Porous yet dense metal-free electro-materials for compact energy storage

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In the last decades, considerable efforts have been made to increase the gravimetric energy density of electro-materials. The volumetric energy density has started to receive more attention only recently with the emergence of miniaturized and on-board energy storage devices. As supercapacitors and batteries go smaller, the main challenge is hence to fabricate new electro-materials that can store more charges per unit volume [1,2].

Metal-based electro-materials, in particular the conducting or semi-conducting ceramic materials (M_xC_y , M_xS_y , M_xO_y), naturally possess high density leading to large volumetric energy density. However, because of the lack of the surface functionality, porosity and texture of ceramics, as well as the low conductivity of semiconductors, the performance of metal-based electro-materials has been restricted due to the blocked mass transfer typically when the electrodes are thick.

Metal-free electro-materials, made of mainly conjugated carbon atoms as well as other elements, allow the development of abundant porosity and good conductivity. Most importantly, metal-free electro-materials are preferential in terms of sustainability, chemical variety and processability (Fig. 1). Nevertheless the challenge of using metal-free materials is to increase the density.

Professor Quan-Hong Yang at Tianjin University and co-workers recently conducted a series of studies on increasing the density of metal-free electro-materials via engineering the porosity and texture at nanoscale and have succeeded in achieving very high volumetric capacities with several graphene-based macro-assemblies and their composites with polymers or sulfur [3–6].

Polyaniline (PANi) has been regarded as a popular electro-material with broad applications in energy, sensing and electrochromic displays. PANi has high electrochemical gravimetric capacitance in theory attributable to the fast redox protonation/deprotonation reactions. To mitigate the low conductivity of deprotonated PANi and its disso-

lution upon cycling, PANi materials are often composited with various carbon materials. This strategy has indeed effectively improved the electrode performance of both PANi and carbon materials. However due to the low density of porous carbons, the volumetric performance of carbon-PANi composites is unsatisfactory.

The dense assembly of reduced graphene oxide sheets,

Figure 1 A comparison of metal-free and metal-based highly dense yet porous electro-materials.

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used as basic units of bulk carbon materials, was achieved by using an evaporation-induced drying (EID) process [5]. In their latest work [1], Yang and his team succeeded in extending the EID method to co-assemble the nanosheets with PANi. This co-assembly has a density over 1.5 g cm^{-3} and exhibits a record volumetric capacitance over 800 F cm^{-3} among metal-free electro-materials.

Yang's main research interests are on the colloidal chemistry and the assembly of graphene oxide derivatives. Yang and his team know well how the extremely tiny objects can be manipulated via chemistry and how to form and tailor the texture of macroscopic assemblies. Most of the dense-assembly techniques developed in Yang's laboratory are at room temperature and ambient conditions, like the co-assembly of reduced graphene oxide with sulfur nanoparticles [5]. This expertise renders the development of advanced forms of metal-free highly dense soft matter and the exploration of their feasibility as compact energy storage materials.

Yang has demonstrated the wide applicability of EID process for engineering the texture of macro-assemblies of one or more soft matters, which as well targets on clean energy technologies resulting in compact energy storage

devices. Because carbon-based materials are very important components in electrodes, this strategy is expected to receive more applications for a range of electrochemical technologies, particularly where metal-free components are required.

**Received 5 January 2016; accepted 6 January 2016;
published online 8 January 2016**

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