



Full Length Article

Pseudocapacitive organic catechol derivative-functionalized three-dimensional graphene aerogel hybrid electrodes for high-performance supercapacitors

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ABSTRACT

Bio-inspired and environmentally friendly chemical functionalization is a successful way to a new class of hybrid electrode materials for applications in energy storage. Quinone (Q)-hydroquinone (QH₂) couples, a prototypical example of organic redox systems, provide fast and reversible proton-coupled electron-transfer reactions which lead to increased capacity. To achieve high capacitance and rate performance, constructing three-dimensional (3D) continuous porous structure is highly desirable. Here we report the hybrid electrodes (GA-C) consisting of 3D graphene aerogel (GA) functionalized with organic redox-active material, catechol derivative, for application to high-performance supercapacitors. The catechol derivative is adsorbed on the surface of GA through non-covalent interactions and promotes fast and reversible Q/QH₂ faradaic reactions, providing large specific capacitance of 188 F g⁻¹ at a current of 1 A g⁻¹ and a specific energy of ~25 Wh kg⁻¹ at a specific power of ~18,000 W kg⁻¹. 3D continuous porous structure of GA electrode facilitates ion and electron transports, resulting in high rate performance (~140 F g⁻¹ at a current of 10 A g⁻¹).

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1. Introduction

Supercapacitors (SCs), also called electrochemical capacitors, have received great interests because of their high charging/discharging rate, exceptional cycle life, low environmental impact, commercial affordability, and high power density [1]. Despite the exceptional attributes of SCs, their low energy densities, an order of magnitude less than typical secondary batteries, remain moderate [2]. It is currently a significant challenge to increase the energy density of SCs while maintaining their intrinsic properties.

Exploration of faradaic electrode materials has been considered as a promising approach for enhancing the energy density of SCs [2,3]. Examples include transition metal oxides [4–7], metal hydroxides [8–10], and conducting polymers [11–14]. Particularly, organic based faradaic materials have the potential for use in electrodes owing to their distinctive properties such as large potential gravimetric energy density, lightweight, low cost,

mechanical flexibility, and chemical tunability, which are particularly appropriate for energy storage [15–17]. In one example of the materials, quinone (Q)-hydroquinone (QH₂) redox couples, inspired by biological electron transfer processes in photosynthesis and respiration, have been well reported as they offer ultrahigh theoretical capacitance of 1751 F g⁻¹ due to their capability to reversibly store two electrons and two protons per quinone in one kinetic step at low pH values that is capable of enhancing capacity [18–24]. The quinone (or hydroquinone) is based on phenolics that make it compatible with the family of aromatic compounds such as carbon nanomaterials (e.g., graphene, carbon nanotube, mesoporous carbon, and activated carbon) [25–28] and aromatic conducting polymers (e.g., polyaniline and polypyrrole) [24,29] through non-covalent interactions (e.g., π - π and hydrophobic interactions) while maintaining their intrinsic properties [30,31]. Although the use of organic pseudocapacitive materials improves the energy of SCs, they are still experiencing some difficulties with the rapid capacity degradation upon cycling and poor power capability due to the slow charge transfer process and the low electronic conductivity, compared to non-faradaic double layer capacitors [32–34]. Thus, the design and optimization of a reliable organic hybrid electrode is particularly important for high energy and

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power densities of SCs as well as long cycle life, which in turn provide broad applications.

Three-dimensional (3D) graphene aerogels have potential as they provide interconnected macroporous architecture, ensuring both high surface area to volume ratio and continuous pathway for electrons and ions [35–39]. Additive/binder-free and self-standing features of graphene aerogels also enable to serve as a host that is integrated with various active materials such as nanoparticles, polymeric, or organic materials [40–44]. Herein we report a hybrid electrode which utilizes the catechol derivative that provides the proton-coupled electron transfer of Q/QH₂ couple incorporated on 3D graphene aerogel scaffold. Benefitting from the synergistic effect of 3D continuous porous structure (provided by graphene aerogel) and reversible faradaic reaction (provided by the catechol derivative), the hybrid electrodes exhibit high specific capacitance, good rate performance, and long cycle life for at least 10000 charge/discharge cycles.

2. Materials and methods

2.1. Preparation of graphene aerogel (GA)

3D GA electrodes were prepared as reported [45]. Briefly, 90 mg of GO powder (Graphene supermarket) was dispersed in 22.5 mL of Millipore water (conc. 4 mg mL⁻¹). 7.5 mL of hypophosphorous acid (H₃PO₂, 50 wt% solution in water, Aldrich) and 900 mg of iodine (I₂, 99.8%, Aldrich) were added to the suspension and then the solution was heated for 6 h at 90 °C. After cooling to room temperature, the monolith was washed three times with Millipore water to remove residues, followed by freeze-dried for 2 days.

2.2. Electrosynthesis of catechol derivative on GA

Catechol (40 mg, 99+%, Across), and lithium perchlorate trihydrate (1.06 g, LiClO₄·3H₂O), 99% extra pure, Across) were added to Millipore water (20 mL) in a 150 mL open beaker where graphene monolith were located and then electrosynthesis was performed for 15 min at 1 mA cm⁻² versus a Ag/AgCl reference electrode and a Pt wire counter electrode. The monolith was removed from the solution and washed with copious Millipore water and then dried overnight at ambient conditions.

2.3. Characterization

The microstructures were imaged using a HitachiS-4700 SEM. XPS data were obtained using a VG Multilab 2000 system (Thermo VG Scientific) with a monochromatic Mg KR X-ray source ($h\nu = 1253.6$ eV) under a vacuum-analysis chamber (10⁻⁷ Torr). The high-resolution scans of C and low-resolution survey scans were analyzed for each sample at least two separated locations. Raman measurements were collected using a Raman confocal imaging microscope (Horiba LabRAM HR 3D, Horiba). Electrochemical characterizations, including CV, GCD, and EIS, were performed using a VMP3 multichannel potentiostat (VMP3, Bio-Logic, USA) in the three-electrode mode with a Ag/AgCl reference electrode, a Pt wire counter electrode, and the electrodes obtained as the working electrodes in 0.1 M of HClO₄ aqueous electrolyte. The mass of electrode was ~5 mg. All potentials in this study are with respect to this reference electrode. In the GCD profiles, the specific capacitance can be estimated using the following equation:

$$C = I / [(\Delta V / \Delta t)m] \quad (1)$$

where I is the current applied, $\Delta V / \Delta t$ is the slope of the discharge curve after a IR drop at the beginning of the discharge curve, and m is the mass of an electrode (in g).

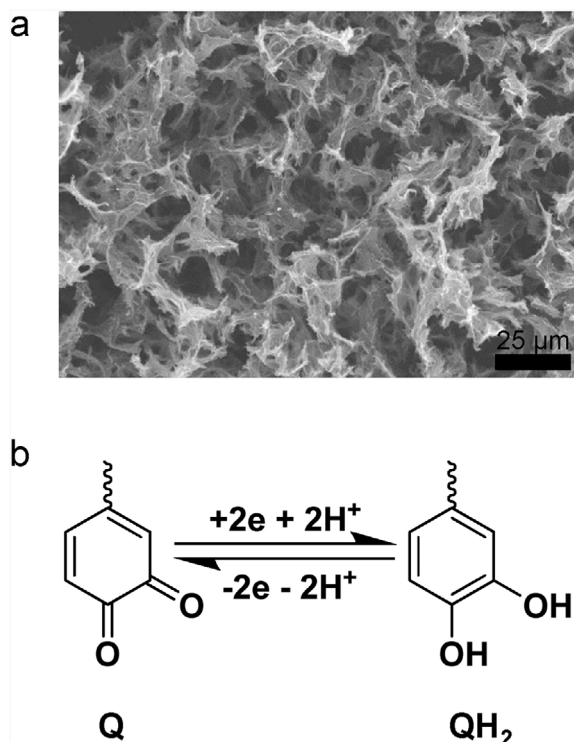


Fig. 1. (a) SEM image of GA. (b) A simplified reversible redox reaction of quinone (Q) and hydroquinone (QH₂) in the catechol derivative during charge/discharge.

The specific power (P , in W kg⁻¹) and energy (E , in Wh kg⁻¹) were calculated using the following equation:

$$P = (\Delta V)^2 / 4R_{ESR}M, E = 0.5C(\Delta V)^2 / 3600M \quad (2)$$

where ΔV , R_{ESR} , M , and C are the potential window obtained from discharge curve after the IR drop, internal resistance from IR drop, the mass of an electrode (in kg), and the measured capacitance, respectively. The internal resistance was computed from the voltage drop at the beginning of each discharge:

$$R_{ESR} = \Delta V_{IR} / 2i \quad (3)$$

where ΔV_{IR} and i are the voltage drop between the first two points in the voltage drop at the top cutoff and applied current, respectively.

4. Results and discussion

Three-dimensional (3D) graphene aerogel, which we term GA here, was prepared via the self-assembly of graphene sheets as reported [45]. Once hypophosphorus acid and iodine converted graphene oxides (GOs) to reduced graphene oxides (RGOs), the electrostatic repulsion between graphene sheets decreased but π - π interaction strengthened, leading to the aggregation of RGOs [45]. The resulting macroporous structure of GA is observed by scanning electron microscopy (SEM) (Fig. 1a). The pore size ranges from a few to hundreds of micrometer with a wall thickness of tens of nanometers. Starting with catechol, its derivative was electrochemically synthesized and hybridized on the as-prepared GA, abbreviated as GA-C, by applying a current of 1 mA cm⁻² for 15, 30, and 60 min in a 0.5 M of LiClO₄ aqueous electrolyte. No significant change in the morphology of these GAs was observed after electrodepositing catechol derivative around GA (Fig. S1 in Supplementary Data). 15 min electrodeposition was used as the resulting GA-C electrode provided the best performance (Fig. S2 in Supplementary Data). The mechanical integrity of GA-C was well conserved as a monolith and

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