



Original Research Paper

An optimum method for uniform synthesis of zirconia on reduced graphene oxide



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ABSTRACT

In this work, efforts have been put to explore an optimum technique for uniform and effective coating of zirconia (ZrO_2) on reduced graphene oxide (rGO) nanosheets. ZrO_2 coated rGO composites have been prepared through chemical precipitation and isothermal hydrolyzation techniques. Morphological characterizations (Scanning Electron Microscopy and Transmission Electron Microscopy) have proved that in chemical precipitation ZrO_2 was agglomerated over the rGO surface and the coating was highly non-uniform. The presence of ZrO_2 agglomerates reduces the effectiveness of coating, as observed through microstructural and thermal characterizations. Moreover, the increase in reaction time during isothermal hydrolyzation offers a more uniform coating and thus enhanced physical, structural and thermal properties. The effect of zirconia coating on charge transport capability of rGO, studied via cyclic voltammetry, also proves that isothermal hydrolyzation is better than conventional chemical precipitation technique for ceramic-coating on rGO.

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1. Introduction

Graphene is a well known advanced carbon material which has imposed itself over other conventional carbon based materials due to π - π interaction of sp^2 hybridized carbon atoms. Since the discovery of graphene in 2004, its high thermal conductivity ($\sim 5000 \text{ Wm}^{-1} \text{ K}^{-1}$), charge mobility ($\sim 200,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), specific surface area ($\sim 2630 \text{ m}^2 \text{ g}^{-1}$) and excellent mechanical strength have drawn worldwide attention [1–5]. In addition, low sludge volume of graphene [6] makes it superior candidate for wastewater treatment and reinforcing element in polymer composites. These superior properties of graphene over carbon nanotubes (CNT) encourage its relevance to various applications such as structural devices, energy storage and conversion devices i.e. fuel cell and Li-ion batteries, sensor optoelectronics, etc. [7–12]. It has been found that graphene oxide (GO) has overcome graphene for its application in composites due to the low-cost of graphite used as raw material and the presence of stable hydrophilic functional groups on its surface which assists for simple, cheap and efficient solution processes [13]. However, the properties of

GO were not up to the mark of graphene. Reduction of GO (rGO) partly restores the thermal and structural properties in close proximity to graphene. Now-a-days, there has been increasing demand of ceramic-GO composites in flame retardant systems and advanced energy storage devices [14]. As a result of extensive research in the field of zirconia (ZrO_2)-CNT composites, it has already been proved that ZrO_2 is highly attractive material for such systems and devices [15–17]. The various methods for preparation of metal-oxide/GO composites includes atomic layer deposition (ALD), two-step annealing process, isothermal hydrolyzing process and chemical precipitation [18–20]. Most of the studies in this area have been carried out for CNT based ZrO_2 composites and a few for applications focused graphene based ZrO_2 composites. To the best of our knowledge, there is no such work where composites have been prepared with the uniformity-focussed synthesis of ZrO_2 on rGO.

In this work, we have focused to achieve a controlled synthesis of ZrO_2 on the surface of rGO using two different techniques. Recently, the growth mechanism of ZrO_2 synthesis on graphene nanosheets through atomic layer deposition (ALD) technique has been studied where the crystallinity of deposited ZrO_2 has been found to decrease with decreasing temperature [21]. Due to the better dispersion ability of rGO, we have presented the growth of ZrO_2 on rGO and our main aim is to explore an efficient procedure which leads to the controlled synthesis and uniform dispersion of

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ZrO₂ coating on rGO sheets for their applications in advanced energy storage and functional devices due to excellent thermal stability and chemical durability.

2. Experimental procedure

2.1. Materials used and sample preparation

GO has been purchased from N-barotech Company, South Korea having the 95% purity. ZrOCl₂·8H₂O was supplied from Sigma–Aldrich, USA and used as a precursor for the coating of ZrO₂ on nanomaterials. Ethanol was brought from Changshu Yangyuan Chemical Co., Ltd., China. Distilled water setup was already there in our laboratory.

Initially, GO was reduced with hydrazine hydrate to remove the oxygen functional groups from exfoliated GO sheets [15]. For this purpose, the GO suspension (1 mg/ml) was sonicated for 1 h under 20 kHz to achieve proper dispersion of the GO sheets. This suspension was heated under condensation in an oil bath for 24 h at 100 °C, after the addition of hydrazine hydrate (1.56 ml, 20.57 mmol). The resulted black precipitate obtained after filtration and washing, was dried under vacuum to obtain rGO.

The processing steps for coating of ZrO₂ on rGO are shown in Fig. 1. Upper trail represents the procedure for chemical precipitation and lower for isothermal hydrolysis technique. Independent of the technique, 0.2 mol/L solution was initially prepared by dissolving solid ZrOCl₂·8H₂O in 100 ml distilled water under stirring. After few minutes, 30 mg rGO was added to this solution and then mixture was introduced to sonicator. A black suspension was observed after about 30 min which indicates proper dispersed of rGO nanosheets in the solution. In chemical precipitation technique, calculated amount of NH₄OH was slowly added to the above suspension, under stirring. This mixture was allowed to stir for 60 min at room temperature to obtain a suspension having ZrO₂ coating on rGO particles. However, in isothermal hydrolysis, dispersed rGO solution was long drawn reflux condensed in a thermostatic water bath at 100 °C and sonicated once in 24 h for about 10 min. This supports for improved dispersion of rGO particles in the solution. To investigate the effect of reaction time, we performed this process for 72 h and 96 h. For 72 h trial, the black suspension was observed to turn into gray, indicating the presence of

some additional layer on rGO particles. The main advantage of this method has been its control over thickness of coating through varying the isothermal hydrolyzation time [22].

2.2. Characterization methods

FESEM Zeiss-Ultra Plus, Gemini Co. was used for investigating the surface morphology and elemental composition. The internal structure of ZrO₂-coated rGO was observed at 200 kV with the help of high-resolution transmission electron microscope (HR-TEM), JEM-2010(JEOL). A charge-coupled digital device camera was employed to record the images. X-ray photoelectronic spectroscopy (XPS) was done on XPS-PHI 5500 spectrometer to observe the effect of coating done via two different techniques. Al K α (1485.6 eV) at anode voltage 13.8 kV, was used as X-ray source. X-ray diffraction (XRD) tests were carried out by means of Bruker AXS Diffractometer D8 having Cu K α radiation ($\lambda=0.154$ nm) at 5°/min scanning rate, 40 mA current and an accelerating potential of 40 kV. Raman spectra were recorded from 800 to 2000 cm⁻¹ on RM-2000 microscopic confocal Raman spectrometer which employ He-Ne laser beam of 514.5 nm wavelength with a CCD detector. It provides structural information about the carbon-based materials. Thermogravimetric analysis (TGA) was carried out from room temperature to 800 °C on TGA SII 6300 Exstar with 10 °C/min temperature ramp to analyze the effect of coating on thermal behavior of rGO. Cyclic voltammetry was used for the electrochemical analysis of specimens using EC epsilon.

3. Results and discussions

FESEM images of ZrO₂-rGO nanocomposites prepared through chemical precipitation of NH₄OH and isothermal hydrolysis at increasing time are shown in Fig. 2 where coating of ZrO₂ on rGO can be clearly observed in subsequent images. The corresponding elemental composition is shown in Fig. 3 and compared in Table 1. This is apparent from Fig. 2(b) that the coating of ZrO₂ through chemical precipitation technique is highly non-uniform and disordered. A portion of rGO particles remained uncoated whereas large clusters of ZrO₂ particles have been observed various sites. This may be due to the dominating amorphous phase in composite. In case of ZrO₂ coating on rGO via isothermal technique, almost same

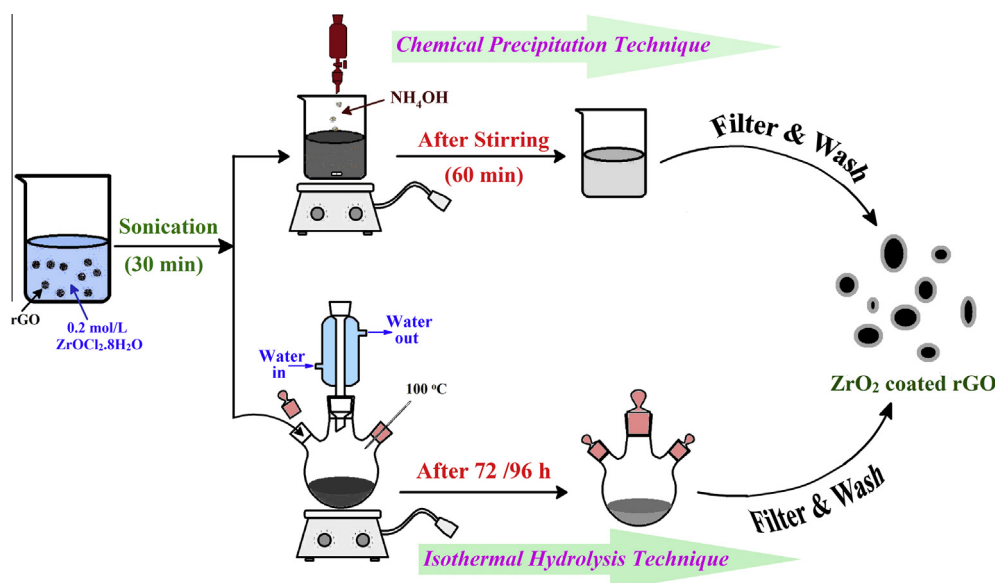


Fig. 1. Experimental set-up for zirconia coating on rGO through chemical precipitation and isothermal hydrolysis techniques.

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