

PREPARATION AND CHARACTERIZATION OF POROUS GRAPHENE-OXIDE FRAMEWORKS

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Introduction

Graphene-based materials have generated great interest owing to their unique properties including large specific surface area, excellent electrical and thermal conductivity, good light transmission, high mechanical strength and life-cycle stability^{1, 2}. More importantly, due to its oxygen containing functional groups (i.e., hydroxyl, carboxyl, carbonyl and epoxy groups), GO has more attractive characteristics than graphene, such as better dispersion in water (higher hydrophilicity), and adjustable micro- and meso-structures because of easy functionalization via chemical modification³. Thus, given the chemical richness of its surface, it is possible to cross-link GO layers with organic ligands in order to obtain pillared graphene-oxide materials or graphene-oxide frameworks (GOFs). In this work we selected diboronic acid ligands of various structures: Benzene-1,4-diboronic acid (DBA), 4,4-Biphenyldiboronic acid (BDBA). They were used to cross-link GO to prepare GOF with varying d-spacing. We also investigated the influence that linkers in the thermal stability and the textural properties.

Materials and Methods

GO was synthesized using the modified Hummers method reported by Cruz-Silva et al.⁴ GOFs were obtained by solvothermal synthesis in mild conditions. Briefly, 1 mmol of the ligands was dissolved in methanol, and mixed with an equal amount (weight) of GO also dispersed in methanol. The suspensions were stirred for 30 minutes at room temperature, and then transferred to a stainless steel autoclave and left for 60 h at 100 °C. The resulting products were washed and centrifuged several times with methanol, in order to remove unreacted starting materials and dried overnight at room temperature. The resulting powders were characterized by means of X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and thermal analysis. The textural properties were characterized by N₂ and CO₂ adsorption at 77 and 273 K, respectively.

Results and Discussion

XRD patterns of the starting GO and the obtained GOF-DBA and GOF-BDBA samples showed a single diffraction (001) peak at different positions. In the case of GO, the expected peak at 9.6° was obtained, corresponding to the interlayer spacing of GO layers. For the GOFs, the peak was still sharp but shifted towards lower values, depending on the boronic acid ligands. This indicates the expansion of the layers of the GO upon the incorporation of the organic linkers, suggesting a successful binding of these to the surface groups of the GO. The characterization by FTIR spectroscopy (Figure 1) also confirmed this finding. As seen, in addition to the characteristic bands of GO present in the all spectra, two bands were clearly observed in the corresponding

spectra of samples GOF-DBA and GOF-BDBA. The first one appears at 1320 cm^{-1} , and is related to the B–O stretch due to cross-reaction of boronic acids with GO layers by boronate-ester formation^{5,6}. The second one at 1080 cm^{-1} corresponds to the prominent B–C vibrations.

The thermal stability of the materials was confirmed by the slightly higher thermal decomposition temperatures of the GOFs, compared to the GO, as well as the slightly smaller total mass loss -due to the stabilization of the functional groups linked to the organic spacer-. Further confirmation was obtained by the analysis of the evolved gases by TPD-MS with the detection of the m/z signals corresponding to the decomposition of the ligands, besides in addition to typical CO, CO₂, H₂O, O₂ and SO₂ m/z signals of GO.

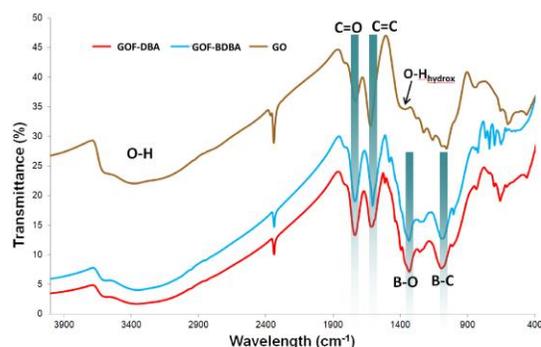


Figure 1. FTIR spectra for GOFs and GO precursor.

Regarding the textural features, the analysis of the gas adsorption data revealed the presence of narrow microporosity in the prepared GOFs, with a strong dependence with the organic linker (composition and dimensions).

Conclusions

We have successfully synthesized graphene-oxide frameworks by grafting linear diboronic acids to GO sheets. As inferred from XRD data, the GOF structures showed an increase in the interlayer spacing of the GO layers, indicating the pillaring of the linkers. This was further supported by FTIR, and TPD-MS, evidencing the occurrence of boronate-ester bonding formation. The so-prepared frameworks exhibit a remarkable increase in the porosity, comprised of narrow micropores, as confirmed from gas adsorption data.

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References

- Liu, S.K., Xie, K., Chen, Z.X., Li, Y.J., Hong, X.B., Xu, J., Zhou, L.J., Yuan, J.F., Zheng, C.M. (2015). A 3D nanostructure of graphene interconnected with hollow carbon spheres for high performance lithium–sulfur batteries. *J. Mater. Chem. A* 3, 11395–11402
- Qiu, Y.C., Li, W.F., Zhao, W., Li, G.Z., Hou, Y., Liu, M.N., Zhou, L.S., Ye, F.M., Li, H.F., Wei, Z.H., Yang, S.H., Duan, W.H., Ye, Y.F., Guo, J., Zhang, Y.H. (2014). High-rate, ultralong cycle-life lithium/sulfur batteries enabled by nitrogen-doped graphene. *Nano Lett.* 14, 4821–4827
- Chen, C., Yang, Q.-H., Yang, Y., Lv, W., Wen, Y., Hou, P.-X., Wang, M., Cheng, H.-M. (2009). Self-Assembled Free-Standing Graphite Oxide Membrane. *Adv. Mater.* 21, 3007–3011
- Cruz-Silva, R., Aaron Morelos-Gomez, A., Kim, H., Jang, H., Tristan, F., Vega-Diaz, S., Rajukumar, L.P., Perea-Lopez, N., Elías, A.L., Suhr, J., Endo, M., Terrones, M. (2014). Super-stretchable Graphene Oxide Macroscopic Fibers with Outstanding Knotability Fabricated by Dry Film Scrolling *ACS Nano* 8(6), 5959–5967
- Côté, A. P., Benin, A. I., Ockwig, N. W., ÓKeeffe, M., Matzger, A. J., Yaghi, O. M. (2005). Porous, Crystalline, Covalent Organic Frameworks. *Science* 310, 1166–1170
- Rambo, B. M., Lavigne, J. J. (2007). Defining Self-Assembling Linear Oligo(dioxaborole)s. *Chem. Mater.* 19, 3732–3739.