

High performance supercapacitors based on thermally reduced graphene oxide

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ABSTRACT

In the present paper, graphene has been addressed as active material for supercapacitor electrodes. In particular we describe an environmental-friendly two stages procedure for the preparation of graphene-based electrodes for supercapacitors. In the first step, graphene oxide was synthesized by means of the modified Hummers method and deposited onto a metallic substrate (titanium, stainless steel and nickel wire meshes) by electrophoretic deposition. The second step consisted in a thermal treatment carried out to remove the functional groups from graphene oxide. The electrodes were finally characterized by cyclic voltammetry in order to measure their electrochemical performances in aqueous electrolytes (0.5 M K₂SO₄, 1M Na₂SO₄ and 6M KOH).

Keywords: supercapacitors, graphene, graphene oxide, energy storage, thermal reduction.

1 INTRODUCTION

Graphene (G) is the name given to individual sheets of two dimensionally-bounded sp²-hybridized carbon atoms, which are usually found in stacks to form crystalline graphite. In recent years, a great deal of attention has been devoted to graphene due to its unique properties, especially from the electrical point of view: its semimetallic nature leads to properties such as the quantum Hall effect [1,2], ambipolar electric field effect [3] and electrical transport via relativistic Dirac fermions [4]. In addition to its fundamental electronic characteristics, graphene has been used to fabricate a number of simple electronic devices [5,6].

Supercapacitors are electrical energy storage devices for applications requiring high power density such as energy back-up systems, consumer portable devices and electrical/hybrid automobiles. Energy can be stored in supercapacitors by means of two different phenomena: the formation of an electrical double layer at the interface of the electrodes (electrical double layer capacitors, EDLCs) or the electron transfer between the electrolyte and the electrode through fast Faradaic redox reactions (pseudocapacitors). Supercapacitors store significantly higher amount of energy than conventional capacitors but less than that of batteries, and are similar in construction to conventional capacitors; the main distinction being that metal electrodes are replaced by a highly porous electrode.

Porous carbon materials such as activated carbon [7], xerogels [8], carbon nanotubes [9] have been investigated for use as electrodes in EDLCs. In the last few years, there has been great interest in the use of graphene in EDLCs.

We investigated the use of graphene as electrode-active material for electrochemical supercapacitors. The graphene-based electrodes were obtained by electrophoretic deposition of graphene oxide (GO) onto metallic substrates, followed by thermal treatment before electrochemical characterization.

2 EXPERIMENTAL DETAILS

The morphology, size and surface topography of the graphene based electrodes were investigated by means of Scanning Electron Microscopy (SEM – Zeiss® EVO 50), operated at 20 kV accelerating voltage in backscattering mode and Atomic Force Microscopy (AFM – Bruker Dimension Edge SPM System). Samples for AFM imaging were prepared by dispersing graphene oxide into distilled water and spreading some drops of the solutions onto a Si/SiO₂ wafer. Imaging was carried out in non-contact mode by using a Si V-shape probe. All images were collected under ambient conditions at a scanning rate of 0.76 Hz.

The distance between layers in graphene was determined by X-ray diffraction (XRD) with Cu K_{α1} radiation at 1.54 Å (Philips PW - 1830).

Reduction progress has been verified by Thermogravimetric Analysis (TGA) using SDT Q600 TA Instruments. TGA was performed in air. Samples were heated from room temperature to 1173 K at 1 K/min in order to avoid thermal expansion of the GO due to rapid heating.

Finally the graphene-based electrodes have been characterized by means of cyclic voltammetry using ModuLab ECS Solartron Analytical equipped with Model Pstat 1MS/s (2087A) in a three electrodes cell configuration using a Saturated Calomel Electrode (SCE) and a Pt foil as reference and counter electrode, respectively.

2.1 Synthesis of graphene oxide

Graphene oxide (GO) has been synthesized from native graphite by modified Hummers method [10,11]. All chemicals were of analytic grade and used as received. Double-distilled water was used throughout.

Graphite powder (<40 μm , Sigma-Aldrich[®]) was added to concentrated (96%) H_2SO_4 and thoroughly stirred. Then concentrated (65%) HNO_3 was slowly dropped into the mixture under ice-cooling and stirring. After cooling down, KMnO_4 was slowly added, the mixed slurry was stirred at room temperature, then deionized (DI) water was slowly added into the reacted slurry. After that H_2O_2 (36%) was added in order to oxidize reagents remained. After stirring, the solution was allowed to deposit on and the supernatant was decanted. To remove the ions of oxidant and other inorganic impurity, the resultant yellow-green slurry was centrifuged (15000 rpm, 30 min) and then washed in 2 L DI water with 10 mL (37%) HCl and 6 mL (36%) H_2O_2 added (5 cycles). After that the resultant slurry was purified with 2 L of pure DI water centrifuged and rinsed again. This procedure has been followed until the pH of the washing solution increased to neutral (6.5) (it took about 5 cycles). The remaining dark-yellow solid was dried under vacuum at 40 $^\circ\text{C}$ for 24 h and ground to a fine powder.

2.2 GO deposition

GO powder and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dispersed in isopropyl alcohol (IPA) and sonicated for 2 h at room temperature. GO was then deposited onto a substrate (titanium, stainless steel and nickel meshes) by electrophoretic deposition.

Electrophoretic deposition has been carried out by using a Pt foil as counter-electrode (CE) and a sheet of the metal desired as substrate as working electrode (WE) (Figure 1). GO was deposited onto the WE by imposing a voltage bias of 120 V for 30 minutes.

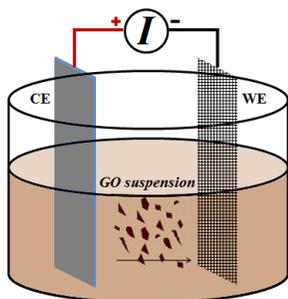


Figure 1: Electrophoresis deposition experimental set up.

2.3 Thermal reduction

As synthesized graphene-based electrodes were then thermally treated at 623 K for 2 h in reductive atmosphere consisting in a mixture of H_2 and N_2 flowing at 100 sccm each.

2.4 Electrochemical characterization

The electrochemical properties of the electrodes were measured by cyclic voltammetry (CV) in aqueous

electrolytes containing either 0,5 M K_2SO_4 , 1M Na_2SO_4 or 6M KOH , at scan rates from 10 to 3000 mV/s.

3 RESULTS AND DISCUSSION

Due to the hydrophilic nature of the oxygenated graphene layers, GO can be easily obtained by exfoliation of native graphite in aqueous media, forming stable colloidal suspensions. SEM images and AFM scans of GO dispersed in DI water revealed the presence of single sheets with uniform thickness of around ~ 1.15 nm (Figure 2). No agglomerates were observed, leading to the conclusion that under the selected experimental conditions complete exfoliation of GO down to single layer graphene oxide was achieved. While a pristine graphene sheet is atomically flat with a well-known van der Waals thickness of ~ 0.34 nm, graphene oxide sheets are expected to be “thicker” due to the presence of covalently bound oxygen-containing functional groups, and the corresponding displacement of the sp^3 -hybridized carbon atoms slightly above and below the original graphene plane.

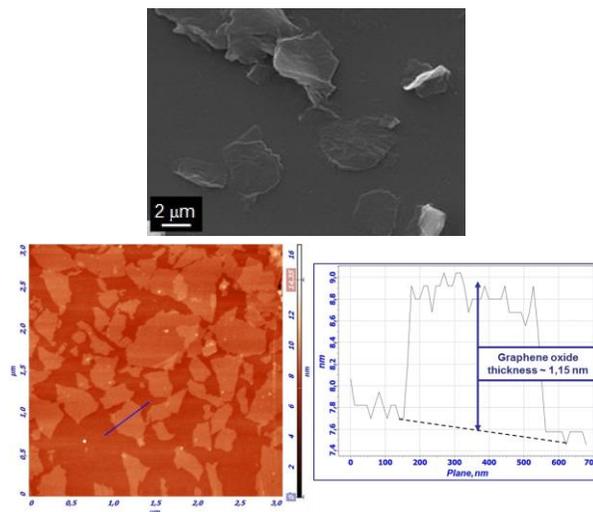


Figure 2: (top) SEM image of GO dispersion onto Si/SiO₂ substrate; (bottom) AFM scan of GO dispersion and profile of a single layer of GO, showing an average thickness of the sheet of about 1.15 nm.

From XRD experiments (Figure 3) it is possible to calculate the interlayer distance in GO powders, which usually varies as a function of the amount of absorbed water from 0.6 to 1.2 nm. In agreement with data reported in literature [12], before thermal treatment the interlayer distance was about 0.88 nm ($2\theta = 10.06^\circ$), after thermal treatment it was 0.37 nm ($2\theta = 24.13^\circ$), meaning that the thermal treatment contributed to minimize the water content and to reduce the oxygen-containing functional groups present in GO.

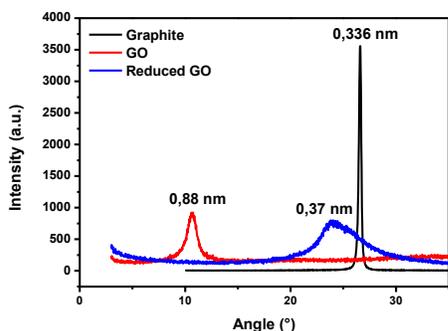


Figure 3: XRD patterns of pristine graphite, graphene oxide (GO) and thermally reduced GO.

The actual reduction of graphene oxide has been verified by TGA, shown in Figure 4. The weight loss (24 wt%) showed by GO below 100 °C could be primarily ascribed to the evaporation of absorbed water molecules. A comparatively small weight loss (3 wt%) measured for thermally reduced GO in the same temperature range indicates that thermally reduced GO contains a lower amount of water. In the region between 100°C and 220 °C, GO exhibited a significant weight loss (48 wt%), due to both further evaporation of water and to the removal of labile oxygen functional groups, while, thermally reduced GO did not lose weight, suggesting that a significant amount of the water and labile oxygen groups were removed by the thermal treatment.

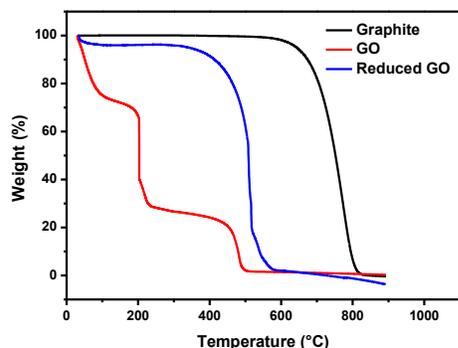


Figure 4: TGA analysis of pristine graphite, graphene oxide (GO) and thermally reduced GO.

In Figure 5 SEM images of graphene oxide electrophoretically deposited onto titanium (a), AISI 316 L (b) and nickel (c) meshes are shown. The electrophoretic deposition was done by adding to the solution $Mg(NO_3)_2 \cdot 6H_2O$, which adsorbs onto the graphene oxide sheets providing a positive charge and allowing cathodic deposition. Wire meshes were used because of their high surface area which is directly proportional to the expected supercapacitors performances.

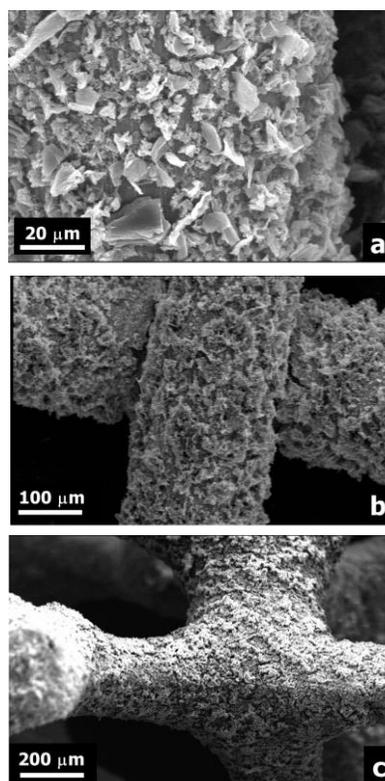


Figure 5: SEM images of graphene oxide electrophoretically deposited onto titanium (a), AISI 316 L (b) and nickel (c) mesh.

As shown in Figure 5, the wire mesh surface was completely covered by graphene oxide, which tend to form agglomerates creating a sort of porous structure which will be useful for our purpose.

After electrophoretic deposition, each electrode has been thermally treated in order to reduce graphene oxide to pristine graphene. All heat treatments have been carried out in reductive atmosphere in order to remove oxygen functional groups from graphene oxide and to avoid oxidation of the metallic substrate. After the heat treatment, all the samples changed in colour from brown to blackish brown, suggesting that graphene oxide has been reduced.

CV curves of the electrophoretically prepared graphene electrodes are shown in Figure 6 under different scan rates, ranging from 10 mVs^{-1} to 3000 mVs^{-1} . The cyclic voltammetries were carried out in different electrolytes depending on the metallic substrate employed: $0.5 \text{ M K}_2\text{SO}_4$ for titanium, $1 \text{ M Na}_2\text{SO}_4$ for AISI 316 L, and 6 M KOH for nickel substrates. All electrodes exhibited fairly rectangular CV curves at low scan rate (below 100 mVs^{-1}), while at higher scan rate a significant resistance has been determined. This effect is probably due both to the resistance between graphene sheets and to the electrical contact between graphene and the metallic current collector.

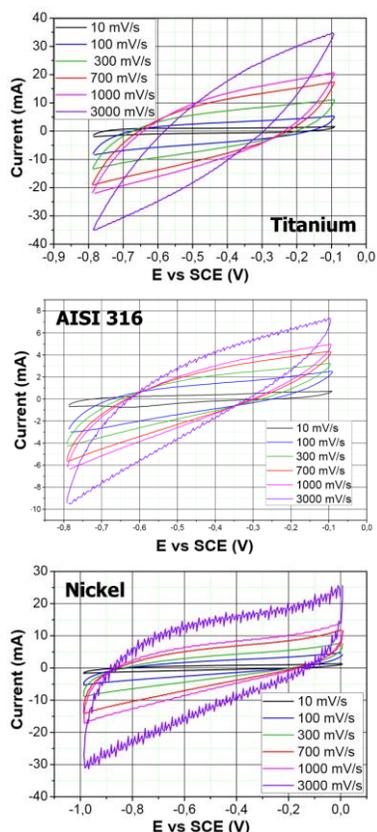


Figure 6: Cyclic voltammetry of titanium (0,5 M K_2SO_4), AISI 316 (1 M Na_2SO_4), nickel (6 M KOH).

At room temperature and 10 mVs^{-1} , a specific capacitance of 92 Fg^{-1} , 68 Fg^{-1} , and 148 Fg^{-1} was measured on titanium, AISI 316 and nickel meshes respectively. Moreover, the electrodes presented high stability over about 10000 cycles (Figure 7). The specific capacitance increased up to 67% compared to the initial value after 2000 cycles. This might be attributed to further electrochemical reduction of the oxygen functional groups not completely reduced by thermal treatment.

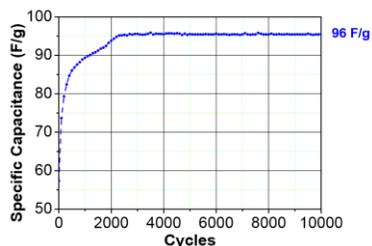


Figure 7: Cycles stability of titanium based electrodes.

4 CONCLUSIONS

In the present work we describe a simple procedure for the preparation of graphene-based electrodes for supercapacitors. Graphene oxide, synthesized by means of the modified Hummers method, was deposited onto a metallic substrate (titanium, stainless steel and nickel

meshes) by electrophoretic deposition and annealed in order to remove the oxygen-containing functional groups from graphene oxide. The electrophoretic deposition led to a complete coverage of the metallic substrates and good adhesion of the GO to the same, both before and after the thermal treatment. The adhesion to the substrate was preserved during both the electrochemical CV experiments and the life-cycle measurements. Based on electrochemical characterization, a maximum specific capacitance of 148 Fg^{-1} was measured onto Nickel substrates into 6 M KOH.

The results described in the present paper suggest that electrophoretic deposition onto metallic substrates followed by thermal reduction can be a highly promising approach to produce graphene-based electrodes having high energy capacity and superior stability for applications in supercapacitors.

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