Umeå University

This is an accepted version of a paper published in *Journal of Physical Chemistry Letters*. This paper has been peer-reviewed but does not include the final publisher proof-corrections or journal pagination.

Citation for the published paper:

Talyzin, A., Sundqvist, B., Szabó, T., Dmitriev, V. (2011)
"Structural breathing of graphite oxide pressurized in basic and acidic solutions"
Journal of Physical Chemistry Letters, 2(4): 309-313
URL: <http://dx.doi.org/10.1021/jz1016476>

Access to the published version may require subscription.

Posted by permission of the Editors.

Permanent link to this version:

<http://urn.kb.se/resolve?urn=urn:nbn:se:umu:diva-39531>

<http://umu.diva-portal.org>

Structural Breathing of Graphite Oxide Pressurized in Basic and Acidic Solutions.

A.V.Talyzin^{†}, B.Sundqvist[†], T.Szabó[§], V.Dmitriev[‡].*

[†]Department of Physics, Umeå University, SE-901 87 Umeå, Sweden,

[§]Department of Physical Chemistry and Materials Science., University of Szeged, H-6720 Szeged,
Hungary

[‡] SNBL, European Synchrotron Radiation Facility, ESRF, 38043 Grenoble, France

AUTHOR EMAIL ADDRESS: alexandr.talyzin@physics.umu.se

RECEIVED DATE

ABSTRACT

Graphite oxide immersed in excess of basic or acidic water media was studied using synchrotron X-ray diffraction at high pressure using diamond anvil cells. The lattice spacing of graphite oxide in excess of NaOH solution increases by the enormous value of 85% at 1.6 GPa. In contrast, structure expansion of graphite oxide immersed in liquid water with added HCl is significantly less pronounced compared to compression in pure water. The point of media solidification correlated with sharp decrease of graphite oxide layers separation due to partial withdrawal of water from the structure. Therefore, pressure induced structural breathing of graphite oxide due to insertion/desertion of water into/from interlayer

space is strongly enhanced in basic media and suppressed in acidic one. The magnitude of structural breathing depends also on relative amounts of graphite oxide powder and solution. Strongly diluted samples with low relative amount of graphite oxide powder in the suspension exhibited less pronounced high pressure anomaly.

TOC figure

KEYWORDS High Pressure • graphite oxide • X-ray diffraction •

Graphite oxide (GO) is a unique material¹⁻⁵ which recently attracted great attention from a broad range of specialists as a precursor for the synthesis of graphene and graphene-related materials⁶⁻¹⁰. The structure of solvent free graphite oxide is non-stoichiometric and even after 150 years of research it is not completely established despite very strong recent interest¹¹⁻¹⁶. Graphite oxide shows a significantly increased inter-layer distance (up to $\sim 6\text{\AA}$), while keeping the planar structure of graphite^{4,15}. Unlike pristine graphite, GO is hydrophilic; water and other polar solvents are easily inserted into interlayer space with formation of an expanded solvated structure¹⁷⁻²⁰. For example, fully hydrated graphite oxide shows a sharp increase of the inter-layer distance (up to $12\text{\AA}$) compared to “dry” state^{4,17}. Graphite oxide can be easily dispersed as separate layers in water solution, deposited as thin films^{10,21-22} and converted into graphene by mild heat treatment, by reduction in solutions (see e.g. ^{6,9,23-24}) or even by light from a camera flash²⁵. Several structural models have been proposed for GO based on NMR, XPS and IR spectroscopy data^{4-8,13,15,26-27}, and some of them suggest that epoxy, carbonyl and -OH groups

are attached to the graphene skeleton which results in some buckling of the planes. Strong disorder and turbostratic packing make it difficult to identify the detailed structure of GO by diffraction methods.

Recently we discovered that graphite oxide immersed in excess amounts of several solvents shows an expansion of the structure due to pressure induced insertion of additional solvent between oxidized graphene layers²⁸. A similar effect has been previously observed for nanoporous materials, e.g. zeolites or pyrochlores immersed in liquid media²⁹⁻³¹. The unit cell volume of these materials shows a jump-like increase at a certain pressure due to pressure induced insertion of water into pores. The volume increase for these materials is relatively small, e.g. about 5-7.5% for defect pyrochlores of various compositions²⁹⁻³⁰. The lattice expansion observed for GO was significantly higher, reaching 25-30%²⁸. The difference is due to the relatively weak van der Waals bonding between oxidized graphene layers which allows easy “structural breathing” upon pressure variation. The inter-planar distance (and unit cell volume) of graphite oxide (GO) pressurized in the presence of water continuously increases, reaching a sharp maximum at 1.3-1.5 GPa. The following downturn is correlated with the solidification point of water. The effect is reversible, resulting in a unique “breathing” of the structure upon pressure variation²⁸. Graphite oxide immersed in methanol, ethanol and acetone also exhibited pressure-induced liquid phase insertion³²⁻³³.

Experimental results indicate that at least part of the water in fully hydrated GO is in a liquid like state and is able to go in and out of interlayer space relatively easily under the influence of external conditions. However, the chemical interaction of the GO structure with solvents is rather complex and contributes to the unusual compressibility of hydrated graphite oxide. It is known that the GO structure is extremely sensitive to changes of pH, and expands in slightly basic solutions²⁴. It should also be noted that GO immersed in aqueous solutions of strong acids and bases degrades irreversibly⁹. Therefore, it could be anticipated that change of pH will influence also compressibility anomaly observed for graphite oxide at high pressure²⁸.

Here we present results of X-ray diffraction experiments with GO immersed in basic and acidic water solutions. Enormous expansion of the lattice due to pressure induced insertion of a basic solution was found.

The GO sample was prepared using Brodie's¹ method and showed a composition $\text{CO}_{0.38}\text{H}_{0.12}$ according to elemental analysis. The XRD pattern recorded for the pristine sample of GO at ambient conditions was indexed by a turbostratic graphite-like hexagonal structure with the cell parameters $a=2.48 \text{ \AA}$ and $c=6.60 \text{ \AA}$ ²⁸. A high pressure study of the GO immersed in various liquid media was performed using synchrotron radiation X-ray diffraction in a Diamond Anvil Cell (DAC).

The results of high pressure experiments performed with graphite oxide powder immersed into NaOH and HCl solutions are shown in **Figures 1-3**.

Figure 1. XRD patterns recorded from GO/NaOH sample on increasing pressure. Indexing of the graphite oxide reflections is shown for the 0.1 GPa pattern. Ice patterns are indexed for the 2.0 GPa and 2.2 GPa patterns.

The (001) spacing of graphite oxide immersed in NaOH solution is higher and for the HCl medium is smaller compared to that of pure water already at near ambient pressure, in good agreement with literature data^{24,34}. Pressure increase results in dramatic changes of interlayer spacing while the oxidized graphene planes are only very slightly compressible and keep their original state (see inset in Figure 2). **Figure 2** shows that changing the chemical composition of the solution results in huge variations of the pressure induced water insertion into graphite oxide interlayer space. Pressurizing of GO in an acidic medium resulted in a relatively small (~ 1.1 Å) increase of the (001) spacing at pressures below 0.5 GPa and at higher pressures remained almost unchanged until the solidification point of the solution at 1.9 GPa, followed by a downturn at higher pressures. In contrast, applying high pressure to GO in NaOH solution resulted in a dramatic increase of the (001) spacing from 11.58 Å at 0.1 GPa up to 21.47 Å at 1.7 GPa. The amplitude of the lattice expansion in NaOH solution media is significantly larger compared to the effect in pure water (from 10.95 Å to 13.08 Å)²⁸. This effect was also reproduced in another high pressure experiment with only slight variations. Considering the size of a water molecule to be ~ 3 Å, The pressure effect on graphite oxide in pure water would correspond to insertion of one monolayer of water while in NaOH solution the change of interlayer distance is about 3 monolayers. No additional reflections from water were observed in hydrated samples either at ambient conditions or at high pressure. The continuous shift of the position of the (001) reflection could be explained by interstratification of layers with different degree of hydration while the number of galleries with a high number of water layers increases with increasing pressure. However, water in the hydrated GO structure is not ordered and considering the insertion of water strictly as insertion of monolayers would be an oversimplification.

The downturn in the pressure dependence of the (001) spacing (see **Figure 2**) correlated with the solidification point of the liquid media independently on pH of the solution. It can also be noted that

pressure points of basic and acidic media solidification are higher compared to pure water. This was also verified in separate experiments performed with pure HCl/water solutions using DTA method (see supplementary materials). The rapid decrease of interlayer spacing above the solidification point of media suggests that water inserted between graphene oxide layers at high pressure conditions remains in a liquid-like state and is squeezed out of the structure. The structural transformations were found to be reversible after rapid decompression. No detailed decompression study was performed for the basic and acidic solutions while for pure water it can be found in our previous study²⁸.

It is clear that water can be inserted and withdrawn from the graphite oxide structure by changing the pressure, thus producing structural breathing. The results presented here prove that the amount of inserted water depends on the chemical composition of the water solutions. It is known that at ambient pressure the addition of NaOH to water results in structural expansion of graphite oxide (or even leads to complete dispersion of individual sheets) while the structure contracts in acidic solutions²⁴.

Figure 2. Pressure dependence of the (001) spacing of graphite oxide immersed in various liquid media: ▲ - NaOH, ■ - pure water, ● - HCl. Inset shows pressure dependence of the (010) reflection for GO immersed in a NaOH pressure medium. Arrows indicate pressure points of liquid media solidification (first pressure point where reflections from ice were observed).

In the case of the NaOH solution the effects are explained by chemical interaction of OH(-) anions from solution with functional groups on the graphite oxide (by deprotonation of COOH and phenolic groups), leaving planes in a negatively charged state¹⁵. The charge on graphene oxide planes is compensated by mobile ions in solution. In contrast, addition of HCl hinders deprotonation of GO planes and results in significantly weaker lattice expansion of the graphite oxide structure.

Let us consider some general effects of pressure on the GO/solvent system. Compression of the system must result in increased densities for both the water medium and for the water confined between the GO layers, but not necessarily with the same rate. It is known that water confined in nanometer

spaces has significantly different properties compared to bulk water, and this includes also a higher density even at ambient pressure³⁵. As was shown in our simple model, a higher density of confined water compared to the density of bulk water should result in an increased separation of GO layers³⁶. Besides the physical effects of an applied pressure one needs to take into account changes in the chemical properties of the materials which compose the system. Weak acids are known to dissociate better under pressure³⁷ and graphite oxide behaves as a weak acid when placed in solution due to dissociation of certain surface hydroxyl groups¹⁵. Water molecules are compacted stronger around ions compared to molecules³⁷ while the concentration of ions should be higher for water confined between GO plates. Therefore, the total density of the solution between GO planes should be higher than the density of the bulk medium due to the excess of ions provided by the dissociation of functional groups. In general, expansion of the GO structure could be expected if the concentration of ions between GO planes exceeds the concentration in the bulk solution. Addition of NaOH to water results in a promotion of dissociation while the addition of HCl hinders it.

This simple model is also able to explain another interesting result obtained in our experiments. **Figure 3** shows that the application of pressure to samples with strongly increased water/GO powder ratio results in a strong decrease in the amplitude of the high pressure anomaly. This result is paradoxical at a first glance since the acidity of the water medium due to dissociation of GO should be lower in the strongly diluted sample. According to the data shown in **Figure 2**, acidic media gives a lower structural expansion for samples with equal proportions of GO powder per volume solution. However, the results observed in compression experiments with strongly diluted samples (and therefore with less acidic water medium) showed smaller magnitude of GO structural breathing.

Figure 3. Pressure dependence of the (001) spacing of graphite oxide loaded with different amount of water: ▲- “standard” GO powder/water proportion, approximately 1:1 by volume; ■- strongly diluted sample with 1:3 proportion between volumes of GO powder and water.

It should be noted that all experiments described above and in previous studies^{28,32-33} were performed with approximately the same loading procedure, in which the gasket hole was filled completely with GO powder after which water was added, thus making the relative volumes of powder (bulk volume) and water approximately 1:1. The pressure dependence of strongly diluted samples (**Figure 3**) shows remarkable differences compared to that observed in experiments with the “standard” 1:1 proportion between GO and water. The difference is observed already for the first pressure point: immediately after closing the cell with pressures 0.1-0.2 GPa the interlayer distance of strongly diluted samples appeared to be approximately 1 Å smaller. The (001) spacing for diluted samples increased only by ~0.5

Å and remained almost unchanged until the solidification point of the liquid medium, and the sharp expansion of the structure typical for GO/water loaded in the “standard” proportions was not observed.

As was suggested above, larger amplitude of the structural expansion of graphite oxide is associated with a higher concentration of ions in the solution confined between its layers. A strong dilution of the sample results in a somewhat less acidic pH of the bulk water but also results in a depletion of confined water from ions produced by dissociation of GO functional groups. Fewer ions between layers should result in a smaller density difference between bulk and confined water upon pressurization and smaller amplitude for the structural expansion.

In general, graphite oxide hydration is remarkably similar to swelling of some clay minerals which exhibit in certain cases “osmotic swelling” when water enters interlayer space in a liquid-like state and the separation of layers depends on osmotic pressure developed in the system due to inserted interlamellar ions (see e.g. ref³⁸). In a simple model, graphite oxide could be considered as a semi-permeable membrane: the interlayer space of the GO structure has a higher concentration of ions compared to the surrounding liquid medium and this causes an osmotic pressure and osmotic flow of liquid inside interlayer space. The pressure increase promotes dissociation of certain functional groups and increases the concentration difference between the pressure medium and the solution confined between GO layers, resulting in a stronger osmotic pressure forcing liquid from the medium to the space between the GO layers. This effect becomes stronger in basic solution due to a more complete deprotonation of GO functional groups while an acidic solution weakens the dissociation.

In conclusion, pressure induced insertion of water into the graphite oxide structure was studied for liquid media with various chemical composition. Experiments revealed an enormous increase in the structural expansion of graphite oxide immersed in basic solution (up to 85% lattice expansion) while using acidic water as medium was found to hinder pressure induced water insertion. It is suggested that a stronger dissociation of GO functional groups stimulated by the pressure increase is responsible for an osmotic inflow of the liquid medium into the interlayer space of the GO structure, resulting in a stronger

structural expansion. The enormous structural expansion observed in graphite oxide pressurized in basic media opens additional possibilities for functionalization of this material: it is obvious that a wider separation of layers allows insertion of larger molecules (e.g. polymers) into the GO structure.

EXPERIMENTAL SECTION

XRD patterns were recorded in situ in DAC with beryllium seats using synchrotron radiation at the Swiss-Norwegian Beam Line (BM1A) at ESRF at the wavelength $\lambda=0.7092 \text{ \AA}$ using a MAR345 image plate detector. Diamond anvils with 0.4-0.6 mm flat culets were used. The samples were loaded into a 0.2-0.3 mm hole in rhenium gaskets together with a ruby ball used for pressure calibration. The pressure was increased gradually in steps of 0.1-0.2 GPa, and XRD patterns were recorded on every step during pressure increase and decrease. The two-dimensional XRD patterns were integrated using Fit2D software. Experiments were performed with GO powder loaded with an excess of NaOH (0.5 mol/l concentration) and HCl solutions (1 mol/l solution) as pressure media. The exact proportions of water and powder cannot be controlled in the DAC experiments due to the extremely small amounts of materials and the rapid evaporation of solvent during the loading procedure. However, a qualitative difference can be achieved by loading various amounts of powder into the gasket hole while filling the remaining space with solution. All experiments described above and in previous studies^{28, 32-33} were performed with approximately the same loading procedure, in which the gasket hole was filled completely with GO powder after which water was added, thus making the relative volumes of powder (bulk volume) and water approximately 1:1. Several experiments were also performed with significantly decreased amount of GO: the gasket hole was loaded by GO powder only to approximately 1/3 of its volume with remaining space filled by water.

ACKNOWLEDGMENT Umeå University acknowledged for financial support provided by Young Investigator Award (A.T.), T.S. acknowledges support from the Magyary Zoltan postdoctoral fellowship funded by the EEA and Norway Grants.

SUPPORTING INFORMATION AVAILABLE High pressure DTA for H₂O-HCl system. Solidification and melting points of water determined in absence on graphite oxide. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

REFERENCES

- (1) Brodie, B. C., Sur le Poids Atomique du Graphite. *Ann. Chim Phys.* **1860**, 59, 466–472.
- (2) Hofmann, U. F., A., Quellung von Graphit und die Bildung der Graphitsäure. *Ber. Deutsch. Chem. Ges.* **1930**, 63, 14.
- (3) Hummers, W. S.; Offeman, R. E., Preparation of Graphitic Oxide. *J Am Chem Soc* **1958**, 80, 1339-1339.
- (4) Scholz, W.; Boehm, H. P., Graphite Oxide .6. Structure of Graphite Oxide. *Z Anorg Allg Chem* **1969**, 369, 327.
- (5) Bourlinos, A. B.; Gournis, D.; Petridis, D.; Szabo, T.; Szeri, A.; Dekany, I., Graphite oxide: Chemical Reduction to Graphite and Surface Modification with Primary Aliphatic Amines and Amino acids. *Langmuir* **2003**, 19, 6050-6055.
- (6) Stankovich, S.; Dikin, D. A.; Dommett, G. H. B.; Kohlhaas, K. M.; Zimney, E. J.; Stach, E. A.; Piner, R. D.; Nguyen, S. T.; Ruoff, R. S., Graphene-Based Composite Materials. *Nature* **2006**, 442, 282-286.
- (7) Stankovich, S.; Dikin, D. A.; Piner, R. D.; Kohlhaas, K. A.; Kleinhammes, A.; Jia, Y.; Wu, Y.; Nguyen, S. T.; Ruoff, R. S., Synthesis of Graphene-Based Nanosheets via Chemical Reduction of Exfoliated Graphite Oxide. *Carbon* **2007**, 45, 1558-1565.
- (8) Gao, W.; Alemany, L. B.; Ci, L. J.; Ajayan, P. M., New Insights into the Structure and Reduction of Graphite Oxide. *Nat Chem* **2009**, 1, 403-408.
- (9) Fan, X. B.; Peng, W. C.; Li, Y.; Li, X. Y.; Wang, S. L.; Zhang, G. L.; Zhang, F. B., Deoxygenation of Exfoliated Graphite Oxide under Alkaline Conditions: A Green Route to Graphene Preparation. *Adv Mater* **2008**, 20, 4490-4493.
- (10) Cote, L. J.; Kim, F.; Huang, J. X., Langmuir-Blodgett Assembly of Graphite Oxide Single Layers. *J Am Chem Soc* **2009**, 131, 1043-1049.
- (11) He, H. Y.; Klinowski, J.; Forster, M.; Lerf, A., A New Structural Model for Graphite Oxide. *Chem Phys Lett* **1998**, 287, 53-56.
- (12) He, H. Y.; Riedl, T.; Lerf, A.; Klinowski, J., Solid-State NMR Studies of the Structure of Graphite Oxide. *J Phys Chem-Us* **1996**, 100, 19954-19958.
- (13) Lerf, A.; He, H. Y.; Forster, M.; Klinowski, J., Structure of Graphite Oxide Revisited. *J Phys Chem B* **1998**, 102, 4477-4482.
- (14) Lerf, A.; He, H. Y.; Riedl, T.; Forster, M.; Klinowski, J., C-13 and H-1 MAS NMR Studies of Graphite Oxide and its Chemically Modified Derivatives. *Solid State Ionics* **1997**, 101, 857-862.
- (15) Szabo, T.; Berkesi, O.; Forgo, P.; Josepovits, K.; Sanakis, Y.; Petridis, D.; Dekany, I., Evolution of Surface Functional Groups in a Series of Progressively Oxidized Graphite Oxides. *Chem Mater* **2006**, 18, 2740-2749.
- (16) Szabo, T.; Berkesi, O.; Dekany, I., DRIFT Study of Deuterium-Exchanged Graphite Oxide. *Carbon* **2005**, 43, 3186-3189.
- (17) Lerf, A.; Buchsteiner, A.; Pieper, J.; Schottl, S.; Dekany, I.; Szabo, T.; Boehm, H. P., Hydration Behavior and Dynamics of Water Molecules in Graphite Oxide. *J Phys Chem Solids* **2006**, 67, 1106-1110.
- (18) Buchsteiner, A.; Lerf, A.; Pieper, J., Water Dynamics in Graphite Oxide Investigated With Neutron Scattering. *J Phys Chem B* **2006**, 110, 22328-22338.

- (19) de Boer, J. B. v. D., A.B.C., Graphite Oxide. V. The Sorption of Water. *Koninkl. Nederl. Akad. Wetenschappen, Ser. B* **1958**, *61*, 10.
- (20) Cervený, S.; Barroso-Bujans, F.; Alegria, A.; Colmenero, J., Dynamics of Water Intercalated in Graphite Oxide. *J Phys Chem C* **2010**, *114*, 2604-2612.
- (21) Gilje, S.; Han, S.; Wang, M.; Wang, K. L.; Kaner, R. B., A Chemical Route to Graphene for Device Applications. *Nano Lett* **2007**, *7*, 3394-3398.
- (22) Szabo, T.; Hornok, V.; Schoonheydt, R. A.; Dekany, I., Hybrid Langmuir-Blodgett Monolayers of Graphite Oxide Nanosheets. *Carbon* **2010**, *48*, 1676-1680.
- (23) Jung, I.; Field, D. A.; Clark, N. J.; Zhu, Y. W.; Yang, D. X.; Piner, R. D.; Stankovich, S.; Dikin, D. A.; Geisler, H.; Ventrice, C. A.; Ruoff, R. S., Reduction Kinetics of Graphene Oxide Determined by Electrical Transport Measurements and Temperature Programmed Desorption. *J Phys Chem C* **2009**, *113*, 18480-18486.
- (24) Boehm, H. P.; Clauss, A.; Fischer, G. O.; Hofmann, U., Das Adsorptionsverhalten Sehr Dunner Kohlenstoff-Folien. *Z Anorg Allg Chem* **1962**, *316*, 119-127.
- (25) Cote, L. J.; Cruz-Silva, R.; Huang, J. X., Flash Reduction and Patterning of Graphite Oxide and Its Polymer Composite. *J Am Chem Soc* **2009**, *131*, 11027-11032.
- (26) Casablanca, L. B.; Shaibat, M. A.; Cai, W. W. W.; Park, S.; Piner, R.; Ruoff, R. S.; Ishii, Y., NMR-Based Structural Modeling of Graphite Oxide Using Multidimensional C-13 Solid-State NMR and ab Initio Chemical Shift Calculations. *J Am Chem Soc* **2010**, *132*, 5672-5676.
- (27) Cai, W. W.; Piner, R. D.; Stadermann, F. J.; Park, S.; Shaibat, M. A.; Ishii, Y.; Yang, D. X.; Velamakanni, A.; An, S. J.; Stoller, M.; An, J. H.; Chen, D. M.; Ruoff, R. S., Synthesis and Solid-State NMR Structural Characterization of C-13-labeled Graphite Oxide. *Science* **2008**, *321*, 1815-1817.
- (28) Talyzin, A. V.; Solozhenko, V. L.; Kurakevych, O. O.; Szabo, T.; Dekany, I.; Kurnosov, A.; Dmitriev, V., Colossal Pressure-Induced Lattice Expansion of Graphite Oxide in the Presence of Water. *Angew Chem Int Edit* **2008**, *4*, 8268-8271.
- (29) Lee, Y.; Vogt, T.; Hriljac, J. A.; Parise, J. B.; Artioli, G., Pressure-Induced Volume Expansion of Zeolites in the Natrolite Family. *J Am Chem Soc* **2002**, *124*, 5466-5475.
- (30) Lee, Y.; Vogt, T.; Hriljac, J. A.; Parise, J. B.; Hanson, J. C.; Kim, S. J., Non-Framework Cation Migration and Irreversible Pressure-Induced Hydration in a Zeolite. *Nature* **2002**, *420*, 485-489.
- (31) Perottoni, C. A.; daJornada, J. A. H., Pressure Induced Water Insertion in the Defect Pyrochlore NH_4NbWO_6 . *Phys Rev Lett* **1997**, *78*, 2991-2994.
- (32) Talyzin, A. V.; Sundqvist, B.; Szabo, T.; Dekany, I.; Dmitriev, V., Pressure-Induced Insertion of Liquid Alcohols into Graphite Oxide Structure. *J Am Chem Soc* **2009**, *131*, 18445-18449.
- (33) Talyzin, A. V.; Luzan, S. M., Pressure-Induced Insertion of Liquid Acetone into the Graphite Oxide Structure. *J Phys Chem C* **2010**, *114*, 7004-7006.
- (34) Boehm, H. P.; Clauss, A.; Hofmann, U., Graphite Oxide and Its Membrane Properties. *J Chim Phys Pcb* **1961**, *58*, 141-147.
- (35) Liu, D. Z.; Zhang, Y.; Liu, Y.; Wu, J. L.; Chen, C. C.; Mou, C. Y.; Chen, S. H., Density measurement of 1-D confined water by small angle neutron scattering method: Pore size and hydration level dependences. *J Phys Chem B* **2008**, *112*, 4309-4312.
- (36) Vakarin, E. V.; Talyzin, A. V., On the Mechanism of Negative Compressibility in Layered Compounds. *Chem Phys* **2010**, *369*, 19-21.
- (37) Tsuda, M.; Shirotani, I.; Minomura, S.; Terayama, Y., Effect of Pressure on Dissociation of Weak Acids in Aqueous Buffers. *B Chem Soc Jpn* **1976**, *49*, 2952-2955.
- (38) Cases, J. M.; Berend, I.; Besson, G.; Francois, M.; Uriot, J. P.; Thomas, F.; Poirier, J. E., Mechanism of Adsorption and Desorption of Water-Vapor by Homoionic Montmorillonite .1. The Sodium-Exchanged Form. *Langmuir* **1992**, *8*, 2730-2739.