

Chemically Modified Graphene Stars as New Electrode Material in Ultracapacitor Cell

Capacitors have numerous technological applications, including energy storage, and researchers are striving to develop more efficient devices (i.e., to increase capacitance per unit mass or per unit volume or both). Some ultracapacitors utilize nanoscopic charge separation at the electrochemical interface between an electrode and an electrolyte, an approach known as electrochemical double layer capacitance (EDLC). They offer superior performance compared to conventional dielectric capacitors because the energy density is inversely proportional to the thickness of the double layer, and this thickness in EDLC is of the order of a nanometer.

In the October issue of *Nano Letters* (DOI: 10.1021/nl802558y; p. 3498), M.D. Stoller, S. Park, Y. Zhu, J. An, and R.S. Ruoff of The University of Texas, Austin have introduced a class of carbon material for use as an electrode material in EDLC ultracapacitors, which they call chemically modified graphene (CMG). The researchers synthesize the CMG by suspending graphene oxide sheets in water, and then reduce the sheets with hydrazine hydrate. During reduction, the graphene sheets agglomerate into 15–25- μm -diameter particles that possess a surface area of 705 m^2/g as measured by the N_2 absorption Brunauer–Emmett–Teller (BET) method, and the oxygen content is greatly reduced by the chemical action of hydrazine, so that the “reduced graphene oxide” sheets have excellent electrical conductivity. The impressively high surface area supports CMG’s promise as a useful material for ultracapacitor electrodes.

The researchers have also built a two-electrode EDLC cell. They form CMG particles into porous electrodes using a polytetrafluoroethylene binder. The cell consists of two such electrodes, isolated by a porous separator, with all of this saturated by an electrolyte that permits ionic current while suppressing electronic current that would otherwise discharge the cell. The high conductivity of the CMG materials permits thicker electrodes that also are free of the conductive fillers that had been previously required. This raises the relative amount of electrode material, and boosts the energy density of the packaged ultracapacitor.

The researchers used cyclic voltammetry and galvanostatic charge/discharge to measure the specific capacitance of the cells. Values between 80–135 F/g are obtained, using three electrolytes commonly found in commercial EDLCs. They also used electrical impedance spectroscopy to

characterize the frequency response and hence the equivalent series resistance (ESR) of the cell. The high conductivity of the CMG materials contributes to the favorable values of ESR and power capability.

“These chemically modified graphenes are cheap and abundantly available, have good electrical conductivity, and very large surface areas,” said Stoller and Ruoff. “Furthermore, they are compatible with common electrolyte systems. Ultracapacitors based on these materials could have the cost and performance to be rapidly adopted for a wide range of energy storage applications.”

RICH LOUIE

First-Principles Calculations Show Ultrafast Electron Injection for Dye Adsorbed on TiO_2 Nanowire

Pragmatic harvesting of solar radiation with dye-sensitized solar cells (DSSC)—the so-called Grätzel cell—requires gains in efficiency. In the past two decades, researchers have sought to separate the light-absorption process from the charge-collection process—thereby mimicking natural photosynthesis—by combining dye sensitizers with inexpensive, wide bandgap semiconductors like TiO_2 . By design, the dye’s highest occupied molecular orbital (HOMO) lies within the semiconductor’s bandgap, and its lowest unoccupied molecular orbital (LUMO) lies within the semiconductor’s conduction band. Efficiency is quantified with the maximum photocurrent density, I_{ph} , a measure of the charge injection rate from the dye HOMO to the semiconductor conduction band, and the open circuit potential, V_{oc} , a measure of the energy difference between the dye HOMO and the conduction band minimum (CBM). While nanoparticle-based and surface-based DSSCs have been well studied, one-dimensional (1D) nanostructures have only recently been investigated. Their large aspect ratios result in enhanced visible light scattering and absorption, and the 1D geometry facilitates rapid, diffusion-free electron transport to the electrodes. Recently, however, S. Meng, J. Ren, and E. Kaxiras of Harvard University used extensive calculations based on time-dependent density functional theory (TDDFT) to investigate the mechanism and electronic coupling between a TiO_2 nanowire and a natural dye molecule.

As reported in the October issue of *Nano Letters* (DOI: 10.1021/nl801644d; p. 3266), Meng, Ren, and Kaxiras used the TiO_2 anatase phase to construct model nanowires with four (101) facets and two (001) facets exposed. The nanowire unit was repeated either along the [010] or the [101]

directions with periodic boundary conditions. The researchers adsorbed onto the nanowire one cyanidin molecule (cyanin without the sugar moiety), and found that the dye assumes a lower energy quinoid structure after a proton transfers to the nanowire. For various nanowire orientations and dye adsorption sites, the researchers found that deprotonation results in shifting the cyanidin HOMO inside the TiO_2 bandgap, and the LUMO shifting to a position very close to but below the TiO_2 CBM. Oxygen vacancy defects, which have been shown to be prevalent in TiO_2 nanowires, were found to further improve dye adsorption. Calculated spectra show that visible light absorption is greatly enhanced by the dye’s presence. Even though the CBM is 0.1–0.3 eV higher in energy than the dye LUMO, the researchers found using real-time TDDFT simulations that excited electrons are injected into the conduction band of TiO_2 at the ultrafast time scale of 50 fs, resulting in both high V_{oc} and large I_{ph} . The researchers said that their “results agree with available experimental absorption spectra and electron injection kinetics,” and that, “further improvements can be achieved by attaching more dye molecules to the facets of the nanowire, forming a high density antenna system similar to natural photosynthesis, which is a unique advantage of the 1D nanowire system.”

STEVEN TROHALAKI

Microemulsion Technique Improves Iron Oxide Loading in Superparamagnetic Silica Composite Nanospheres

Superparamagnetic composite nanospheres are useful for a variety of environmental and biological separation applications. Often, functional ligands are bound to the surface of these particles to improve their separation capabilities. Particle surface functionalization is facilitated by encapsulation of the nanospheres in a layer of silica. One problem, though, with superparamagnetic silica composite nanospheres (SSCNs) is that they typically have small magnetic saturation values, a result of low magnetic material loading, making separations inconvenient and time-consuming. Recently, a group of researchers led by J.M. Xue at the National University of Singapore developed a new oil-in-diethylene glycol (DEG) microemulsion technique that has potential to improve SSCN performance. The researchers report their findings in the October 28 issue of *Chemistry of Materials* (DOI: 10.1021/cm8012107; p. 6292).

A variety of synthetic approaches are