



Facile hydrothermal synthesis of lanthanum oxide/hydroxide nanoparticles anchored reduced graphene oxide for supercapacitor applications



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ABSTRACT

This paper reports the synthesis of lanthanum oxide/hydroxide nanoparticle (LaNPs)-doped rGO nanosheets. The uniform distribution of LaNPs on the rGO nanosheets was confirmed by FESEM, TEM, and elemental analysis. A dramatic change in electrochemical behavior was observed by adjusting the concentration of LaNPs in rGO (LaG ratio = 1:2, 1:1 and 2:1). The LaG 12 showed a better areal capacitance of 889.29 F cm^{-2} than LaG 11 (428.58 F cm^{-2}) and LaG 21 (260.72 F cm^{-2}). Further, improved cycle stability (84% after 1000 cycles) with good impedance behavior confirms LaG 12 is a suitable electrode material for high-performance supercapacitor fabrication.

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Introduction

In recent years, the fast-growing energy demands, limited fossil fuel reserves, and emerging ecological concerns have provoked a quest for environmentally friendly and sustainable energy storage devices with high energy and power densities [1,2]. The supercapacitor (SC) or electrochemical capacitor (EC) is an ultra tech modern energy storage device that has been highlighted for next generation sustainable energy storage devices owing to its high power density ($>10 \text{ kW/kg}$), excellent charge–discharge rates, and long cycle life ($>1,000,000$ cycles) compared to conventional capacitors and batteries [3]. On the other hand, the energy density of SCs is quite low and needs to be improved before SCs can be used in current electronic devices, such as electronic vehicles, portable electronics, etc. The improvements in energy density can be achieved by increasing the specific capacitance or cell voltage of the supercapacitor [4]. A promising way to increase the energy density is to find a suitable electrode material with a high specific capacitance. Therefore, the performance of supercapacitors depends strongly on the electrode materials. Transition metal oxides, carbonaceous materials, and conducting polymers have been used for electrode fabrication [5–7]. These materials store the energy based on the mechanism of Helmholtz electrostatic double

layer adsorption (EDLC), Faradic oxidation–reduction (pseudocapacitance) and doping – de doping process, respectively [8,9].

Various carbonaceous materials, such as graphene, carbon nanotubes, activated carbon, etc., have been used as electrode materials in EDL capacitors. Among them, graphene-based materials have attracted considerable attention among researchers owing to its ultra-large surface area, low internal resistance, and high mechanical stability. One atom thick and honeycomb structurally arranged sp^2 hybridized carbon atoms make graphene a promising candidate for supercapacitor electrode fabrication. On the other hand, the van der Waals forces and interplanar π – π interactions cause the graphene sheets to aggregate together. The resulting aggregated graphene sheets have a lower specific surface area and electrolyte ion diffusion, which reduce the electrochemical performance of graphene electrodes. The aggregation between the graphene sheets can be reduced by decorating the surface of graphene layers with nanoparticles; these nanoparticles increase the space between the graphene nanosheets, which enhances the electrolyte ion diffusion [10,11]. The excellent electrical conductivity of graphene provides good electron transport between the dispersed nanoparticles.

Various transition metal oxide nanoparticles (TMO NPs), such as MnO_2 , RuO_2 , SnO_2 , and Co_3O_4 , have been used for the decoration of graphene nanosheets. The resulting nanocomposite exhibited extraordinary electrochemical behavior with a combination of electric double layer and pseudocapacitance [12–17]. Hamid and co-workers prepared MnO_2/NrGO nanocomposite by the

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sonochemical method and studied its electrochemical properties. The prepared MnO₂/rGO nanocomposite exhibited the high specific capacitance value of 522 F g⁻¹ at the scan rate of 2 mV s⁻¹, which is higher than individual MnO₂ nanoparticles (298 F g⁻¹) and rGO nanosheets (122 F g⁻¹), respectively [18]. Similarly, Liu et al. enhanced the specific capacitance value of graphene from 220.5 F g⁻¹ to 274 F g⁻¹ by adding Fe₂O₃ nano-dots [19]. Recently, rare earth metal oxide (REMO)-doped graphene nanocomposites have attracted considerable attention owing to its incomplete 4f shell with many oxidation states, and these REMOs are expected to enhance the specific capacitance and cycling stability [20]. Recently, Dezfuli et al. synthesized samarium oxide nanoparticle-anchored rGO by a sonochemical-assisted, self-assembly process and achieved a high capacitance of 268 F/g at a current density of 2 A/g [21]. PPy/nanoG/Gd nanocomposites were prepared via an in-situ polymerization process and the resulting electrode exhibited a specific capacitance of 175 F/g at a current density of 1 A/g [22]. Lanthanum and cerium are the most abundant, environment-friendly rare earth elements and are favorable for supercapacitor applications owing to their excellent redox characteristics. Many researchers examined the electrochemical behavior of cerium oxide and cerium oxide nanoparticle-decorated graphene materials [20,23,24]. Deng et al. synthesized the cerium oxide nanoparticles through chemical precipitation method and improved the specific capacitance value of cerium oxide nanoparticles from 81.18 F g⁻¹ to 382.94 F g⁻¹ by adding graphene oxide nanosheets [25]. In the same way, Vanitha and co-workers achieved the high specific capacitance value of 710.42 F g⁻¹ at an applied current density of 0.2 A g⁻¹ from cerium doped graphene nanosheets with the addition of silver [26]. Surprisingly, lanthanum oxide doped/decorated graphene oxides have not been used for supercapacitor electrode fabrication.

In the present study, the lanthanum oxide/hydroxide-anchored reduced graphene oxide was synthesized using a facile hydrothermal process. In this process, the hydrothermal reaction induced the uniform dispersion on the graphene surface and assisted in the self-assembly process. The electrochemical behavior of the lanthanum oxide/hydroxide nanoparticle-anchored reduced graphene oxide composite was investigated by cyclic voltammetry (CV), galvanostatic charge/discharge measurements, and electrochemical impedance spectroscopy (EIS) in a 1 M Na₂SO₄ aqueous electrolyte.

Experimental

Graphite powders, potassium permanganate (KMnO₄), sulfuric acid (H₂SO₄), hydrogen peroxide (H₂O₂), hydrazine hydrate (N₂H₄), lanthanum nitrate (La(NO₃)₃·6H₂O), and sodium hydroxide (NaOH) were purchased from Sigma-Aldrich. All chemicals were used as received.

Synthesis of reduced graphene oxide

Reduced graphene oxide (rGO) was synthesized from graphite powders using a modified Hummer's method [27]. Briefly, 1 g of graphite powder and 50 ml of concentrated H₂SO₄ were mixed and stirred for 30 min. The mixture was cooled to 0 °C and stirred moderately for 1 h. KMnO₄ (6 g) was added to the above mixture with continuous stirring and the reaction temperature was maintained below 15 °C. After continuous stirring for 2 h, 90 ml of distilled water was added drop-wise. At this point, the reaction temperature was strictly maintained below 30 °C and stirred for a further 2 h. Finally, 280 ml of distilled water and 6 ml of H₂O₂ was added with vigorous stirring. As a result, the reaction mixture was turned to a bright yellow color, which confirmed the formation of graphene oxide (GO). The synthesized GO was washed with

distilled water and a 10% HCl solution, filtered, and dried in an oven. The reduction of graphene oxide was achieved by a chemical reduction method. Here, 50 mg of graphene oxide was dispersed in 50 ml of double distilled water, and 1 ml of hydrazine hydrate (60%) solution was then added. The resulting solution was stirred continuously at 70 °C for 8 h to achieve the complete reduction. The product was then washed with copious amount of water followed by ethanol and filtered. Finally, the reduced graphene oxide was air dried at 80 °C for 12 h.

Synthesis of lanthanum oxide/hydroxide nanoparticles anchored rGO

The lanthanum oxide/hydroxide nanoparticle-anchored, reduced graphene oxide was prepared by a simple hydrothermal method. First, 50 mg of La(NO₃)₃·6H₂O was dissolved in 100 ml of double distilled water. Subsequently, 50 mg of reduced graphene oxide nanosheets were dispersed in the above solution and sonicated for 20 min. During this process, the reduced graphene oxide nanosheets were allowed to mix completely with the La³⁺ ions. The above mixture was then transferred to a magnetic stirrer and stirred at 300 rpm for 10 min. To this, 1 M of NaOH solution was added drop-wise to the mixture with constant stirring until the reaction mixture reached pH 10. After constant stirring for another 30 min, the mixture treated hydrothermally at 100 °C for 12 h. The resulting product was washed with distilled water and ethanol followed by air drying at 80 °C overnight. During the above process, the weight ratio of La(NO₃)₃·6H₂O and reduced graphene oxide was maintained at 1:1 to produce a product called LaG 11. The same experiment was carried out by altering the La(NO₃)₃·6H₂O to reduced graphene oxide weight ratio to 1:2 and 2:1; the resulting products are called LaG 12 and LaG 21 respectively. For comparison, pure lanthanum oxide/hydroxide nanoparticles (LaNPs) were synthesized without reduced graphene oxide using the above procedure. Fig. 1 presents a schematic diagram for the preparation of the LaNP-anchored rGO nanosheets.

Characterization of lanthanum oxide/hydroxide nanoparticles anchored rGO

The physiochemical properties of the lanthanum oxide/hydroxide decorated rGO were examined using various techniques. The crystal structure and phase of the nanomaterials were studied by X-ray diffraction (XRD, Rigaku-Ultima (IV)) using Cu K α radiation with a wavelength of 1.5406 Å. The associated functional groups of the lanthanum hydroxide-decorated rGO nanocomposite were analyzed by Fourier transform infrared (FTIR, IR Affinity-1S, Shimadzu) spectroscopy. The surface morphology and elemental composition of the materials were studied by field emission scanning electron microscopy (FESEM, Jeol-JSM7600F) with energy dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM, Jeol-JEM-2100F). The valance distributions and oxidation states of the elements were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo scientific) using an Al K α X-ray source.

Electrode preparation and electrochemical measurements

All electrochemical measurements were carried out on an IVIUMSTAT instrument. The working electrode was prepared using a drop casting technique. Briefly, 1 mg of active material was dispersed in 1 ml of ethanol and sonicated for 10 min. Subsequently, 10 μ l of the mixture was drop cast on the glassy carbon electrode at 80 °C and the electrode was dried at 80 °C for 3 h. This active material-coated glassy carbon electrode, Pt strip, and Ag/AgCl in saturated KCl were used as the working, counter, and reference electrodes, respectively. The cyclic voltammograms of the

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