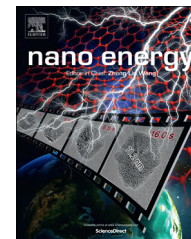


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RAPID COMMUNICATION

Functionalized graphene aerogel composites for high-performance asymmetric supercapacitors

Zenan Yu¹, Matthew McInnis¹, Jean Calderon, Sudipta Seal, Lei Zhai*, Jayan Thomas**

NanoScience Technology Center, Department of Materials Science and Engineering, Department of Chemistry, and CREOL, College of Optics and Photonics, University of Central Florida, FL 32826, United States

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Abstract

Asymmetric supercapacitors (ASCs) have played a leading role in realizing energy storage devices with high energy and power densities. While both anode and cathode materials are important for high performance ASCs, more research effort has been devoted to developing cathode materials because the energy source of an ASC is mostly attributed to the cathode. However, the development of anode materials is essential in order to achieve high power density as well as stable long-term cycle life of ASCs. In this study, functionalized graphene aerogel (GA) decorated with palladium (Pd) nanoparticles is used as an efficient ASC anode material. The high surface area ($328 \text{ m}^2 \text{ g}^{-1}$) and low electrical resistivity (50 times lower than one without Pd) of the GA composite grants a high specific capacitance (175.8 F g^{-1} at 5 mV s^{-1}), excellent rate capability (48.3% retention after a 10 fold increase of scan rate), and remarkable reversibility. ASCs assembled from manganese dioxide (cathode) and GA composite (anode) show stable extended cell voltage, fast charge-discharge capability, excellent cycle stability (89.6% retention after 3000 cycles), and high energy and power densities (average of

*Corresponding author. 12424 Research Parkway, Suite 400, Orlando, FL, USA 32826. Tel.: +1 407 882 2847.

**Corresponding author. 12424 Research Parkway, Suite 400, Orlando, FL, USA 32826. Tel.: +1 407 882 0196.

E-mail addresses: lzhai@ucf.edu (L. Zhai), jayan.thomas@ucf.edu (J. Thomas).

¹These two authors contributed equally to this work.

13.9 Wh kg⁻¹ and 13.3 kW kg⁻¹). These results demonstrate the great potential of the GA composite as an efficient anode material for high performance energy storage devices.
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Introduction

Bridging the properties of batteries and conventional capacitors, supercapacitors (SCs) are an emerging technology that fills a crucial gap in today's rapidly evolving energy storage needs. With desirable properties of high power density, fast charge-discharge rate, and excellent cycle stability [1-5], SCs can be used in a wide range of applications such as hybrid vehicles, portable electronics, pacemakers, etc. [6-9]. Improving the energy density of SCs is critical for its widespread use. The energy density of a SC is calculated using the equation $E=1/2CV^2$, where E is the energy density, C is the cell capacitance, and V is the cell voltage [10,11]. Obviously, the exponent of 2 in the above equation makes the cell voltage to play an essential and efficient role in enhancing energy density. There are two major approaches to broaden the cell voltage. One is to use organic or ionic liquid electrolytes which raise the voltage window up to 3 V [12,13]. However, the toxicity, high-cost, and poor ionic conductivity of organic electrolytes and the working temperature limitations of ionic liquid electrolytes make this approach unfavorable. Second is to develop aqueous electrolyte-based asymmetric supercapacitors (ASCs), which include a battery-type Faradic cathode as an energy source and a capacitor-type anode as a power source [14-16]. An ASC takes advantage of the different voltage windows of both the cathode and anode so that an enhanced operation voltage in a cell system can be readily achieved, resulting in an improved specific capacitance and substantially boosted energy density.

Despite the considerable effort dedicated towards the development of cathode materials such as MnO₂ [17], NiO [18,19], Ni(OH)₂ [20,21], CoO_x [22], etc., less attention is focused on anode material development. Carbon-based materials commonly serve as an anode in ASCs including activated carbon [23,24], carbon nanofiber [25], carbon nanotube (CNT) [26], graphene [27], etc. Among them, graphene has stood out due to its outstanding characteristics such as large surface area, solution processability, high electrical conductivity, excellent mechanical properties, and superior electrochemical stability [28-34]. However, a significant surface area loss is normally observed during processing because of the aggregation of graphene nanosheets [35-37], resulting in a reduced electrochemically active area which considerably limits the specific capacitance. A feasible approach is to fabricate graphene nanosheets into a graphene aerogel (GA); a stable 3D network which can effectively hamper the aggregation of graphene nanosheets [38-40]. The GA electrode's open 3D network structure provides maximal active surface area while the honeycomb structure (~10 μm pore diameter) facilitates effective electrolyte ion transportation [41]. One significant limitation is that the oxidation-reduction process lowers the electrical conductivity relative to pristine graphene due to defect site formation [29,42]. Therefore, it is advantageous to

fabricate a GA with enhanced electrical conductivity. Functionalization of the GA with metal nanoparticles increases the bulk electrical conductivity as the metal nanoparticles preferentially anchor at the otherwise electrical impeding defect sites [43], and lowers the work function of the composite [44].

Here we report a novel functionalized GA fabrication method of producing a high surface area electrode material (328 m² g⁻¹) for ASCs. In this method, palladium (Pd) nanoparticles are introduced into the 3D network structure of GA (denoted as P-GA), which reduces the electrical resistivity from 950 to 16 Ω cm (more than 50 times improvement). Although Pd is a relatively expensive metal, it is environmentally and electrochemically stable, making it a potential candidate to improve the device performance. Electrodes prepared based on P-GA show high specific capacitance (175.8 F g⁻¹ at 5 mV s⁻¹), excellent rate capability, superior coulombic efficiency, and remarkable reversibility. Moreover, ASCs assembled using this functionalized GA show stable extended cell voltage, fast charge-discharge capability, excellent cycle stability, and high energy and power densities. In addition, we have further demonstrated the applicability of our ASC in energy storage by lighting up a LED, highlighting the significant potential of our functionalized GA for high performance energy storage devices.

Material and methods

Preparation of Pd salt-loaded GO aerogels

GO was prepared by modified Hummers method starting from graphite powder [45]. Briefly, graphite was oxidized using concentrated H₂SO₄ and KMnO₄ and the resulting GO was purified and isolated via successive centrifugation and dispersion cycles in water, then dried under vacuum. A 100 mM stock solution of ligated palladium ions was prepared by slowly adding 0.002 mol of palladium chloride (PdCl₂) into 20 mL of a 100 mM ethylenediaminetetraacetic acid (EDTA) solution while stirring. This mixture was refluxed for 30 min to achieve dissolution and to degas the solvent, and was then used immediately after cooling to room temperature. After appropriate dilution of the metal ligand complex to the desired concentration with a total volume of 500 μL, 500 μL of a freshly sonicated (30 min Branson S-450D horn sonicator at 10% amplitude) 20 g/L suspension of GO was added and thoroughly mixed in a 1 cm × 1 cm plastic cuvette. Parafilm was used to seal the bottom, to better facilitate freezing. Each solution was then placed onto a block of dry ice and allowed to freeze fully (~20 min) before lyophilization. Lyophilization was carried out using a Labcono freeze drying chamber at 20 μbar with a collector set at -52 °C.

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