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Short Communication

Gold nanoparticle embedded paper with mechanically exfoliated graphite as flexible supercapacitor electrodes

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ABSTRACT

We report a new method for the fabrication of flexible supercapacitor electrodes wherein mechanically exfoliated graphite on paper containing gold nanoparticles is used as supercapacitor electrodes. It has been found that the supercapacitor electrode made of paper containing gold nanoparticle with graphite exfoliation yields a capacitance, which is about 4.3 times higher than that of the electrodes without gold nanoparticles.

1. Introduction

Supercapacitors have attracted immense attention as a component for energy storage in recent years due to their high capacitance, exceptional energy density and cycle reliability [1,2]. With the increasing demand of power storage requirements within limited cost, flexible and disposable supercapacitors have come into existence that have higher charge storage capacity as well as good flexibility and can be used in micro-nanoscale devices such as flexible sensors, wearable devices, and roll up displays. Supercapacitors consist of two electrodes with very high surface area and a separator, which contains materials that either contribute to EDL (electrochemical double layer) or pseudo capacitance or both [3–5].

Whereas commonly used materials for electrode fabrication such as activated carbon, carbon nanotubes and exfoliated graphite prepared using different physiochemical routes, the electrolytes comprise of organic or inorganic solvents such as acetonitrile, and aqueous solution of KOH 6–10]. A number of reports are available which emphasize on various techniques for generating few layers of exfoliated graphite and carbon nanotubes (CNT) [11] on flexible polymeric substrates for fabrication of supercapacitor electrodes like microwave exfoliation [12], thermal exfoliation [13], in-situ reduction of graphene oxide to graphene using laser irradiation [14], and flame induced reduction to graphene [15]. Exfoliated graphite has a very high surface area (2630 m^2/g) whereas theoretically, single walled CNTs have a surface area of 1300 m^2/g [16,17]. However, the exfoliation process of graphite to prepare supercapacitor electrode material is complex and CNTs are difficult to be fabricated on polymeric substrates making the fabrication process expensive. Furthermore, CNTs have a high areal resistance, [18] which adversely affects the discharge characteristics and energy density of the supercapacitor by increasing the equivalent series resistance (ESR).

An approach to fabricate supercapacitor electrode using VACNTs (vertically aligned carbon nanotubes) grown on Si substrate with sputtered nickel and further transferring the entire system to polycarbonate film has been reported recently [19]. In this work the sputtered nickel on VACNT was instrumental in reducing the electrode resistance. This reported work indicated the feasibility towards enhancing supercapacitor characteristics employing conducting materials in the electrode matrix. However, the reported device houses polymeric materials and uses fabrication procedure like chemical vapour deposition technique which requires exact process conditions. In order to enhance the supercapacitor characteristics for a polymer free supercapacitor electrode with easily exfoliated graphite, we have synthesized supercapacitor electrodes with gold nanoparticles soaked in paper substrate and subsequent controlled mechanical exfoliation of graphite in this work.

In the present supercapacitor cell, gold nanoparticle embedded paper substrate was mechanically exfoliated with graphite layers and used as electrodes. Pencil lead was used as graphite containing material and mechanically rubbed on paper in controlled fashion. The gold nanoparticles embedded in paper matrix are used to decrease the resistance of mechanically exfoliated graphitic layers (pencil lead) as nanoparticles possess profuse number of free electrons generating a charge

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pool. Pencil lead is a mixture of natural graphite and clay wherein clay is used as a binder. It is a crystalline material which exhibits fair electrical conductivity. The crystalline nature of exfoliated graphite layers from pencil lead on paper has recently been reported using TEM (transmission electron microscope) images of pencil lead manually rubbed on a solid substrate [20,21]. The separator was a paper soaked in a Ni–Cu hydroxide complex containing excess KOH. Ni–Cu complex was used as these transition metal oxides and hydroxides possess high pseudocapacitance [22], are of low cost, abundant and non-toxic. The use of Ni hydroxide as a pseudo capacitive material is well known as it possesses a high value of pseudo capacitance. The presence of Cu along with Ni enhances the electrochemical activity of the supercapacitor which may be attributed to the charge imbalance and imperfections in the Ni–Cu lattice. In one of the earlier studies [23], it has been demonstrated that Ni–Cu double hydroxides have higher pseudo capacitance when compared to the individual double hydroxides. The fabricated supercapacitor cell shows high specific capacitance of the order 790 mF/cm^2, which assures the applicability of these simple devices in micro-nanoscale flexible electronics.

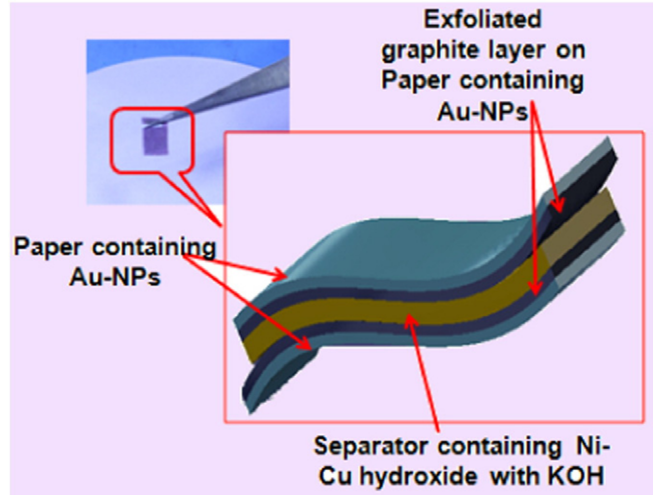

Fig. 1. Figure showing the details of the fabricated supercapacitor.

2. Experimental

The fabrication of supercapacitor electrode employs the following steps. Filter paper with 10 μm pore size (Whatman) was cut into 1 × 1 cm pieces (area 1 cm^2). Two pieces of the stated size were dipped into AuNPs solution for 24 h. The AuNPs were prepared using 50.0 μl of 0.1 M $HAuCl_4$ and 5.0 mg/ml sodium citrate solutions stirred at 90 °C as in the reported literature [24]. The paper pieces were dried in an oven at 60 °C. Graphitic layers were then exfoliated on the AuNP-paper surface mechanically using a set up designed for this purpose (Fig. S1). The setup consists of 2-motion stages that can move in two directions and is similar to existing CNC (computer numerically controlled) machines used in metal machining. A rectangular shaped graphitic pencil lead (Flair Company, 2B) was fixed on a cartridge and was attached to the Z axis stage. An electronic weighing system was rigidly fixed to the X-axis stage. The paper containing AuNPs was placed on the electronic weighing system, which rests on the X-axis stage. The Z axis stage was lowered gradually to touch the paper surface. This was continued till the electronic weight showed a mass of 200 g. The X-axis stage was now actuated which generated graphitic layers as pencil markings on the paper substrate. Unlike manual rubbing of pencil on paper to generate uncontrolled growth of turbostratic graphitic layers on paper surface, this method uses controlled pressure (in terms of mass) to generate pencil markings. The setup is shown in the ESI (Fig. S1).

The separator containing Ni–Cu hydroxide with excess KOH was prepared using the same procedure which was used for AuNP-paper preparation wherein Ni–Cu hydroxide with excess KOH was used instead of AuNPs. Pencil markings were not present and the drying process was not followed during this step. The detailed procedure for synthesis of Ni–Cu hydroxide in excess KOH can be found in the ESI. The fabricated electrodes and the separator were pressed in a hydraulic press at 150 Kg/cm^2 pressure for 1 min. This leads to a sandwiched structure ready to be tested for supercapacitor characteristics. The fabricated supercapacitor two electrode cell has an average thickness of 230 μm. A schematic for the fabricated supercapacitor cell, electrodes and the separator layers is shown in Fig. 1. For comparison, a supercapacitor cell without AuNPs was also fabricated employing the above procedure wherein the electrodes were not dipped into AuNPs solution prior to graphite exfoliation.

The fabricated electrodes, the separator and the pencil lead used in the experiment were subjected to FESEM (field emission scanning electron microscopy) for material characterization. The size of AuNPs in solution was found using NanoSight NS500 Instrument. The electrical characterization for the electrodes and the supercapacitor cell was carried out using Parstat 4000 potentiostat. The resistance of the exfoliated graphite layers on normal filter paper and filter paper containing AuNPs was estimated using I–V plots for five repeated sets of exfoliation process at 200 g weight using the stated set up in Fig. S1. Cyclic voltammetry (CV) tests were carried out with the fabricated supercapacitor cell in order to test their performances. The areal resistance for graphite exfoliated paper with KOH solution and graphite exfoliated on AuNP-paper with KOH solution is obtained from the slope of the I–V plot followed by multiplying the value with the surface area (1 cm^2 in this case) [20].

3. Results and discussions

3.1. Material characterization

The FESEM images for the pencil lead, the paper soaked in Ni–Cu hydroxide, the paper soaked in AuNPs solution and the paper with exfoliated graphite containing AuNPs are shown in Fig. 2.

The FESEM images of the paper soaked in AuNP solution show the entrapment of gold nanoparticles in the paper fibres having sizes in the order of 30–40 nm (Figs. 2, S2). The size of gold nanoparticles in solution has a mean 30 nm. This study indicates that the gold nanoparticles are embedded as well as stabilized in the paper matrix without any agglomeration. The FESEM image of graphite exfoliated on the AuNP-paper shows that the turbostratic thin layers of graphite rest on the gold nanoparticles which were embedded in the paper matrix.

3.2. Electrical characterization

The current vs. voltage plots at different scan rates (5, 10, 50 and 100 mV/s), the comparative current vs. voltage plots for the supercapacitor with electrodes containing AuNPs and without it, the galvanostatic charge discharge curves at constant currents (4, 6, 8 and 10 mA/cm^2), the impedance spectroscopy for the supercapacitor containing AuNPs and without it, the cyclic charge–discharge capacitance retention curve at different discharge rates and the variation of current–voltage characteristics with bending are shown in Fig. 3.

3.3. Calculation of electrical parameters

The calculated areal resistance for graphite exfoliated paper with KOH solution was 110 Ω cm^2 whereas the resistance of graphite exfoliated on AuNP-paper with KOH solution was 19 Ω cm^2. This indicates that the entrapment of gold nanoparticles in the paper matrix reduces the resistance of graphene exfoliated electrodes significantly. Furthermore, the resistance of the electrodes generated using controlled exfoliation of graphite on AuNPs embedded paper as well as on normal