

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

available for SSCN synthesis; however, each has its own set of drawbacks. One synthetic technique, the Stöber sol-gel method, leads to uniform silica-coated nanospheres but it suffers from low loading of magnetic material and requires an extra surface functionalization step. With aerosol pyrolysis, another approach, combustion of iron and silica precursors forms high-loading composites but the process requires high temperatures that can lead to nanosphere aggregation. In another technique, reverse microemulsion, magnetic material loading is determined by the amount of hydrophilic iron oxide dispersed in water droplets that are suspended in a continuous oil phase. High-quality hydrophilic iron oxide particles are an important part of this technique, but their synthesis is still a challenge. The oil-in-DEG microemulsion technique described in this report uses high-quality hydrophobic iron oxide, does not require high temperatures, and is capable of high magnetic material loading.

In the described microemulsion technique, hydrophobic iron oxide nanoparticles are dispersed in a discrete tetraethylorthosilicate (TEOS) phase. The magnetic material-containing oil droplets are stabilized in a DEG continuous phase using a nonionic surfactant. The use of DEG instead of water eliminates premature hydrolysis and condensation of the TEOS giving the researchers greater control over particle size and agglomeration. Ammonia is added which diffuses into the oil droplets causing the hydrolysis and condensation reactions to occur only in the oil droplets. This eliminates the possibility of empty SSCNs. As a result, the researchers have made SSCNs with saturation magnetizations as high as 33.6 emu/g (compared to pure superparamagnetic iron oxide nanoparticles with a saturation magnetization of ~42 emu/g), much higher than reverse microemulsion methods that typically provide less than 5 emu/g. In the search for highly magnetic silica-coated particles, the research group has introduced a synthetic method that holds great potential for improving future biological and environmental separations.

KEVIN HERLIHY

Novel Hydrogel Membrane Enables Demonstration of Water Transpiration in a Synthetic Tree

Transpiration—the motion of water from the soil into the air through a vascular plant—involves differences in pressure about a hundred times larger than those currently achieved in synthetic wicks. T.D. Wheeler and A.D. Stroock from Cornell University recently overcame this chal-

lenge by designing and operating a synthetic tree, a microfluidic system formed in a cross-linked organic hydrogel.

As the researchers reported in the September 11 issue of *Nature* (DOI:10.138/nature07226; p. 208), the system captures the main attributes of transpiration in plants: transduction of subsaturation in the vapor phase of water into negative pressures in the liquid phase, stabilization and flow of liquid water at large negative pressures (down to -21 MPa), continuous heat transfer with the evaporation of liquid water at negative pressure, and continuous extraction of liquid water from subsaturated sources.

The researchers first created 1-mm thick sheets of poly(hydroxyethyl methacrylate) (pHEMA); a sheet was imprinted with microfluidic channels by soft lithography, and then another sheet was bonded on top of it by repolymerization. The system contained all the elements required by a synthetic tree: a root membrane of pHEMA in contact with the water source, the liquid-filled xylem capillary, and a leaf membrane of pHEMA exposed to air.

A steady-state flow through the synthetic tree was achieved by exposing the leaf to air flow. The root was exposed either to vapor or liquid water, and it was demonstrated that the leaf network can act alone as a pump due to the highly negative pressure differences. Pressures 15-fold higher than any previously reported synthetic pumped system were recorded when the root membrane was punctured for easier access to the source, and separate experiments with an intact root membrane demonstrated the capacity of the system to reproduce the transpiration of water in a plant.

Through a series of experiments, the researchers demonstrated that the system offers a platform not only for realistic investigations of different aspects of plant physiology, but also for applications in processes demanding large pressure differences (that can move liquid tens of meters above a reservoir), in cooling a heat source by transpiration, a mechanism that will greatly increase the heat flux compared to other technologies, and in the extraction and purification of water from subsaturated soils.

EUGEN PANAITESCU

Hydrogels Stimulated by Antibiotics to Release Vascular Endothelial Growth Factors

Polymeric hydrogels can be triggered to release pharmacological agents by chemical, biological, and physical means. However, a significant therapeutic level is difficult to achieve because the stimulus concentration required to elicit a polymer

response cannot easily be applied *in vivo*. A hydrogel based on pharmacologic processes has been designed and validated by M. Ehrbar of the University Hospital Zurich, R. Schoenmakers and W. Weber of ETH Zurich, and their collaborators to release the protein vascular endothelial growth factor (VEGF) upon interaction with the antibiotic Novobiocin.

As described in the October 2008 issue of *Nature Materials* (DOI: 10.1038/nmat2250; p. 800), the researchers designed an antibiotic-sensing hydrogel by grafting bacterial gyrase subunit B (GyrB) onto polyacrylamide, then dimerizing GyrB with the antibiotic Coumermycin to stabilize the structure. The hydrogel was designed to release its contents when it came in contact with a secondary antibiotic, Novobiocin. Novobiocin binds to the GyrB and competitively inhibits the GyrB-Coumermycin interaction. Once GyrB is uncoupled, the hydrogel structure is loosened and dissolution occurs. To validate the feasibility of the hydrogel, swelling behavior and cell activity was examined.

The release of protein from prepared hydrogels was determined by incubating the hydrogels in a phosphate buffered saline (PBS) solution containing concentrations of Novobiocin, ranging from 0 mM to 1 mM. The hydrogels were monitored for a period of 120 h, and the release profile showed that as concentrations of Novobiocin increased, the amount of protein released also increased. This effect was due to the rapid dissolution of the hydrogel in the presence of higher concentrations of Novobiocin, and slower release at lower concentrations. A cell proliferation assay, using human embryonic kidney cells, was used to study possible cytotoxic effects of the hydrogel components. The assay showed that no cytotoxic effects were present at hydrogel quantities sufficient to release VEGF concentrations of >500 ng ml⁻¹. To determine the bioavailability and bioactivity of VEGF after release from the hydrogel, a cell proliferation assay was performed using human umbilical vein endothelial cells (HUVEC). After incubating the hydrogels in the cell medium with and without Novobiocin for 96 h, the assay showed in the absence of Novobiocin that there is no difference in cell proliferation compared to the negative control. However, when Novobiocin is present, there is a marked increase of HUVEC growth.

The novel stimuli-responsive hydrogel in this study has demonstrated the ability to release therapeutic treatments within physiological limits, without sacrificing the activity of its contents.

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