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# Electrochemical performance of $Bi_2O_3$ decorated graphene nano composites for supercapacitor applications

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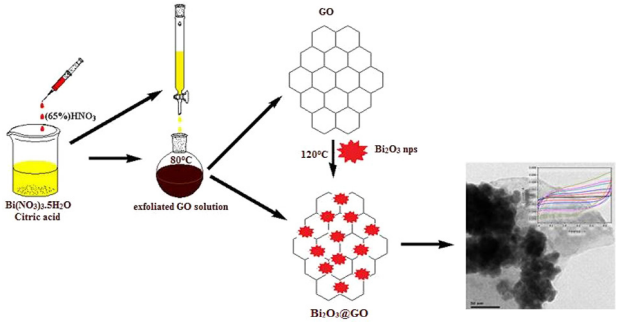
## HIGHLIGHTS

- Synthesis of graphene/$Bi_2O_3$ nanocomposite material by simple sol–gel process is reported.
- Graphene/$Bi_2O_3$ nanocomposite material shown a specific capacitance of 136.76 $Fg^{-1}$ at current density of 0.5 $Ag^{-1}$ which is found to be good for supercapacitor applications.
- The composite electrode exhibited an excellent cycling stability (>95% over 1000 cycles).

## GRAPHICAL ABSTRACT

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## ABSTRACT

Graphene based supercapacitors are being developed as potential devices for large scale energy storage applications with physical flexibility, because of their low cost and high electrochemical performance. This paper is mainly focused on the preparation of pure $Bi_2O_3$ and graphene / $Bi_2O_3$ based nanocomposite materials via sol–gel method and their physical / electrochemical characterization towards application in supercapacitors. The physical characterization like crystallinity, structure, morphological studies etc. were carried out by XRD, FTIR, SEM, EDAX and HR-TEM techniques. The capacitance behaviour of the prepared electrode materials was examined by cyclic voltammetry, galvanostatic charge–discharge and impedance analysis respectively. Among the two samples studied, $Bi_2O_3$/graphene nanocomposite electrode material has exhibited higher specific capacitance of 136.76 $Fg^{-1}$, which is much higher than the specific capacitance of pure $Bi_2O_3$ based electrode (81.03 $Fg^{-1}$). Moreover, the synthesized nanocomposite electrode material has exhibited good cyclic stability (>95% over 1000 cycles) which may lead to applications in high-performance energy storage devices such as super capacitors.

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## 1. Introduction

Supercapacitors or electrochemical capacitors or ultra-capacitors have attracted a worldwide research now-a-days when compared to the secondary batteries because of their high power density, long cycle life, cleanliness, low maintenance cost and their potential applications in different scientific arena [1–3]. Generally, supercapacitors can be classified based on their two different charge storage mechanisms: electrical double layer capacitance (EDLC) and pseudocapacitance. In EDLC based capacitor, charges are stored at the electrode/electrolyte interface which may result in double-layer and in case of pseudocapacitor, the storing of energy may be due to the redox reactions which take place at the surface of the electrodes [4–6]. Supercapacitors have the advantage over other renewable energy storage devices because on their high power density (>10 kW/kg) and high cyclic stability ($10^5$ cycles). However, the supercapacitors developed till now resulted in low energy density which limits their electrochemical performance and therefore supercapacitors are being developed with new alternate electrode materials having high surface

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area [7]. It was reported that suitable modifications carried-out in the electrode material of supercapacitors can result in high performance [3]. The electrode materials based on carbon, conducting polymers and transition metal oxides have been developed till now [1,2]. Nanostructured materials with graphene composites have attracted greater attention recently for the application as electrode materials in supercapacitors because of their high surface area and excellent electrochemical properties [8–11]. The electrode materials like carbon, graphite and graphene with high specific area may deliver high capacitance because of charge separation at the electrode/electrolyte interface either with aqueous or organic electrolytes [12–15]. These materials may suffer from some drawbacks like high resistivity, poor cyclic performance and volume shrinkage/enlargement during the charge–discharge process. However, the researchers still pay attention more to these materials because of their remarkable capacitance and low cost. Composites combining metal oxides and carbonaceous materials respectively, have been studied to solve the intractable problem reported with ordinary electrode materials [16–18].

Graphene having 2D monolayer of $sp^2$-carbon atoms with high surface area (2675 $m^2/g$) and good mechanical strength ($\sim$1 TPa) [19] possessed high electrical conductivity and excellent electrochemical stability [20]. Because of these unique properties, a good number of research works are being focussed on the preparation of electrode materials in combination with graphene for application in supercapacitors. From these outstanding features, graphene is being studied as a promising material for various applications including transparent conducting films [21], actuators [22], sensors [23], nanoelectronics [24] and energy storage devices [25]. It was reported that graphene may undergo aggregation during the fabrication of electrode materials which may lead to affect its capacitance characteristics [26]. Because of these characteristics, the researchers now have started anchoring metal oxides/hydroxides onto graphene sheets as composites in order to exhibit better capacitance behaviour in which metal oxides/hydroxides may act as a spacer to prevent the aggregation on graphene. Based on this proposed design, nanocomposites of graphene and metal oxides / hydroxides have been successfully reported on the basis of either GO or rGO, which includes graphene / $Co_3O_4$ [27], graphene / $Fe_2O_3$ [28], graphene/NiO [29], graphene / $Ni(OH)_2$ [30] and so on. In addition to this, a good focus has been given also on bismuth based materials like $Bi_2WO_6$ [31], $BiVO_4$ [32], $Bi_2O_3$ [33], and $Bi_2S_3$ [34] and which exhibited good electrochemical properties. Among which, $Bi_2O_3$ is found to be good alternate electrode material due its good thermo-chemical stability and electrochemical characteristics [33].

In this work, we demonstrate a simple sol–gel method to synthesize $Bi_2O_3$ and graphene/$Bi_2O_3$nanocomposites. The physico-chemical and electrochemical characteristics of these electrode materials were studied and compared. Based on the results, it was found that graphene/$Bi_2O_3$electrode material exhibited a good specific capacitance and better cyclic stability. Hence, this may be considered as an alternate electrode material for supercapacitor applications.

## 2. Experimental

### 2.1. Materials

The chemicals such as, bismuth (III) nitrate (99%, Merck), citric acid (97%, Merck), nitric acid (97%, Merck), sulphuric acid (97%, Merck), graphite ($\geq$ 97%, Merck), ethanol (99.9%, Changshu Yangyuan), N-Methyl-2-pyrrolidone (NMP) (99%, Sigma) and polyvinylidene fluoride (PVDF) were as used in the experiment. All the chemicals were used as such without any further purification.

### 2.2. Synthesis of graphene oxide

Graphite oxide was synthesized by modified Hummer's method [35]. Initially, graphite powder (2 g) was added in 100 mL of concentrated $H_2SO_4$ (98%) in a 1000 ml volumetric flask kept under ice bath (maintained at 0–5 °C) with continuous stirring. The mixture was stirred for 4 h at this temperature range and $KMnO_4$ (6 g) was added to the suspension very slowly. The rate of addition of $KMnO_4$ was carefully controlled to keep the reaction temperature lower than 15 °C. The mixture was diluted further with very slow addition of 150 mL double distilled water and it was kept under stirring for 2 h. The ice bath was then removed, and the mixture was stirred at 35 °C (in a mantle) for 2 h. The solution was finally treated with 40 ml $H_2O_2$ which will result in the colour change from dark brown to bright yellow. To this reaction mixture, 150 ml of double distilled water was added and the solution was stirred for another 2 h. It was then kept without stirring for about 3–4 h, where the precipitates are settled at the bottom and the remaining filtrate is filtered-off. The resultant precipitate was washed repeatedly by centrifugation process with 10% HCl and then with deionized (DI) water several times until the formation of gel like material having neutral pH. The gel-like material was centrifuged and vacuum dried at 60 °C for more than 6 h to get graphene oxide (GO) powder.

### 2.3. Synthesis of bismuth oxide composites

Simultaneously two solutions were prepared, one containing 20 mg of GO powder in 50 ml of ethanol and kept on ultra-sonication to obtain an exfoliated GO. The other one containing 0.5 g of $Bi(NO_3)_3{\cdot}5H_2O$ in 50 ml ethanol with the addition of 65% $HNO_3$ (approximately 5–10 mL) until the transparent solution was formed. To this transparent solution, 0.5 g of citric acid was added to get the solution of bismuth citrate mixture. Then, the solution containing bismuth citrate mixture was added drop-wise to the exfoliated GO solution and the resultant solution was continuously stirred for about 2 h to get a sol. The sol thus formed was heated to 80 °C for 3–4 h to get a yellowish gel. This gel was further dried at 120 °C for 2 h and then final calcination was carried-out at 300 °C for about 3 h to obtain graphene/$Bi_2O_3$ nanocomposite material. The schematic diagram for the preparation of graphene/$Bi_2O_3$ nanocomposite is indicated in Fig. 1. The same procedure was repeated to prepare pure $Bi_2O_3$ nanoparticles with the absence of GO for comparative study.

### 2.4. Fabrication of working electrode

Initially, 9 wt% of the obtained active electrode material with 1 wt% of poly(vinylidenefluoride) (PVDF) in N-Methyl-2-pyrrolidone (NMP) ($\sim$5 ml) to form a slurry. Then, the obtained slurry was coated onto a thin graphite sheet (having specific area of 1 $\times$ 1 $cm^2$) with the active materials loading of around 0.5 $mg/cm^2$. The slurry coated electrode was dried at 50 °C in order to remove the organic constituents present in the micropores of the working electrode [36].

### 2.5. Materials characterization

The heat treated nanocrystalline materials were characterized by Shimadzu XRD6000 X-ray diffractometer using Cu$K\alpha$ radiation. Shimadzu IR Prestige-21 model FTIR spectrometer was employed to record the FTIR spectra of materials in the range of 4000–400 $cm^{-1}$. The surface morphology of the particles was studied by means of JEOL Model JSM-6360 scanning electron microscope. EDAX analysis was also performed with JEOL Model JSM-6360 to find out the atomic weight percentage of elements present in the

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