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HYDROTHERMAL SYNTHESIS OF REDUCED GRAPHENE OXIDE/ZIRCONIA NANOCOMPOSITE AND ITS PHYSICOCHEMICAL CHARACTERIZATION

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Abstract

In this paper, we present a technique for the effective fabrication of reduced graphene oxide with nanostructured zirconia (rGO/ZrO_2) composites using a hydrothermal method. The objective this work was to provide simpler and efficient method for the synthesis of rGO/ZrO_2 which highly required for industrial applications. Powder X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and UV-visible spectroscopy was used to characterize the obtained nano-hybrid structure materials. These techniques confirmed the presence of rGO and the uniform distribution of zirconia nanoparticles on graphene oxide sheets during synthesis. This has created new opportunities and prospects for the use of this simple and low-cost technique in the development of zirconia/graphene nanocomposite powders.

Keywords: Hydrothermal synthesis, Reduced graphene oxide, Zirconia nanocomposite.

1. Introduction

Development of zirconia (ZrO_2) and zirconia-based ceramics have received significant attentions as a potential material for various structural applications. The physicochemical characteristics of the zirconia related with the thermal stability, corrosion resistance and zero toxicity are the most acceptable considerations for future applied fields. Furthermore, many modifications were attempted for improving the performances [1-4].

The formation of composite with some other solid supports were reported, and from various possible materials, the combination of zirconia with graphene and its derived materials were reported to give significant improvements. The enhanced performances related with mechanical, tribological, electrical, and thermal properties was successfully obtained, and therefore, the graphene-reinforced composites are got many attentions. In more technical studies, the various graphene synthesis techniques and processing methods including the ceramic/graphene composition, sintering methods and sintering variables were optimized [5-8].

The exploration on a homogeneous distributed graphene in the composite with an optimum sintering is an interesting attention. Moreover, several methods for preparing nanocrystalline zirconia-based nanocomposites have been proposed, including the sol/gel method [9], the vapor phase method [10], pyrolysis [11], spray pyrolysis [12], hydrolysis [13], and microwave plasma [14].

Some drawbacks of those methods are related with a high production costs and poisonous constituents and by-products, causing the difficulties to scaling up. Therefore, hydrothermal methods are mentioned as having great potential for producing effectively isolated nanoparticles with a narrower size distribution [15].

Hence, the primary goal of this work is to (a) develop a simple and easy method for synthesizing ZrO_2/rGO nanocomposites, (b) examine their morphological and chemical structures using powder X-ray diffraction (XRD), Fourier transform infrared (FTIR), scanning electron microscopy (SEM), and Energy Dispersive X-Ray Analysis (EDAX) techniques, and (c) optical properties.

2. Materials and Method

2.1. Materials

Chemicals utilized in this research consist of GO, $ZrOCl_2{\cdot}8H_2O$, $N_2H_4{\cdot}H_2O$, purchased from Merck (Germany). All chemicals are in analytical grade.

2.2. Preparation of ZrO_2/rGO nanocomposite

The hydrothermal process was adapted for the synthesis of reduced graphene oxide-nano zirconia (ZrO_2/rGO) composites. The GO suspension served as the rGO precursor, $N_2H_4{\cdot}H_2O$ served as the reducing agent, and as ZrO_2 precursor, $ZrOCl_2{\cdot}8H_2O$ was used, respectively. Previously, the mixture of 20 mL of 0.01 M $ZrOCl_2$ solution and 40 mL of colloidal suspension of GO was prepared, followed by sonication for 30 min. Into the mixture, 1 mL of hydrazine hydrate was then added and poured into a 200 mL stainless steel Teflon-lined autoclave. The autoclave was kept at 180 °C for 18 h before was cooled at room temperature. The obtained black products were centrifuged and repeatedly washed with ultrapure water before being freeze-dried for 12 h.

Figure 1 describes the schematic representation of the synthesis method.

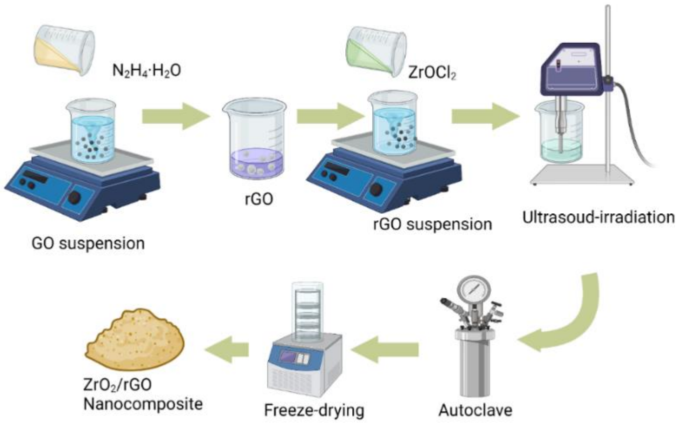

Fig. 1. Synthesis of ZrO_2/rGO nanocomposite.

2.3. Characterization of material

The characterization was conducted on Shimadzu X6000 X-ray diffraction (XRD), Perkin-Elmer Fourier transform infrared (FTIR), and scanning electron microscopy-Energy Dispersive X-Ray Analysis (EDAX) of Phenom-X. A Ni-filtered-$K\alpha$ ($\lambda = 1.5406$ A°) was utilized as radiation source in XRD analysis, meanwhile FTIR analysis for was carried out over the spectral range of 400-4000 cm^{-1}.

3. Results and Discussion

The XRD patterns of the prepared rGO/ZrO_2 nanocomposite are shown in Fig. 2. The reflection at about 25° represents a major (002) peak of rGO pattern, which corresponding to an ordered crystalline structure as the result of GO sheets reduction[16]. The crystal structure of ZrO_2 nanoparticles is tetragonal and monoclinic but the former has the dominant position of relative intensity and quantity. The rGO/ZrO_2 nanocomposite exhibits tetragonal peaks of rGO (002) and ZrO_2, indicating the presence of ZrO_2 nanoparticles over the rGO nanosheets.

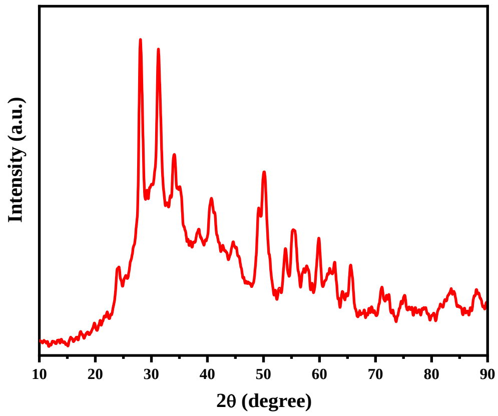

Fig. 2. XRD pattern of rGO/ZrO_2 nanocomposite.

Figure 3 depicts the use of an FTIR technique to determine the presence of functional groups in rGO/ZrO_2 nanocomposite. Some characteristic bands are the identification for the composite formation. The presence of C=O functional group was located at 1725 cm^{-1} which specifically related with stretching frequency, and it was shifted to 1745 cm^{-1} in the ZrO_2/rGO nanocomposite as the interaction of C=O group and Zr causing the increasing vibration energy [17]. The hydroxyl functional groups are identified the vibrational spectra at 1465 and 1390 cm^{-1}, which are assigned to the formation of either a monodentate or bidentate complex coming from the interaction of Zr (IV) and the oxygen-containing groups of GO [18-21]. The vibrational bands at 1684 and 472 cm^{-1} can be assigned to the C=C stretching mode and Zr-O vibration, respectively [22].

Furthermore, there is additional evidence to support the findings after the various characterization techniques - the SEM images in Figs. 4(a)-(c) show the rGO sheets and ZrO_2 nanoparticles. The ZrO_2/rGO SEM image revealed a homogeneous distribution of ZrO_2 nanoparticles that are dispersed onto a flat rGO sheets. In addition, elemental analysis based on the EDX spectrum (Figs. 4 (d)-(h)) depicts the presence of Zr, C and O in nanocomposite suggested that ZrO_2 nanoparticles were bonding on the graphene oxide surface.

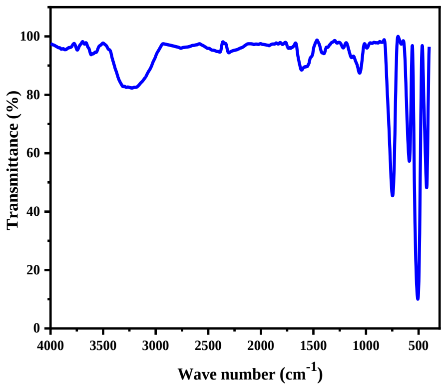

Fig. 3. FTIR spectrum of rGO/ZrO_2 nanocomposite.

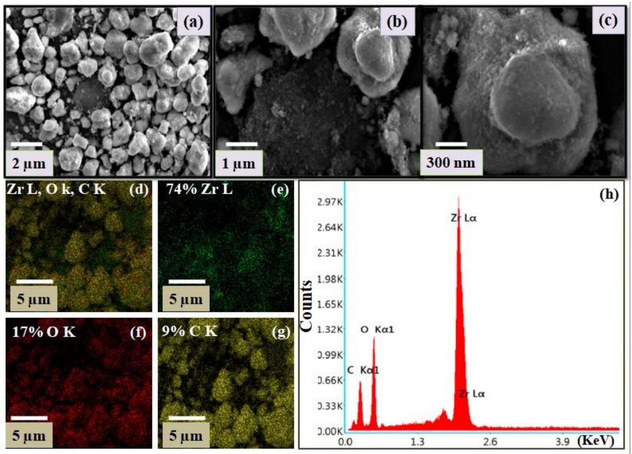

Fig. 4. (a-c) SEM images and (d-h) EDX spectrum of rGO/ZrO_2 nanocomposite.

Figure 5 depicts the UV-visible absorption spectrum of an rGO/ZrO_2 nanocomposite. The peak at 232 nm is attributed to the aromatic carbon-carbon (C-C) bonds π to π* (π →π*) transition. A broad peak centred at 232 nm was observed in the rGO/ZrO_2 nanocomposite. As a result of the hydrothermal and chemical reduction processes, the conjugation network of the rGO/ZrO_2 nanocomposite has been partially restored.

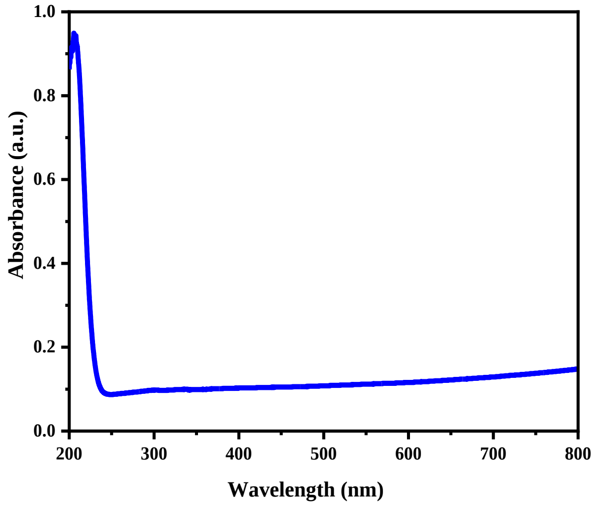

Fig. 5. UV absorption spectrum of rGO/ZrO_2 nanocomposite.

The present study used a low-cost and simple hydrothermal synthesis technique for the fabrication of ZrO_2/rGO nanocomposites. XRD, FTIR, SEM, and UV measurements were used to characterize the as-prepared nanocomposite. During the hydrothermal reaction, zirconia nanoparticles were successfully bonded into the reduced graphene oxide sheets, according to all characterizations. The SEM also clearly demonstrated the uniform distribution of ZrO_2 nanoparticles that completely covered the graphene oxide sheets.

4. Conclusions

The present study used a low-cost and simple hydrothermal synthesis technique for the fabrication of ZrO_2/rGO nanocomposites. XRD, FTIR, SEM, and UV measurements were used to characterize the as-prepared nanocomposite. During the hydrothermal reaction, zirconia nanoparticles were successfully bonded into the reduced graphene oxide sheets, according to all characterizations. The SEM also clearly demonstrated the uniform distribution of ZrO_2 nanoparticles that completely covered the graphene oxide sheets.

Nomenclatures

C_o	Initial concentration
DE	Degradation efficiency
D	Crystallite size
K	Diffraction factor
k	Kinetics constant

R^2	Determination coefficient
Greek Symbols	
λ	wavelength
θ	Diffraction angle
Abbreviations	
FTIR	Fourier-Transform Infra-Red
JCPDS	Joint Committee of Pure Diffraction Spectra
SEM-EDX	Scanning Electron Microscope-Energy Dispersive x-ray Spectroscopy
UV	Ultraviolet
XRD	x-ray diffraction

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