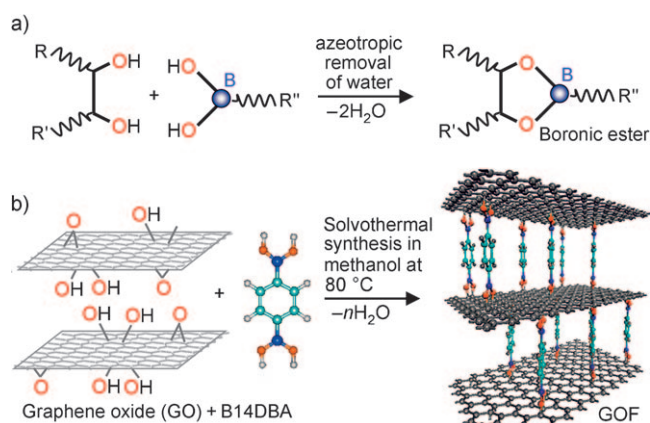# Graphene Oxide Framework Materials: Theoretical Predictions and Experimental Results**

Jacob W. Burress, Srinivas Gadipelli, Jamie Ford, Jason M. Simmons, Wei Zhou, and Taner Yildirim*

The reduction of fossil fuel use in vehicles is key to reducing greenhouse emissions.[1] Vehicles and other systems powered by hydrogen have the advantage of emitting only water as a waste product. An important challenge, however, is storing enough hydrogen on board to give it a range comparable to a vehicle powered by fossil fuels.[1] Unfortunately, current materials still lack the ability to store necessary amounts of hydrogen under technologically useful conditions. Thus, there is urgent need for new ideas and materials to solve the hydrogen storage problem.

Herein, we show that graphene oxide[2] (GO) can be easily turned into a potentially useful gas storage material. GO, the existence of which has been known for over 150 years, is a sheet of carbon atoms with many hydroxy, epoxide, and carboxy surface groups.[2] In principle, hydrogen can be stored between layers of this lightweight material. However, the challenge is to separate the layers without filling the space between them.[3,4] Even though there has been extensive research on gas adsorption properties of graphite/graphene,[5,6] there has been little work carried out on the gas adsorption properties of GO.[7] Furthermore, intercalated GO and GO layers stitched with different functional groups have been studied without attention to their porosity or gas adsorption properties.[8] Herein we show that by using the well-known reactivity between boronic acids and hydroxy groups,[9] GO layers can be linked together to form a new layered structure (Scheme 1 and Figure 1). Such GOF structures can have tunable pore widths, volumes, and binding sites depending on the linkers chosen, and could exhibit interesting gas sorption properties.

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Scheme 1. Representations of a) boronic ester and b) GOF formation. Idealized graphene oxide framework (GOF) materials proposed in this study are formed of layers of graphene oxide connected by benzenediboronic acid pillars.
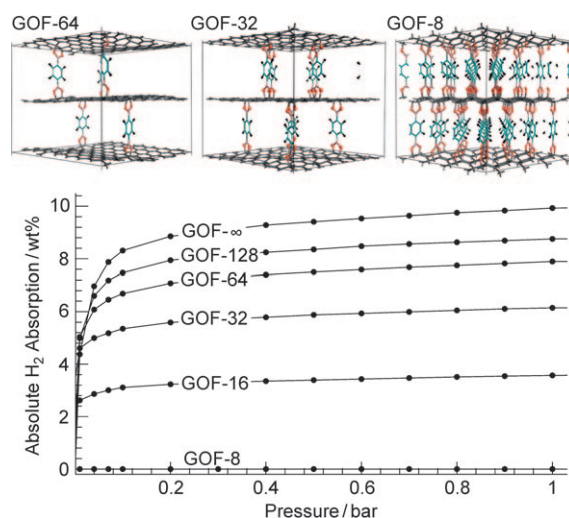

Figure 1. Grand canonical Monte Carlo simulations for ideal GOF-*n* structures with *n* graphene carbons per linker. The structures of three examples with *n* = 64, 32, and 8 are also shown.

To evaluate the potential of GOF materials for H_2 storage, we performed theoretical grand canonical Monte Carlo (GCMC) simulations.[10] A series of idealized model systems with various diboronic acid linker concentrations (and consequently different pore size, pore volume, and surface areas) were examined (see Supporting Information for details). Structural optimization yielded a circa 1.1 nm interlayer separation for these ideal structures. The simulated absolute

hydrogen adsorption isotherms at 77 K for several representative GOF structures are shown in Figure 1. Similar calculations for H_2 uptake in MOF-5 gives 1.67 wt%, which is reasonably close to the experimental value of about 1.3 wt%, giving confidence for the accuracy of GCMC simulations for GOF. When the linker concentration is too high, the GOF structure is too dense and contains no accessible pores. Consequently, there is no H_2 uptake. As the linker concentration decreases, the GOF specific pore volume increases and eventually reaches the limit of no linker present (that is, a hypothetical pure layered graphene structure with about 1.1 nm interlayer separation). Naturally, a GOF structure with lower linker concentration would possess higher H_2 adsorption capacity. However, low linker concentrations will lead to low structural stability and reduced graphene interlayer separation. For example, for bare graphene planes, the natural interlayer distance is around 0.34 nm and there is no room for H_2 adsorption. Similarly, for GO the natural interlayer distance is around 0.7 nm, but owing to the presence of O and OH groups, there is again no room for H_2 uptake. It is important that we expand the interlayer distance without filling the space between them. Therefore, these factors must be balanced to optimize the linker concentration. The GOF-32 structure with one linker per 32 graphene carbon atoms (Figure 1) appears to be one reasonable choice, as it is structurally stable (according to density functional theory lattice dynamics calculations; see the Supporting Information), and it is predicted to have an H_2 adsorption capacity (ca. 6.1 wt% H_2 uptake at 77 K and 1 bar), which is higher than any other porous material known. Overall, our simulation results were quite encouraging and strongly motivated us to experimentally pursue these materials.

We synthesized samples containing varying amounts of linker and characterized them with powder X-ray diffraction (PXRD). As shown in Figure 2, we observed a controllable, monotonic increase in the interlayer spacing in the GOF samples, from 0.75 nm to 1.05 nm. This, combined with prompt gamma activation analysis (PGAA) shown in Figure 3a, indicates that the boronic acid is intercalated in the
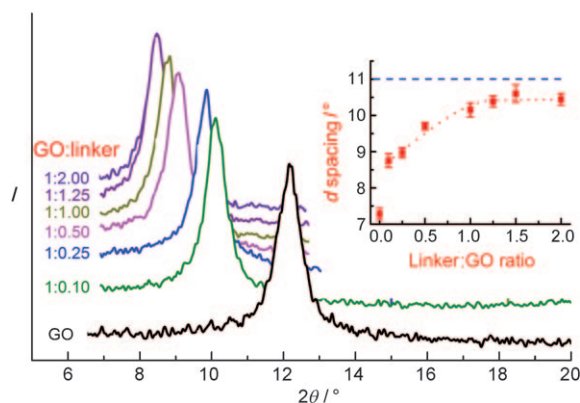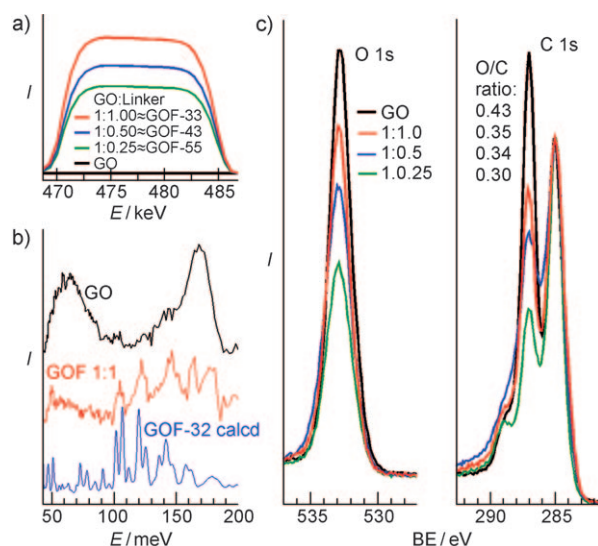

Figure 3. a) The major boron peaks normalized to carbon peak in PGAA spectra, indicating the approximate relations between GO:linker samples and the ideal GOF-n structures. b) INS spectra of GO, a GOF 1:1 sample, and a model calculation based on a GOF-32 structure. c) XPS O1s and C1s core level spectra for GO and three different GOFs.

GO and that the sample prepared with a 1:1 ratio of GO:linker roughly corresponds to GOF-33. As shown in Figure 3b, the inelastic neutron scattering (INS) spectra of GOF differs significantly from the INS spectra of GO and resembles the calculated INS spectra of GOF-32, thus further supporting that the synthesized materials are structurally very close to our ideal GOF systems shown in Figure 1. The X-ray photoelectron spectroscopy (XPS) normalized to the graphitic carbon peak at 285 eV is shown in Figure 3c. It indicates that the O/C ratio of 0.43 in GO decreases down to about 0.33 in the GOF materials. The peak near 287 eV corresponds to carbon with a singly-bonded C−O moiety, and its intensity increases with linker concentration, as expected for graphene layers with increased boron ester cross-linking. The detailed discussion of PGAA, INS, and XPS can be found in the Supporting Information. Thermogravimetric analysis revealed a 100°C increase in the exfoliation temperature of the GOFs, again supporting interlinking of GO planes. FTIR spectroscopy shows new B−O bond formation with no evidence of boroxine rings, thus further supporting pillar-like boronic ester type linkages.

To show that the boronic ester linkage is the key for GOF synthesis, we tested many other linkers using the same solvothermal synthetic steps and found that none of them intercalate between the GO layers (Supporting Information, Figures S12, S13). The fact that benzene-1,4-dicarboxylic acid (Supporting Information, Figure S12b) does not intercalate the GO layers is quite interesting as it is of similar size and shape as B14DBA, but with different reactivity. These results strongly support our theory that the diboronic acid interacts with the OH groups on graphene oxide to form some kind of ester bonding that interlinks the planes and forms a 3D framework structure.

Figure 2. X-ray diffraction and the corresponding interlayer *d* spacing (inset) versus linker concentration. The dashed blue line indicates the optimized *d* spacing (11 Å) that was calculated for GOF-32 shown in Figure 1.

The porosity and gas storage capacity of GOF samples were measured with nitrogen, hydrogen, and carbon dioxide sorption isotherms (see Figure 4; Supporting Information, Figures S3, S5). The nitrogen BET surface area reaches a maximum for the 1:1 linker/GO GOF at 470 m^{2}g^{-1} compared to about 20 m^{2}g^{-1} for the GO control. Despite this low surface area, GOF exhibits 1 wt% H$_2$ uptake at 1 bar, whereas the GO-control sample adsorbs only 0.2 wt%. The initial isosteric heat of hydrogen adsorption was determined to be $Q_{st} \approx 9$ kJ mol^{-1}, which is twice as large as typical metal–organic framework (MOF) materials, such as MOF-5,[13] and comparable to MOFs with open metal centers, such as HKUST-1.[14] The INS spectra of H$_2$-loaded GOF (Supporting Information, Figure S11) shows a peak at around 10 meV, suggesting very strong hindered rotation owing to a strong binding potential, consistent with the large Q_{st} value. Compared to the simulation results, the experimental H$_2$ uptake achieved so far in our GOF material is less than expected for an ideal GOF structure, which is most probably due to presence of unreacted functional groups in our initial GOF materials. This is supported by the large O/C ratio that we obtained from XPS data (Figure 3c). The O/C ratio for our ideal GOF-32 is $4/32 \approx 0.13$, which is significantly smaller than the current experimental ratio of 0.35. Clearly, there is significant room for optimization. Figure 4b shows the CO$_2$
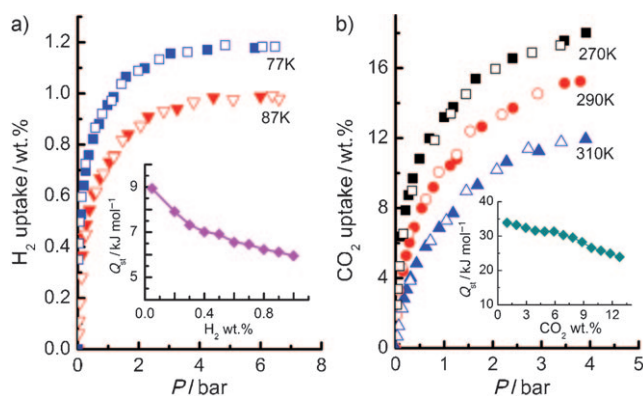

Figure 4. a) Excess H$_2$ and b) CO$_2$ isotherms at various indicated temperatures. Insets: Isosteric head of adsorption as a function of gas uptake.

isotherms at various temperatures. Again, the adsorption capacity is comparable to MOFs, whilst the heat of adsorption is among the largest observed in MOFs[15] and is almost comparable to amine-functionalized MOFs.[16]

In conclusion, we have successfully shown that graphene oxide layers can be used as building blocks for new nanoporous materials by interlinking them with diboronic acid. Considering the rich boron chemistry and large number of different types of boronic acids, it is quite possible that there are other linkers that will perform better than the B14DBA linker used in this study. Our next challenge is to reduce the O/C ratio in GOF materials to optimize the hydrogen uptake.

Different activation procedures other than heat treatment, such as chemical reduction, to remove unreacted functional groups could reduce the O/C ratio shown in Figure 3c and improve the surface area and adsorption capacity of GOFs significantly. We are currently carrying out more detailed research along these lines. We hope that our theoretical predictions and the first experimental results presented herein will start a new research direction based on cheap and environmentally friendly GO as a building block for new nanoporous materials with better gas adsorption properties.

Experimental Section

Full details of the synthesis of GO and GOFs are provided in the Supporting Information. Briefly, GO was synthesized using a modified Hummer's method[11] from synthetic graphite powder. For the initial GOF materials, benzene-1,4-diboronic acid (B14DBA) was used. Initial attempts to make these materials used a similar synthesis as for covalent organic frameworks (COF).[12] However, powder X-ray diffraction (PXRD) revealed a mixed phase of COF-1 and GOF (Supporting Information, Figure S1). After many trials, we found that a solvothermal reaction of GO with B14DBA in methanol yields single-phase GOF materials.

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