FIRST Center Research Perspective:

Brick and mortar approach to hierarchical electrode materials synthesis and performance

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Research Summary: Self-assembly of phenolic resins and a pluronic block copolymer via the soft-template method enables the formation of well-organized polymeric mesostructures, providing an easy way for preparation of ordered mesoporous carbons (OMCs). The final OMCs have high surface areas and accessible pores for energy storage in the form of ions, as in supercapacitors (Zhai, 2011). Their electrical conductivities, however, are less than those of graphitic carbon materials, namely graphite, carbon nanotubes, and graphene. To address this issue, the "brick and mortar" method for preparing high surface area OMCs, having graphitic domains without high temperature graphitization, was developed (Fulvio, 2011). Graphitic nanomaterials such as onion-like carbons, carbon black (Fulvio, 2011), carbon nanotubes (Guo, 2011), graphene, and carbon nanohorns (Fulvio, 2013) are dispersed in the OMC precursors. After low temperature carbonization, an OMC "mortar" with graphitic "bricks" is obtained. The electronic conductivity of the OMC is sufficient to allow for electronic transport between highly conductive graphitic "bricks", thus improving the rate performance of the final supercapacitors (Fulvio, 2011).

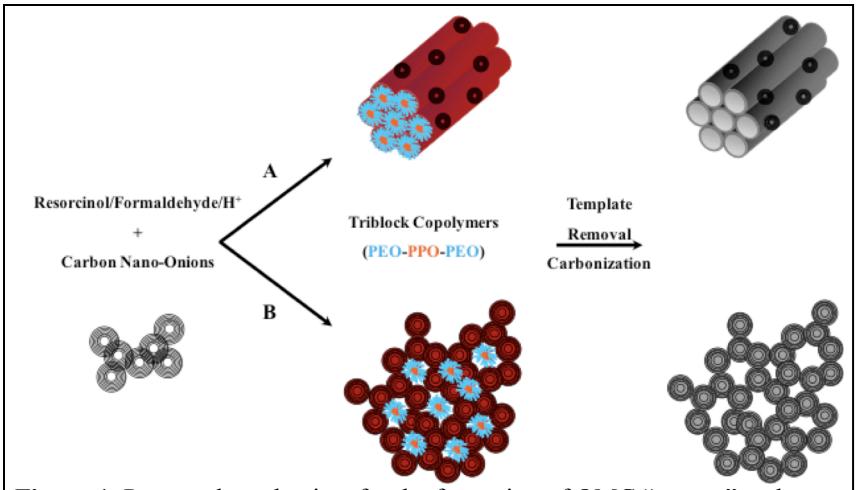

Figure 1. Proposed mechanism for the formation of OMC "mortar" and graphitic "bricks" nanocomposites.

Technical Details: Mesoporous carbon materials lack sufficient ordering at the atomic scale to exhibit good electronic conductivity. To date, ordered mesoporous carbons (OMCs) having uniform mesopores and high surface areas have been prepared from partially-graphitizable precursors in the presence of templates (Zhai, 2011). High temperature thermal treatments above 2000ºC required to increase conductivity, result in a partial or total collapse of the mesoporous structures and reduced surface areas induced by growth of graphitic domains, limiting their applications in supercapacitors. In this research, we successfully implemented a "brick and mortar" approach to obtain ordered graphitic mesoporous carbon nanocomposites with tunable mesopore sizes below 850ºC without using graphitization catalysts or high

temperature thermal treatments (Dai, US Patent Appln.). Phenolic resin-based mesoporous carbons act as mortar to highly conductive carbon blacks (CBs) and onion-like carbons (COs, Cebik, 2013 & McDonough, 2012) as bricks, shown in **Figure 1**. The adsorption properties, the capacitance and the resistivity of final materials (**Figure 2**) can be tailored by changing the mortar to brick ratios. All samples were prepared by combining the soft-template method for the synthesis of mesoporous carbons using resorcinol-formaldehyde resins and pluronic triblock copolymers of general formula poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) and in the presence of CB and CO additives.

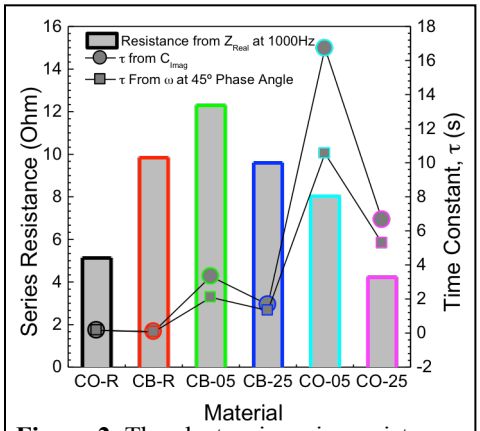

Figure 2. The electronic series resistance and time constants for the supercapacitor cells assembled with graphitic "bricks", in comparison to composites prepared using the "brick and mortar" method.

Significant Impacts on Science and Technology: these results show it is possible to largely improve and tailor the electrochemical performance of low-temperature mesoporous carbons that, in general, lack sufficient ordering at the atomic level thereby having moderate electrical conductivity. The addition of graphitic carbon nanomaterials to the synthesis gels of mesoporous carbons also provides a general methodology to tune the pore widths of the final materials, which is difficult to attain for pure resin based carbons (Dai, US Patent Appln.). Such nanocomposites may further be prepared as powders, monoliths and as films. Furthermore, the ability to prepare soft-templated carbons with mesopores in the range of 10-20nm without organic additives represents a major economical advantage of the present method. Carbon materials with such large pores are extremely attractive for the design of of future electrode materials for energy storage applications ranging from portable electronic devices to hybrid vehicles.

Publications and Manuscripts:

1. Cebik, J., McDonough, J. K., Peerally, F., Medgrano, R., Neitzel, I., Gogotsi, Y., Osswald, S., Nanotechnology, 2013, 24 (20), 205703.
2. Dai, S., Fulvio, P. F., Mayes, R. T., Wang, X. Q., Sun, X.-G., Guo, B., "Mesoporous Carbon Materials" (U.S. Patent Appln. No. 13/349,162).Fulvio, P. F., Mayes, R. T., Wang, X. Q., Mahurin, S. M., Bauer, J. C., Presser, V., McDonough, J., Gogotsi, Y., Dai, S., Adv. Fucnt. Mater., 2011, 21 (12), 2208-2215.Fulvio, P. F., Veith, G. M., Adcock, J. L., Brown, S. S., Mayes, R. T., Wang, X. Q., Mahurin, S. M., Guo, B., Sun, X.-G., Puretzky, A. A., Rouleau, C. M., Geohegan, D. B., Dai, S., J. Mater. Chem. A, 2013, 1, 9414-9417.
3. Guo, B., Wang, X., Fulvio, P. F., Chi, M., Mahurin, S. M., Sun, X. G., Dai, S., Adv. Mater. 2011, 23 (40), 4661-4666.
4. McDonough, J. K., Frolov, A. I., Presser, V., Niu, J., Miller, C. H., Ubieto, T., Fedorov, M. V., Gogotsi, Y., Carbon, 2012, 50 (9), 3298-3309.
5. Zhai, Y., Dou, Y., Zhao, D., Fulvio, P. F., Mayes, R. T., Dai, S., Adv. Mater. 2011, 23 (42), 4828-4850.