

Supporting Information

Self-assembled hierarchical nanostructure comprising carbon spheres and graphene nanosheets for enhanced supercapacitor performance

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Experimental Section

Preparations of graphene oxide and functionalized carbon spheres

Graphene oxide was prepared from natural graphite by a modified Hummers method using NaNO₃, H₂SO₄, and KMnO₄, the details of which have been described in previous reports.^{S1,S2} Carbon spheres were synthesized by a hydrothermal method.^{S3,S4} 6 g of glucose was first dissolved in 40 mL of de-ionized water to form a clear solution, which was transferred to a Teflon autoclave and treated at 180 °C for 12 hr. After cooling naturally to room temperature, the product was isolated by three cycles of centrifugation/washing/redispersion. The freshly prepared carbon spheres were functionalized with Poly(diallyldimethylammonium chloride) (PDDA) to own surface positive charges. First, carbon spheres were dispersed into an aqueous solution of 0.5 wt% PDDA that contained 20 mM NaCl and 20 mM Tris solution and the resulting dispersion was stirred for 2 hr at room temperature. Free PDDA was removed by three cycles of centrifugation/washing/redispersion.

Fabrication of self-assembled hierarchical nanostructure

Hierarchical nanostructure was fabricated by a self-assembled approach via the electrostatic interaction between positively charged functionalized carbon spheres and negatively charged graphene oxide. 100 mL of functionalized carbon sphere aqueous

solution (1 mg mL^{-1}) was first sonicated for 30 min and then added to 100 mL of aqueous graphene oxide suspension (different concentrations) under mild stirring at room temperature. After 6 hr, hydrazine (65 wt%, weight ratio of 7:10 for hydrazine/graphene oxide)^{S2} was added into the above suspension to chemically reduce graphene oxide. The hierarchical nanostructure comprising graphene and carbon spheres was obtained after high-speed centrifugation ($>10000 \text{ rpm}$) and washing with de-ionized water. Plain graphene was fabricated by using the same procedures as that of the hierarchical nanostructure but without carbon spheres.

Fabrication of supercapacitor devices

Electrode films were constituted of 95wt% of active material and 5wt% of poly(tetrafluoroethylene) binder. The active material was compressed into a thin film with a round shape (with diameter around 13 mm) and loaded onto a nickel foam current collector. PTFE plates and stainless clamps were used to maintain the stack under pressure. A porous polymeric separator ($50 \mu\text{m}$ thick) was inserted between the two electrodes. The cells were immersed into an electrolyte consisting of a 6 M KOH aqueous solution.

Material characterizations and supercapacitor device measurement

Graphene oxide nanosheets were characterized by atomic force microscopy (AFM, Nanoman, Veeco, Santa Barbara, CA) using tapping mode. The morphology and microstructure of the samples were investigated by field emission scanning microscopy (SEM, JSM-6700F, Japan). The zeta potentials were measured with a Malvern Instruments Zen 3600 Zetasizer. Cyclic voltammograms and electrochemical impedance spectra were measured by Autolab PGSTAT30 electrochemical working station. Galvanostatic charge/discharge measurements were carried out using a NEWARE battery testing system.

Reference

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