Intrinsically unstacked double-layer graphene for high-rate lithium-sulfur batteries

March 4 2014

By introducing a large number of protuberances on graphene layers during chemical vapor deposition (CVD) synthesis, scientists have fabricated intrinsically unstacked double-layer graphene with a high specific surface area, excellent electrical conductivity, and mesoporous structure. The unstacked double-layer graphene, described in the journal *Nature Communications*, could be excellent cathode materials for high-power lithium-sulfur batteries.

Graphene is a promising functional material for a variety of applications including energy storage because of its extraordinary electrical and mechanical properties. However, graphene layers tend to stack with each other because of their huge surface area and strong π-π interactions between multi-layered graphene with an interlayer distance of ca. 0.334 nm. This stacking results in a much smaller surface area of the obtained graphene, with poor energy-storage performance. It is necessary to avoid stacking to amplify the intrinsic properties of graphene and facilitate practical application.

Researchers have explored numerous novel approaches to inhibit the stacking of graphene. Most of them are based on the introduction of spacers such as metal oxides, conducting polymers, carbon black, or carbon nanotubes into the interlayer spaces. However, such hybridization processes inevitably cause changes in the intrinsic properties of graphene and/or induce poor interfaces.

Scientists in Tsinghua University (China) have now successfully fabricated intrinsically unstacked double-layer graphene through template-directed CVD. A team led by Prof. Qiang Zhang and Fei Wei explored the idea of using mesoporous nanoflakes as the template. The graphene layers are deposited onto the mesoporous template and cast into its mesoporous structure, where the carbon atoms deposited in the mesopores form the graphene protuberances and act as spacers to prevent the stacking of the graphene layers deposited on both sides of the mesoporous flakes. Consequently, double-layer template graphene composed of two graphene layers with a large number of protuberances can be recovered after the removal of the mesoporous flakes.

"The presence of a large number of mesopores in the nanoflake template gives rise to protuberances with a high density of ca. 5.8×10^{14} m^{-2} and sizes ranged from 2 to 7 nm between graphene layers," first-author Meng-Qiang Zhao tells Phys.org. "The protuberances play an important role in preventing the stacking of graphene layers. Besides, the presence of such protuberances on the surface of graphene can weaken the π-π interactions between graphene layers and thus prevent the stacking of neighboring double-layer template graphene to a certain extent." As a result, the double-layer graphene shows a high specific surface area of 1628 m^2 g-1, abundant mesopores with the size ranging from 2 to 7 nm, and a total pore volume of 2.0 cm^3 g^{-1}.

Lithium-sulfur batteries are one of the most promising energy storage technologies due to high energy density. However, their power density and poor cycling stability have always been a key obstacle for their practical application. When using the unstacked double-layer graphene as the cathode materials, scientists were able to fabricate lithium-sulfur batteries with excellent high-power performance. High reversible capacities of 1034 and 734 mA h g^{-1} were achieved at high discharge rates of 5 and 10 C, respectively. Even after 1000 cycles, high reversible capacities of ca. 530 and 380 mA h g^{-1} were retained at 5 and 10 C, with

coulombic efficiencies constants at ca. 96 and 98 %, respectively.

"The excellent high-power performance can be attributed to the extraordinary electrical conductivity and unique mesoporous structure of the unstacked double-layer graphene," Prof. Zhang explained. The unstacked double-layer graphene's unique porous structure allows the effective storage of sulfur in the mesosized lamellar interlayer space, which gives rise to an efficient connection between the sulfur and graphene and prevents the diffusion of polysulfides into the electrolyte. Consequently, an excellent high-power performance of the lithium-sulfur cells with a high capacity and good stability is achieved.

"We expect that the unstacked double-layer graphene materials hold potential in applications for environmental protection, nanocomposites, electronic devices, and personal healthcare because of their intrinsic large surface area, extraordinary thermal and electric conductivity, robust 3D scaffold, tunable surface chemistry, and biocompatible interface," said Prof. Zhang, "Because unstacked layered nanostructures are not limited to graphene, we foresee a new branch of chemistry evolving in the stabilization of nanostructures through 3D topological porous systems."

More information: Zhao MQ, Zhang Q, Huang JQ, Tian GL, Nie JQ, Peng HJ, Wei F. "Unstacked double-layer templated graphene for high-rate lithium sulfur batteries." *Nature Communications* 2014, 5, 3410, DOI: 10.1038/ncomms4410.

Provided by Tsinghua University

unstacked-double-layer-graphene-high-rate.html