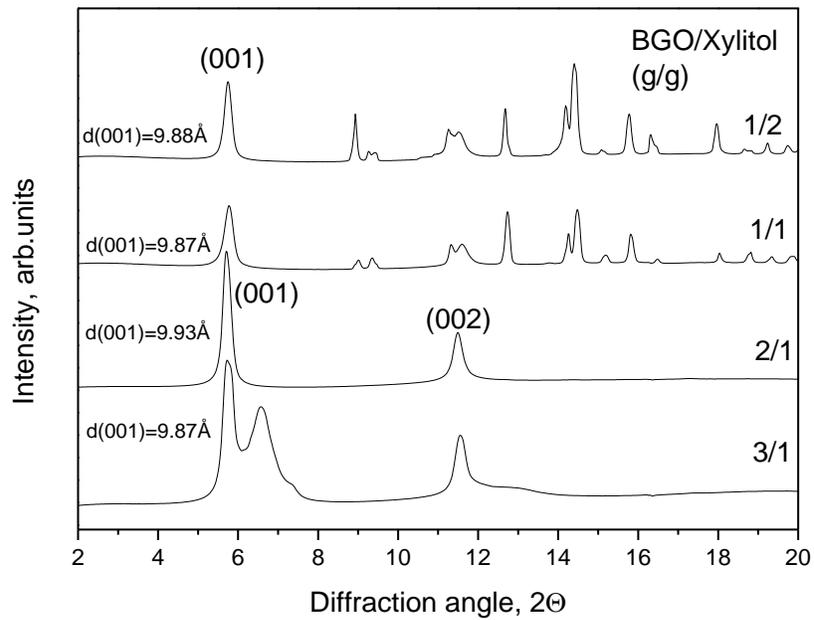
region of (001) reflection which is found at 6.64 Å for precursor BGO at ambient conditions. Sugar alcohols are well crystalline powders which provide high number of rather sharp reflections in XRD patterns and orthorhombic structures. [58-59]

Annealing of BGO in molten sugar alcohols resulted in formation of new phase with expanded lattice. The sample of BGO/Xylitol premixed in 2:1 (g/g) proportion exhibited XRD pattern of reasonably pure intercalated BGO structure with $d(001) = 9.93 \text{ \AA}$ and strongly enhanced intensity of (002) reflection. The samples mixed with BGO/xylitol ratios of 1:2 and 1:1 (g/g) showed also numerous reflections from solidified xylitol, while the sample with 3:1 loading exhibited additional reflection with d-spacing of 8.63 Å. It can be concluded that the composition of saturated BGO/xylitol solvate is very close to the 2:1 (g/g). Molten xylitol is absorbed by BGO structure and excess of solvent crystallize upon cooling. In case if too little xylitol is loaded (1:3), the amount of molten solvent is not sufficient to saturate the BGO/xylitol solvate structure and the sample is inhomogeneous. Note that (001) reflections of intercalated BGO structure are significantly less broad compared to (001) peak of precursor BGO powder. Swelling-induced ordering is reflected in almost twice smaller FWHM of (001) reflection is rather typical for BGO and was reported earlier also for other solvents (e.g. alcohols).[60]

Nearly the same $d(001)$ of 9.93 Å and 9.96 Å are found for BGO intercalated with xylitol and sorbitol, Figure 1b. Both intercalated structures also show remarkably high intensity of (002) reflection which will be discussed in more details below. It can be concluded that sugar alcohols intercalate BGO structure with formation of a new structure which is stable after cooling below the melting points of xylitol or sorbitol. The composition of solid solvate phase is about 2:1 (g/g) for both BGO/Xylitol and BGO/sorbitol.

Test experiments were also performed with HGO samples annealed in excess of xylitol and sorbitol. These experiments revealed that expansion of inter-layer lattice is larger compared to BGO providing $d(001)=16.0-16.2 \text{ \AA}$ for HGO/sorbitol and 15.7-16.4 Å for HGO/xylitol. However, the reflections from HGO/xylitol and HGO/sorbitol were relatively weak and broad compared to precursor HGO. Therefore, we focused our next experiments on study of BGO intercalation. Note that different swelling properties of HGO and BGO were reported in our earlier studies for several solvents. For example $d(001) = 8.9 \text{ \AA}$ and $d(001) = 13.2 \text{ \AA}$ were found for BGO and HGO immersed in methanol respectively.

a



b

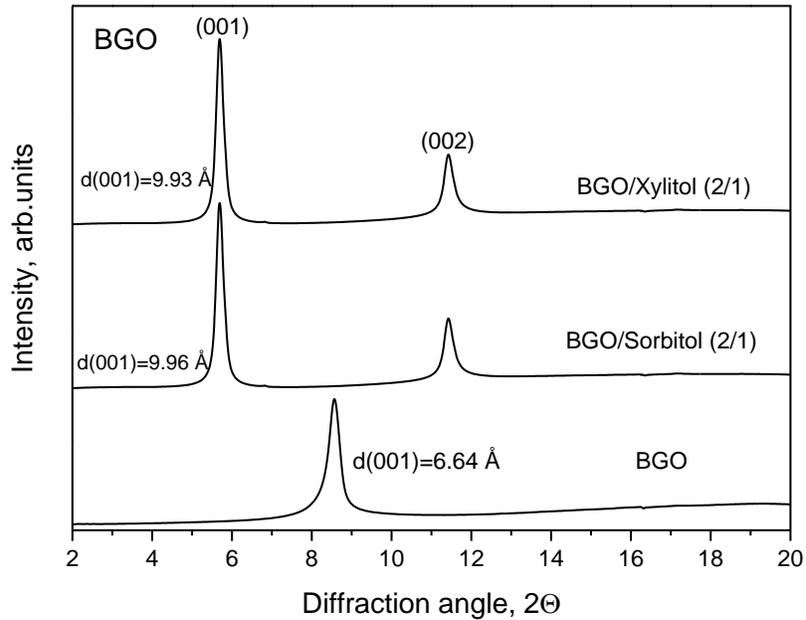


Figure 1: a) XRD patterns recorded at room temperature from samples of BGO/xylitol mixed in different weight proportions and annealed at 110°C, above the melting points of xylitol; b) XRD patterns of BGO/xylitol and BGO/sorbitol materials synthesized using 2/1 (g/g) loading and precursor BGO Synchrotron radiation with $\lambda = 0.98987 \text{ \AA}$ was used.

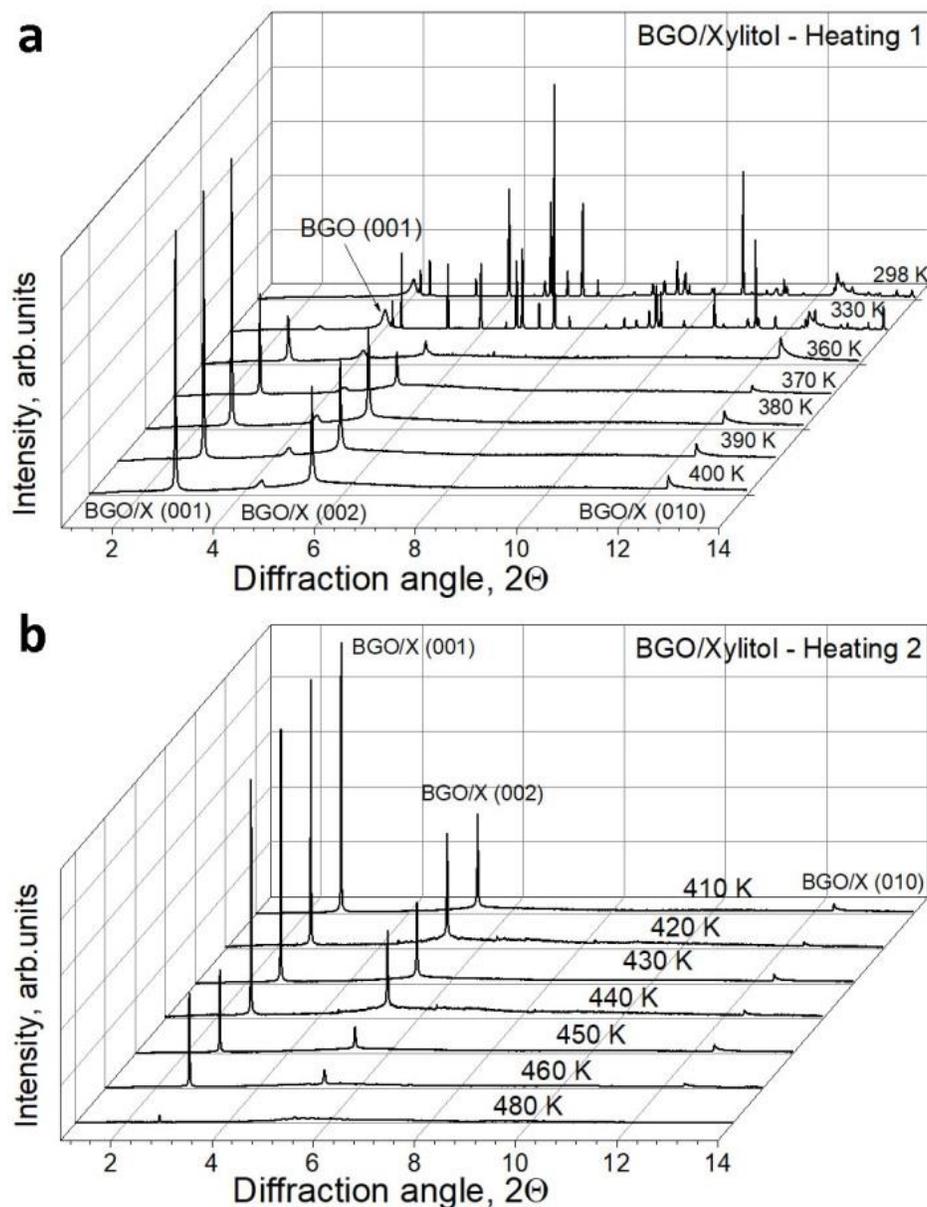


Figure 2. XRD patterns recorded from BGO/xylitol powder mixture: a) heated above melting point of xylitol up to 400 K and cooled down to ambient temperature b) heated second time up to 480K. Pristine BGO shows only two reflections: (001) and (010), all other peaks are form xylitol powder. Intercalated BGO/X phase shows (001), (002) and (010) reflections.

Next set of experiments was performed using in situ synchrotron radiation XRD recorded during the heating of BGO mixed with xylitol or sorbitol. The first heating cycle was performed up to 400 K to verify the structure of BGO in molten sugar alcohol and keeping temperature below the point when thermal deoxygenation of GO could be expected ($\sim >130^{\circ}\text{C}$, [60]), Figure 2a. Analysis of XRD data shows that the same phase with $d(001) \sim 9.9 \text{ \AA}$ is formed in molten sugar alcohols. The sample was then cooled down to room temperature. The intercalated phase of BGO is found to be stable after solidification of melt. Note that strong change in composition of GO solvates was observed in our earlier studies

around the point of solvent freezing/melting for BGO/water system[55] and not observed for BGO in methanol and several other solvents.[44, 61]

A second heating cycle with the same sample was then performed to verify stability and possible phase transformations at higher temperatures. The same phase of BGO/xylitol and BGO/sorbitol was observed in this experiment up to the highest temperature point of 480 K which is just below the temperature of explosive exfoliation of BGO. However, intensity of XRD reflections went down at highest temperatures reflecting start of thermal degradation of GO.

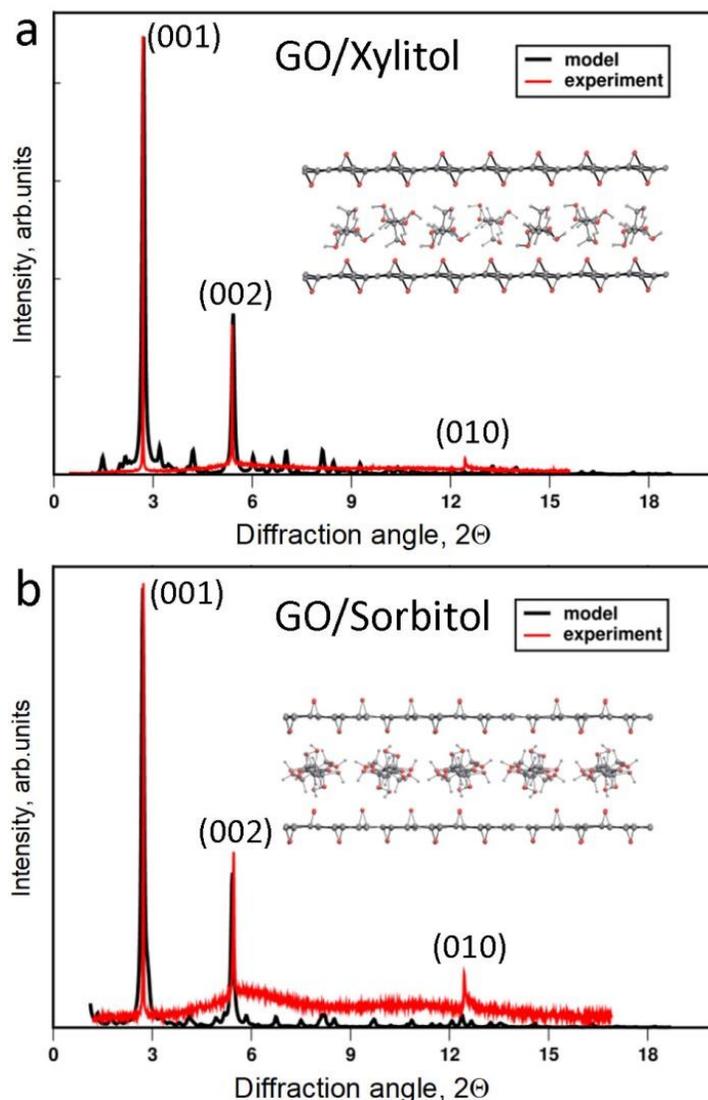


Figure 3. Structural models of BGO intercalated with xylitol and sorbitol, XRD patterns simulated using these models and experimental XRD patterns recorded from melt-intercalated samples (at 450 K for sorbitol and at 410 K for xylitol).

The theoretically simulated structures of BGO intercalated with xylitol and sorbitol are shown in Figure 3. To build up the structure models, we used the simplified GO structure similar to the Hoffmann

model and close-packed monolayers of sugars which were cut from their crystal structures. The unit cells of the intercalated structures were chosen to be commensurate with both GO and monolayers of sugars.

The distance between GO-planes in the model structures was fixed to $d(001)$ -spacing from experimental XRD patterns (9.8943 Å for xylitol and 9.8914 Å for sorbitol). To minimize in-plane strain, geometry optimization was performed using the SIESTA program package.[62] For the stacks of GO and close-packed monolayers of sugars, the intensity of the (002)-reflection was as high as for (001) (Figure 3S in SI). To match relative intensities with experimental data, ca. 50% of the sugar molecules had to be removed from close-packed monolayers. This could be an indication that intercalated sugar molecules tend to form separate “islands” rather than to be uniformly distributed in the interlayer space.

The structure shown in Figure 3 is idealized assuming regular distribution of functional groups over graphene oxide planes and ordered xylitol layer. The real structure of GO is known to be non-periodic with functional groups attached to planes randomly. As a result, intercalation of sugar alcohols will also be in disordered state. Despite very strong oversimplification, the XRD pattern simulated using idealized BGO/xylitol structure shows rather good agreement with experimentally recorded data. The main feature of XRD patterns recorded for BGO intercalated with sugar alcohols is high intensity of (002) reflection which is barely observed in pristine BGO. The theoretically simulated XRD pattern shows rather high intensity of (001) and (002) reflections relative to all other peaks which originate from ordered xylitol layer (see also Figure S3 in SI). Introducing some disorder in the location of functional groups of GO and positions of sugar alcohol molecules will result in smearing of all weak reflections into background. The interlayer distance of 9.93 Å and relative intensity of (001) and (002) reflections are in perfect agreement with experimentally observed XRD pattern.

Intercalation of sugar alcohols into GO structure can be achieved also using aqueous solutions (Figure 4). Note that swelling of GO in water is completely reversible and pristine structure is recovered once the powder is dried (Figure 4a). However, swelling of GO in sugar alcohols is found to be not reversible which can be explained only by intercalation of solute molecules into inter-layer space of GO structure. Immersing BGO powder ($d(001) \sim 6.5$ Å) into 10% xylitol solutions resulted in swelling caused by water and expansion of interlayer distance $d(001)$ up to 9.93 Å, similar to the value observed for BGO in pure water (Figure 4b). However, air drying of the sample does not result in recovery of pristine BGO. Even after vacuum drying the $d(001)$ of BGO/xylitol sample shows $d(001) = 9.44$ Å and increased intensity of (002) reflection. Similar result is found also for BGO immersed in sorbitol solution (Figure 4c). Intercalation of sorbitol results in expanded inter-layer distance of BGO structure and pristine BGO is recovered after washing the BGO/sorbitol with water.

Similarly to swelling in molten sugars, the intercalation of HGO powder with xylitol and sorbitol exhibited larger inter-layer distances of about 14.2 Å which correspond to insertion of at least two layers of sugar alcohol molecules (Figure 1S in SI).

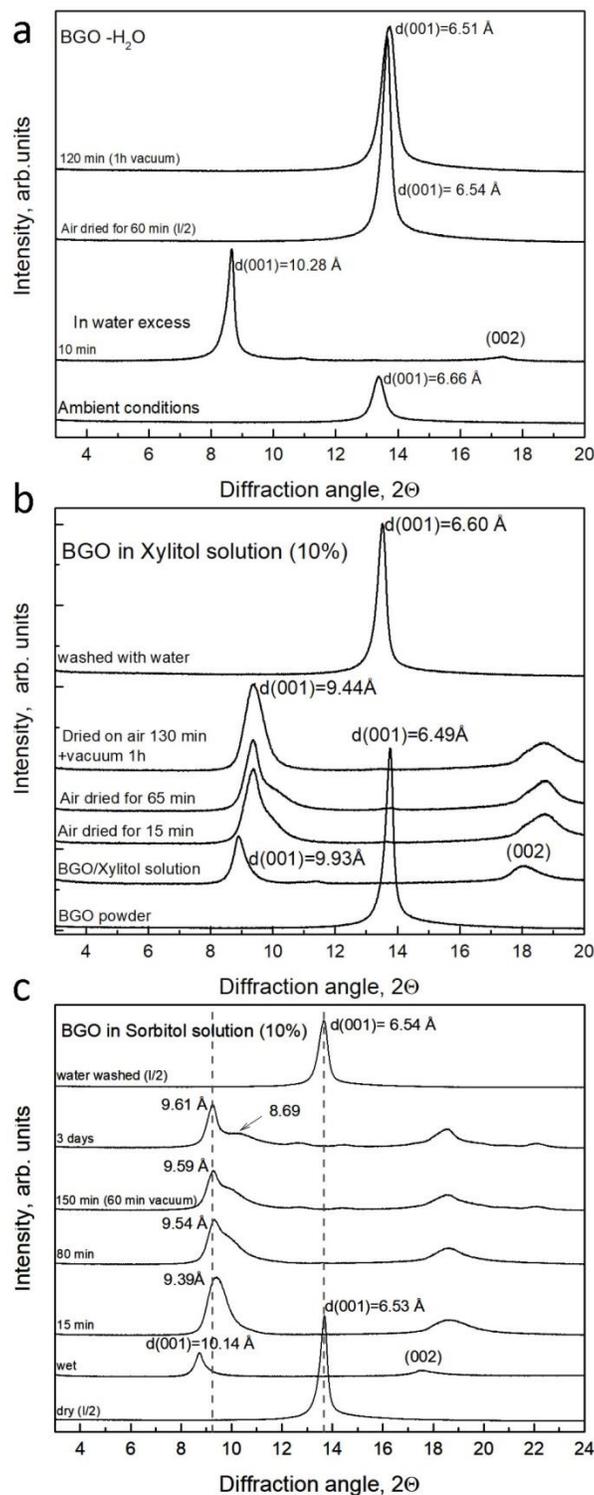


Figure 4. a) XRD patterns recorded from BGO powder, the same powder in water excess and after drying on air and under vacuum conditions; b) Intercalation of BGO powder using aqueous 10% solution of xylitol. XRD patterns recorded for pristine powder, solution immersed powder and patterns recorded

after on air drying up to 80 min and after one hour of vacuum drying. Water washing of BGO intercalated with xylitol resulted in recovery of pristine BGO c) Intercalation of BGO powder using aqueous 10% solution of sorbitol. Intensity of some patterns was reduced by two times ($I/2$) for better representation.

It can be concluded that intercalated BGO/xylitol and BGO/sorbitol structures formed in solution and in melt are nearly identical. However, XRD reflections recorded from solution-intercalated BGO were much broader reflecting stronger disorder of intercalated sugar alcohol molecules. Evaporation of water from BGO structure intercalated with sugar alcohols is likely reason for stronger disorder of resulting material reflected by stronger broadening of (001) and (002) reflections. In contrast, swelling in molten sugar alcohols is water free process and provides better ordered layers in BGO structure evidenced by rather sharp (001) and (002) reflections. It is important to emphasize that xylitol and sorbitol molecules are not covalently attached to graphene oxide planes and not chemically modified in the process of intercalation. Intercalation of sugar alcohols both from melt and from aqueous solution is completely reversible. Xylitol and sorbitol can be removed by sample washing with water which results in recovery of pristine GO.

GO intercalation with sugar alcohols presented in this study is very similar to swelling of GO in methanol and ethanol reported in our earlier studies. Immersion of BGO powder into alcohols at ambient temperature results in swelling and lattice expansion up to $d(001) \sim 9.0 \text{ \AA}$ for methanol and 9.2 \AA for ethanol [30, 41-42]. It can be concluded that intercalation of methanol, ethanol, xylitol and sorbitol results in insertion of one layer of molecules. Solvent induced ordering of BGO structure is reflected in smaller FWHM of the swelled structures. Note that below $\sim 250\text{K}$ transition into two-layered structure occurs for BGO immersed in methanol and ethanol. No similar transitions were observed for BGO in xylitol and sorbitol melts.

For HGO powder the similarity is also rather remarkable: the swelling in both alcohols (at room temperature) and sugar alcohols results in expansion of inter-layer distance which corresponds to insertion of at least two solvent molecule layers ($\sim 13\text{-}14 \text{ \AA}$)[30, 46, 48] and solvent induced disorder reflected in larger FWHM of swelled structures.

Detailed characterization of precursor graphite oxides used in this study (BGO and HGO) was performed in our earlier study [60]. Both materials showed similar oxidation degree ($C/O=2.7$ and $C/O=2.6$ respectively) but rather different vapour sorption properties, thermal stability (revealed by TGA), certain difference in FTIR and NMR spectra. Based on these data we suggested that Brodie graphene oxide has less defects (holes and vacancies) and functional groups are more homogeneously distributed over the surface of BGO flakes. Inhomogeneous hydration of HGO on nanometer size scale was also earlier confirmed by direct SFM observations.[49] Smaller number of defects in Brodie GO relative to Hummers GO is also supported by superior mechanical properties measured on individual Brodie graphene

oxide flakes and multilayered membranes.[33] However, one needs to note that the effect of different impurities (first of all sulphur in HGO) on swelling properties of graphite oxides is not yet completely clear.

The results provided by comparing intercalation of sugar alcohols in aqueous solutions and using molten water free method allow new insights into the mechanism of GO intercalation. It is rather remarkable that swelling of BGO in xylitol and sorbitol solutions results in the lattice expansion of only up to $\sim 9.8\text{-}10.0$ Å which is nearly identical to the inter-layer distance observed in melt-swelling of BGO in sorbitol and xylitol. The swelling of GO in solution is caused by water and sugar alcohol molecules must be inserted between graphene oxide sheets together with water. Sugar alcohol molecules dissolved in water are surrounded by hydration shell and their diameter must be larger compared to the size of molecules in melt. Nearly identical inter-layer distance in melt swelled and solution swelled BGO suggests that molecules must be de-hydrated before insertion into the GO structure. Note that drying of BGO samples immersed in xylitol and sorbitol solutions resulted in rather small decrease of inter-layer spacing by ~ 0.5 Å. Therefore, the insertion of sugar alcohol molecules into GO inter-layers occurs without full hydration shell in aqueous solutions. It can be considered as a selective sorption of sugar alcohols from aqueous solution. This in turn can be extremely important result for understanding of permeation through multilayered graphene oxide membranes. Several previously published studies suggested that permeation of membranes is controlled by the distance between graphene oxide layers provided by swelling and by the size of molecules in hydrated state.[63-64] Our experiments demonstrate that intercalation of sugars into GO structure occurs in not hydrated state. At least partial dehydration of molecules is required in order to explain observed inter-layer distance of $\sim 9.5\text{-}10$ Å in solution immersed BGO.

CONCLUSIONS

In conclusion, swelling of BGO and HGO in molten sugar alcohols and in their aqueous solutions was studied using in situ XRD. Solid solvates of BGO intercalated with xylitol and sorbitol are formed in melt and remain stable at ambient conditions. Very similar solid solvates with expanded structure of GO are formed also by intercalation of sugar alcohols in aqueous solutions of xylitol and sorbitol. The inter-layer distance observed for BGO swelled in molten sugar alcohols and in their aqueous solutions shows that xylitol and sorbitol molecules can diffuse into inter-layer space of GO structure in not hydrated state. Therefore, the diffusion of molecules between graphene oxide layers in multilayered membranes should not be correlated with the hydration radius of molecules. Partial dehydration suggests that smaller molecules can permeate through GO inter-layers given the same expansion of lattice due to swelling.

ASSOCIATED CONTENT

Supporting Information. XRD patterns of Hummers GO annealed at 110°C with Sorbitol and Xylitol, structural models with saturated and diluted layers of xylitol

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ABBREVIATIONS

HGO - Hummers Graphite Oxide, BGO - Brodie Graphite Oxide

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