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Tunable Pressure Effects in Graphene Oxide Layers

Van der Waals interactions in the pores of micro-porous materials are known to generate a confinement effect for guest species.[1-3] Confinement effects, in particular pseudo-pressure effects, are of importance to the development of characteristic states and unique phases of materials in pores under mild conditions. For example, single-walled carbon nano-horns produce a pseudo-pressure effect corresponding to ca. 1.9 GPa on KI nanocrystals in the pores, giving rise to a structural transition to a high pressure KI phase under ambient pressure.[4] Similar effects have been demonstrated for gas molecules accommodated in metal-organic frameworks. O^2 molecules behave in a similar manner to their solid state above the freezing point of O^2 in nano channels of $[\{[Cu_2(pzdc)_2(pyz)]\cdot 2H_2O\}n]$ (pzdc = pyrazine-2,3-dicarboxylate), with the simultaneous formation of $(O_2)_2$ dimers having also been reported.[5] Recently, stacking structures of two-dimensional (2D) nano-sheets of graphene have been shown to act as a 'field' that produces similar effects to confinement effects.[6,7] For example, in highly ordered pyrolytic graphite (HOPG), mixtures of water and methanol form a stable 2D) molecular assembly that is similar to a transient assembly that occurs in the bulk liquid.[6] In the graphene sheet case, an extended H-bond network forms between water and methanol, also giving rise to the formation of such a stable 2D structure. In these cases, the relationship between the resulting pressure (P) and the **interlayer distance (d) is given by** $P \approx E_w/d$, where E_w is the adhesion energy.[7] Although there are many types of porous materials, tunable confinement effects arising from pore size tuning within a single (composite) material remains largely unexplored. In most cases, materials with different size pores need to be prepared one by one to obtain desired pseudo pressure effects.[8] Clearly materials that are capable of exhibiting tunable confinement effects would potentially provide a useful means for precisely controlling particular physical properties of nanomaterials confined in the pores. In this study, we have focused on the structural transformation from graphene oxide (GO) to reduced graphene oxide (rGO) for the development of such tunable confinement effects.

GO, an oxidation product of graphene, consists of 2D layers incorporating oxygen functional groups such as epoxy, hydroxyl and carboxyl groups. Our group has demonstrated its high proton conductivity,[9] and developed composites with cationic species that include metal ions and metal complexes.[10] Oxygen functional groups on GO are removed by thermal treatment, yielding rGO. At the same time, the interlayer distances decrease progressively from 7-9 Å in GO to 3-4 Å in rGO.[11] Importantly, interlayer distances are influenced by the quantity of functional groups on the layers which, in turn, can be controlled by changing the temperature employed for the thermal treatment. In the present study, we anticipated that the above structural transformation between GO and rGO would lead to tunable pressure effects that reflect changes in the respective interlayer distances (Figure 1).

In order to demonstrate the presence of confinement effects in GO/rGO layer structures, we have focused on spin-crossover (SCO) phenomena that occurs for $[Fe(Htrz)_2(trz)](BF_4)$ nanoparticles (NPs) confined in the interlayer spaces. Iron(II) complexes show SCO phenomena in which electron configurations are switched between high-spin (HS) and low-spin (LS) states with thermal hysteresis.[12] SCO temperatures ($T_{1/2}$) have been shown to be sensitive to the presence of a hydrostatic pressure that acts to restrict a structural transformation synchronized with the SCO. A correlation between $T_{1/2}$ and pseudo-pressures for various compounds has been reported.[13,14] In a prior study Colacio and co-workers have described a $T_{1/2}$-pressure correlation for $[Fe(Htrz)_2(trz)](BF_4)$ NPs.[14] Thus, it appeared feasible that we could estimate pseudo-pressure values arising from the confinement effect using $[Fe(Htrz)_2(trz)](BF_4)$ NPs confined within GO/rGO layers by investigating changes in $T_{1/2}$, with the latter changes mirroring changes in the corresponding interlayer distances. The interlayer separation along the GO to GO/rGO-NPs composites to rGO series decreases smoothly from 9.00 Å

(for GO) to 3.50 Å (for rGO) as the temperature employed for the thermal reduction treatments of the GO-NP composites is increased. At the same time, $T_{1/2}$ increases from 351 K to 362 K along the series. This $T_{1/2}$ increment of 11 K corresponds to that observed for pristine $[Fe(Htrz)_2(trz)](BF_4)$ NPs under a hydrostatic pressure of 38 MPa. In regular rGO, a pseudo-pressure value of 38 MPa was obtained corresponding to an adhesion energy of 0.86 meV $Å^{-2}$. Our findings provide insight towards the application of GO materials exhibiting tunable pressure effects for provision of reaction fields for molecular conversions as well as for the development of new composites incorporating functional nano-materials such as quantum dots, metal complexes or even 2D nanosheets.

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Figures
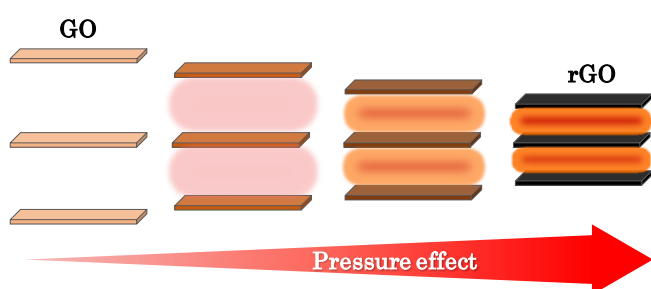
Figure 1: Schematic illustration of the tunable pressure effects caused by the transformation of GO to rGO.