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One-step green synthesis of graphene/ZnO nanocomposites for electrochemical capacitors

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Abstract

A facile, green and efficient approach consisted of a novel liquid phase exfoliation and solvothermal synthesis method has been adopted to prepare graphene/ZnO nanocomposites as electrode material for electrochemical capacitors. Highly pristine graphene was produced from mild sonication treatment of raw highly pyrolytic graphite in a solution at a proper ratio of ethanol and water. The X-ray diffraction (XRD) analysis revealed the formation of pure ZnO structure from the zinc nitrate hexahydrate precursor during solvothermal synthesis. The surface characteristics and elemental composition of the nanocomposites have been studied by means of field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS) and transmission electron microscope (TEM). The electrochemical properties of the graphene/ZnO nanocomposites were examined by cyclic voltammetry (CV), galvanostatic charge–discharge tests and electrochemical impedance spectroscopy (EIS). The graphene/ZnO nanocomposites displayed an improved capacitive performance of 236 F/g at a scan rate of 10 mV/s, excellent cyclic performance, and an average energy density of 11.80 W h/kg. The improved electrochemical performance of the nanocomposites can be ascribed to the high electrical conductivity of the synthesized pristine graphene and the good electroactive property of ZnO.

Keywords: Green approach; Pristine graphene; Solvothermal synthesis; Graphene/ZnO nanocomposites; Electrochemical capacitor

1. Introduction

There are concerns over the limited availability of fossil fuels and its association with global warming and environmental pollution. This growing interest has generated the need for the advancement of renewable energy sources along with new technologies related to effective, facile, and environmental friendly method for energy conversion and storage [1–3]. Energy conversion and storage systems may embrace the technology and systems of an external thermal interface or that of an external electrical interface [4] and they are categorised into groups by the amount of energy and power available for the load [5] which includes batteries, fuel cells, capacitors and supercapacitors [1,5].

Supercapacitors also known as electrochemical capacitors have been a subject to many applications, research and development due to its high power density, environmental friendliness, long shelf life, long life cycle [3,4] and it bridges the energy gap between capacitors (high power output) and fuel cells/batteries (high energy storage) [1,2]. Much research and development have been carried out to improve the overall performance of supercapacitors via the use of carbonaceous compound, metal oxides, conducting polymers and the associated hybrids/ composites as promising electrode materials [1–3,6,7].

Graphene is highly anticipated to be an excellent electrode material due to its notable characteristics such as high surface area to volume ratio, good electrical conductivity, good flexibility, fast electron mobility and good thermal and electrochemical

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properties [8–11]. The introduction of graphene and metal oxide composites has demonstrated a better energy density, power density and capacitance for supercapacitors [3,8,12]. The synergetic effect between the metal oxide and graphene clearly indicates that metal oxides play the roles of spaces to expand the surface area of graphene and improves capacitance as a result of the redox reaction while graphene reduces the resistance by providing a conductive pathway for the easy diffusion of ions and movement of electrons [8]. Among the many metal oxides available, zinc oxide (ZnO) has attracted much attention as a promising electrode material for supercapacitors due to its low cost, abundant availability, environmental friendly nature and electrochemical activity [13]. ZnO is a battery active material which attains an energy density of 650 A/g. It has a large exciton binding energy (60 meV) and a wide band-gap (3.37 eV) [14–16]. In addition, it has strong emission of light at room temperature and it is transparent in nature [15].

In view of the outstanding individual properties of graphene and ZnO as electrode materials, the combination of graphene with ZnO nanoparticles as electrodes may result in improved supercapacitor performance. Several methods employed in preparing graphene–ZnO nanocomposites for supercapacitors have been reported. Lu et al. [17] prepared graphene–ZnO nanocomposites via a microwave-assisted system, where the composite compound exhibited an improved electrochemical capacitance of 146 F/g at a scan rate of 2 mV/s. Li et al. [18] reported a hydrothermal technique to grow ZnO nanorods that were distributed homogeneously on the graphene nanosheets. The nanocomposite materials were found to possess a specific capacitance of 156 F/g at a scan rate of 5 mV/s. Zhang et al. [19] synthesised graphene–ZnO composites films for supercapacitors application by depositing ZnO on graphene by ultrasonic spray pyrolysis (USP). They reported that graphene/ZnO composites had demonstrated a better reversible capacitive process than graphene material alone. Wang et al. [3] reported a successful synthesis of graphene nanosheets/ZnO composites prepared by an in situ crystallization method which displayed an improved capacitance of 62 F/g at a current density of 5 mA/cm^2. However, most of these studies had utilised graphene nanomaterials synthesised via the modified Hummers method, followed by chemical reduction producing the reduced graphene oxide (rGO). By using this conventional method, the graphene produced are less pristine due to the used of harsh acids in the synthesis processes, resulting in many oxygenated groups formed on the graphene surface [20,21]. The presence of these oxygenated groups results in significant compositional and structural defects which affects its electrical properties. Though the reduction process is aimed at removing the oxygen moieties, literatures have indicated that in general, this chemical reduction processes are incomplete and that the oxygenated groups cannot be completely removed resulting in less superior electrical properties or greater crystal defects when compared to the pristine graphene [20–24].

Consequently, the development of a facile green approach for synthesising high-quality graphene is essential and crucial for practical sustainability. Therefore in this work; a novel green synthesis method is used to produce the graphene material. This method involves the liquid phase exfoliation of graphite through the sonication of raw highly pyrolytic graphite flakes in an optimum ratio of ethanol and de-ionized water, as reported in our previous work [25]. Such method does not require strong oxidizing agents (potassium permanganate, sodium nitrate and concentrated sulphuric acid) and reducing agents (hydrazine) thereby making the process simple and fast. The use of a common reagent (ethanol) as the exfoliation medium which has a low boiling point of 78.37 °C for the synthesis of graphene makes the synthesis process relatively safe and preserves the pristine structure of graphene material.

Our composite synthesis method incorporates such simple and green method of synthesising graphene–ZnO nanocomposite material using facile solvent exfoliation and low temperature solvothermal processing approaches. It is our aim to fully harvest the desired high electrical conductivity of graphene and the good electrocatalytic property of ZnO in the nanocomposites material. In this work, the surface characteristics, structural and electrochemical properties of the graphene/ZnO nanocomposites as an electrode material for supercapacitors were evaluated thoroughly.

2. Experimental

2.1. Materials

Commercially available raw highly pyrolytic graphite (HOPG) flakes (99% carbon purity) were purchased from Bay Carbon, zinc nitrate hexahydrate $Zn(NO_3)_2 \cdot 6H_2O$ (reagent grade 98%) were bought from Sigma Aldrich. Activated carbon ($\propto$CH-0020) was purchased from RHE resources, ethanol was obtained from Merck and sodium hydroxide (NaOH) was purchased from R&M Chemicals. All chemicals were used as received without further purification. Deionized water (DI) from the Millipore system was used throughout the experiment.

2.2. Synthesis of graphene

The graphene nanomaterial was prepared via a facile green solvothermal synthesis of graphene and ZnO as illustrated in Fig. 1. Graphite was used as the starting reagent for synthesis of graphene via liquid phase exfoliation method [25]. Typically graphite (50 mg) material was dispersed in 100 ml solution of ethanol and deionized water (2:3 ratio) and sonication treatment was carried out in a conventional ultrasonic bath with working frequency of 50/60 Hz at room temperature for 3 h to form a darkish black suspension. The solution was centrifuged under 1000 rpm for 30 min to remove aggregates and the remaining residue was dried at a temperature of 80 °C for 10 h.

2.3. Preparation of graphene–ZnO composites

Graphene (0.2 g) nanomaterial was then re-dispersed in 50 ml solution of ethanol and deionized water (2:3) under sonication for 30 min. Zinc nitrate hexahydrate was added to