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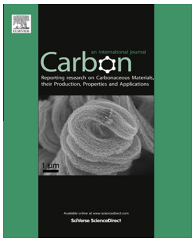

Nanodiamond particles/reduced graphene oxide composites as efficient supercapacitor electrodes

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ABSTRACT

The paper reports on the preparation of reduced graphene oxide (rGO) modified with nanodiamond particles composites by a simple solution phase and their use as efficient electrode in electrochemical supercapacitors. The technique relies on heating aqueous solutions of graphene oxide (GO) and nanodiamond particles (NDs) at different ratios at 100 °C for 48 h. The morphological properties, chemical composition and electrochemical behavior of the resulting rGO/NDs nanocomposites were investigated using UV/vis spectrometry, Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, transmission electron microscopy (TEM) and electrochemical means. The electrochemical performance, including the capacitive behavior of the rGO/NDs composites were investigated by cyclic voltammetry and galvanostatic charge/discharge curves at 1 and 2 A g^{-1} in 1 M H_2SO_4. The rGO/ND matrix with 10/1 ratio displayed the best performance with a specific capacitance of 186 ± 10 F g^{-1} and excellent cycling stability.

1. Introduction

With the growing demand for portable systems and hybrid electrical vehicles requiring high power in short-time pulses, the electrochemical capacitors are gaining increasing interest. Carbon materials such as activated carbon, mesoporous carbon and carbon nanotubes usually display good stability, but the capacitance values are limited by the microstructures in the materials [1,2]. Graphene, a two-dimensional all sp^2 hybridized carbon with unique electronic and mechanical properties, has received a rapidly growing interest as material in supercapacitors [3]. To exploit the potential of graphene-based materials for supercapacitor applications, different approaches have been considered. Chemically reduced graphene oxide (rGO), synthesized through hydrazine reduction of graphene oxide (GO), has been the first reported graphene-based electrochemical double-layer capacitor with specific capacitance values of 135 F g^{-1} in aqueous electrolytes [4]. Chen et al. investigated the capacitive properties of partially reduced graphene oxide, prepared by the reaction of GO with hydrobromic acid. The presence of oxygen functional groups on the rGO facilitated the penetration of the electrolyte, introducing additional pseudo-capacitive effects. As a result, specific capacitance values of 348 and 158 F g^{-1} have been

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measured in 1 M H_2SO_4 and 1-butylimidazolium hexafluorophosphate ($BMIPF_6$), respectively at a current density of 0.2 A g^{-1} [5]. Graphene-based electrodes prepared simply through chemical and/or thermal reduction still do not have sufficient large pores due to rGO sheets agglomeration and thus do not facilitate the access of the electrolyte. Consequently, high specific capacitance values were in most cases only achievable by charging/discharging at current densities below 1 A g^{-1} [6,7]. Less-agglomerated graphene-based electrodes with suitable pore sizes are still highly demanded. Self-assembled graphene hydrogels formed by hydrothermal reduction of GO has shown to possess well-defined and cross-linked 3D porous structure with specific capacitance of 175 F g^{-1} at a discharge current density of 10 mV/s in 1 M H_2SO_4 [7].

To inhibit agglomeration of rGO through electrostatic interactions and providing at the same time open nanochannels, incorporation of intercalating spacers is a promising strategy. Organic molecules such as 1-pyrenecarboxylic acid [33] or tetrabutylammonium hydroxide [9] as well as metallic nanoparticles [10] were used as spacers and resulted in specific capacitances of 120 F g^{-1} (in 6 M KOH) [8], 194 F g^{-1} (at 1 A g^{-1} in 2 M H_2SO_4) [9] or 269 F g^{-1} in 0.5 M H_2SO_4 [10]. The use of carbon nanotubes as spacer in graphene-based hybrid films has shown to increase the specific capacitance to 385 F g^{-1} at a scan rate of 10 mV s^{-1} in 6 M KOH [11].

Diamond nanoparticles (also referred to as nanodiamonds, NDs) have received considerable interest for applications in tribology and nanobiotechnology owing to their chemical inertness, biocompatibility and high specific area [12]. The average diamond particle size in typical detonation diamond is ≈10 nm, but depends strongly on the surface functionalization [13,14]. As NDs have shown electrochemical activity, we investigated the possibility to use them as intercalating material into GO nanosheets as well as their ability to reduce GO into rGO [15].

In this paper, we report on the preparation of reduced graphene oxide/nanodiamonds (rGO/NDs) composites using a solution phase process. The direct reaction of aqueous solutions of GO and NDs at different GO/NDs ratios at 100 °C for 48 h gave the corresponding composites with enhanced properties. The GO matrix was partially reduced to rGO under these conditions, while the NDs particles were intercalated into the rGO sheets. Incorporation of NDs into rGO matrix resulted in a significant improvement of the dispersibility of the rGO/NDs composite in solvents such as ethanol and DMF with the suspensions being stable for several weeks. The rGO/NDs composites have been successfully used as electrodes in supercapacitors with a maximum specific capacitance of 186 ± 10 F g^{-1} in 1 M H_2SO_4 at a current density of 1 A g^{-1}.

2. Experimental part

2.1. Materials

Graphite powder (<20 microns), hydrogen peroxide (H_2O_2), sulfuric acid (H_2SO_4), dimethylsulfoxide (DMSO), acetonitrile (CH_3CN), ethanol (EtOH), acetone, hydrazine, potassium chloride (KCl), potassium ferricyanide ($[K_3Fe(CN)_6]$), potassium ferrocyanide ($[K_4Fe(CN)_6]$), *N*-methyl-2-pyrrolidone (NMP) and polyvinylidene fluoride (PVDF) were purchased from Sigma–Aldrich and used as received. Glassy carbon electrodes (3 mm in diameter) were obtained from Cambria Scientific.

Hydroxylated diamond particles (ND-OH particles) were obtained from the International Technology Centre, Raleigh, NC, USA.

Zirconia beads were obtained from Tosoh Co. (YTZ Grinding Media, 0.05 mm).

2.2. Preparation of reduced graphene oxide/nanodiamonds (rGO/NDs)

Graphene oxide was synthesized from graphite powder by a modified Hummers method [16] and the detailed experimental conditions are reported in [17]. GO was exfoliated in Milli-Q water (0.5 mg/mL) by ultrasonication for 3 h until it became clear with no visible particulate matter.

The as-received hydroxylated nanodiamond (ND-OH) particles were treated by the bead-assisted sonic disintegration process (BASD) to break down the persistent particle agglomerates. An ultrasonicator equipped with a horn-type sonotrode (Branson, Ultrasonic-Homogenizer Sonifier II W-450 with a 4.8 mm microtip) was used. The ultrasonication vial was charged with 40 g of zirconia beads, 200 mg of ND–OH particles and 20 mL of DMSO and treated two times for 60 min (amplitude: 70%; pulse on/off, 0.3 s/0.2 s). During the BASD process the slurry in the vial was cooled with ice. Zirconia beads were removed by centrifugation at 10,000 rpm and the ND-OH particles were purified by consecutive washing/centrifugation cycles in water.

The BASD treated ND-OH particles were mixed with GO (0.5 mg/mL) at different GO/NDs ratios: (1/1, 2/1, 4/1, 10/1, 20/1) and ultrasonicated in a Fisher Transonic TI-H-10 ultrasonication bath for 6 h. Then the mixture was heated at 100 °C for 48 h. The resulting black precipitate was separated from the aqueous supernatant by centrifugation at 14,000 rpm for 20 min. After washing with water (3 times), the precipitate was dried at 80 °C.

In a control experiment, the BASD treated ND-OH particles were mixed with GO (0.5 mg/mL) at GO/NDs ratio = 10/1 and ultrasonicated in a Fisher Transonic TI-H-10 ultrasonication bath for 6 h. Then hydrazine (10 mM) was added to the mixture and heated at 100 °C for 48 h. The resulting black precipitate was separated from the aqueous supernatant by centrifugation at 14,000 rpm for 20 min. After washing with water (3 times) and methanol (3 times), the precipitate was dried at 80 °C.

2.3. Electrode preparation

Glassy carbon electrodes (GCEs) were polished with alumina and diamond paste and then sonicated in a mixture of ethanol/acetone for 15 min before modification. GCE/rGO-NDs electrodes were prepared by casting drops of 20 μL of rGO/NDs (0.5 mg/mL in ethanol) 5 times followed by drying in an oven at 80 °C.

2.4. Instrumentation

2.4.1. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) experiments were performed on a PHI 5000 VersaProbe-Scanning ESCA