Synthesis And Optical Properties Of Zirconia (Zro₂)-Polyacrylicacid (PAA) Nanocomposites

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Abstract: In this paper, we present the synthesis of ZrO₂ (Zirconia) nanoparticles by hydrothermal method and the synthesis of Zirconia (Zro₂)-polyacrylicacid (PAA) nanocomposite. The structural, morphological and optical properties of ZrO₂-polyacrylicacid nanocomposite have been investigated through XRD, SEM, EDX, FTIR, UV–Vis absorption and photoluminescence (PL) spectroscopy. X-ray diffraction (XRD) spectra confirms the formation of ZrO₂ and crystallinity of samples. SEM and EDX performed the surface morphological and elemental characterizations. Scanning electron microscope (SEM) shows the irregular morphology of the particles and chunks of ZrO₂ distributed throughout the sample. Energy Dispersive X-ray (EDX) spectroscopy and Fourier transform infrared (FTIR) spectra confirms the formation of ZrO₂ in crystalline phase. Ultraviolet-visible (UV-Vis) spectroscopy and photoluminescence (PL) spectroscopy gives optical properties. Absorption spectra shows a well-defined peak in absorbance curve. Photoluminescence (PL) spectra exhibits an additional emission peak may be due to interstellar defect created by ZrO₂ in the polyacrylicacid film.

Index Terms: nanocomposites, hydrothermal, optical property, polyacrylicacid (PAA), zirconia (ZrO₂), UV-Vis spectroscopy, Photoluminescence (PL)

1 INTRODUCTION

Nanocomposite is a mixture of different component materials, in which at least one being of nanometer scale. Such materials may display combined features of all components or quite new properties resulting from mutual interactions between components. Organic-inorganic polymer composites have recently found wide technological applications. In the last years, a special interest has been focused on nanocomposites based on polymer networks involving nanoparticles being characterized by different, electric, magnetic or optical features. Different kinds of materials, among which are sulfides, organic compounds and oxides nanocrystals, have been proposed as nano-fillers in these composites [1, 2]. Polymer nanocomposites are materials in which nanoscopic inorganic particles are dispersed in an organic polymer matrix in order to improve the performance properties of the polymer. Polymer nanocomposites represent a new alternative to conventionally filled polymers [3]. Because of their nanometer sizes, filler dispersion nanocomposites exhibit markedly improved properties when compared to the pure polymers or their traditional composites [4]. Nano-size zirconia has attracted much attention due to its specific optical and electrical properties as well as other potential applications in transparent optical devices, electro- chemical capacitor electrodes, oxygen sensors, fuel cells, catalysts and advanced ceramics [5]. ZrO₂ is a technologically important material due to its superior hardness, high refractive index, optical transparency, chemical stability, photothermal stability, high thermal expansion coefficient, low thermal conductivity, high thermostability and corrosion resistance [6]. These unique properties of ZrO₂ have led to their widespread applications in the fields of optical [7], structural materials, solid-state electrolytes, gas-sensing, thermal barriers coatings [8], corrosion-resistant, catalytic [9].

In present paper, ZrO₂-polyacrylicacid nanocomposites were prepared by hydrothermally synthesised ZrO₂ was mixed with polyacrylicacid. The purpose of introducing ZrO₂ with polyacrylicacid was to enhance its optical properties as ZrO₂ has better optical properties.

2 EXPERIMENTAL PART

2.1 Materials

Acrylicacid monomer was purchased from Merck chemicals. Zirconium oxichloride was purchased from Sigma-Aldrich. All chemicals used are of analytical grade and used as obtained.

2.2 Synthesis of ZrO₂ by hydrothermal method

In which zirconium oxichloride and acrylicacid were initial chemicals. The ZrO₂ was prepared by hydrolysis of zirconium oxichloride and then drop wise addition of ammonium hydroxide into the above solution to make pH=10 of the solution. Add hydrogen peroxide (20% volume of solution) to make 50 ml of solution which kept under vigorous stirring at room temperature. The ZrO₂ nanoparticles were obtained by transferring the solution into Teflon lined autoclave at 160 °C for 24h. Then, wash the solution for 2-3 times by ethanol and distilled water and was calcinated in oven at 100 °C for 1h.

2.3 Preparation of ZrO₂-Polyacrylicacid nanocomposites

ZrO₂-Polyacrylicacid nanocomposites was prepared by introducing hydrothermally synthesized ZrO₂ to the acrylicacid (monomer) using oven as a conventional polymerization technique [10]. Thus, synthesized ZrO₂ with various concentrations (0.1 & 0.5 mol%) were ultrasonicated with acrylicacid. With drop wise addition of potassium persulfate (KPS) as an activator, initiate the polymerization. And the solution kept in the oven for 20 min. at 120 °C for desired nanocomposites. The preparation of film can be done by deep coating method [11].

2.4 Characterization technique

As prepared and calcinated ZrO₂ nanopowder and ZrO₂-polyacrylicacid (PAA) characterised through various techniques, namely XRD, SEM, EDX, FTIR, UV–vis absorption spectroscopy and photoluminescence studies. The crystalline nature and phase purity of ZrO₂ nanoparticles was recorded by Bruker D8 Advance X-ray diffractometer. Surface morphology and grain size distribution of samples is analysed.
through JEOL make Model JSM 5810 LV scanning electron microscope. Nicolet iS10 FTIR Spectrometer of Thermo Scientific in the wave number region between 4000–400 cm\(^{-1}\) studies the quality and occurrence of functional group in ZrO\(_2\)-polyacrylicacid nanocomposites. Evolution 600 UV-Vis Spectrometer of Thermo Scientific recorded the UV–Vis absorbance spectra and Photoluminescence spectra were recorded using Horiba Jobin Yvon make Fluoromax-4 Spectrophotometer at room temperature with excitation wavelength 300 nm.

3 RESULTS AND DISCUSSION

3.1 X-ray Diffraction (XRD)
The XRD patterns were recorded on Bruker D8 Advance X-ray diffractometer in 2\(\theta\) range of 20\(^{\circ}\) to 90\(^{\circ}\) at room temperature with a least count of 0.05\(^{\circ}\). The 2\(\theta\) values are mentioned in degrees. In order to investigate the crystallization process of zirconia, Fig. 1. shows XRD of as-prepared products. This figure indicates that a mixture of monoclinic (m) and tetragonal (t) phases of zirconia was obtained. The distinguishing characteristic peaks occurred at 2\(\theta\) 30.161, 35.021, 50.371 and 60.021 for (1 1 1), (2 0 0), (2 2 0) and (3 1 1) reflections respectively. This is very close to the values in the literature (JCPDS no. 003-0640).

![Fig. 1. XRD spectra of pure ZrO\(_2\)](image)
The crystallite size of the as-prepared ZrO\(_2\) calculated with the Scherer formula, was found 12.1 nm and XRD results showed that the phase of ZrO\(_2\) nanoparticles were monoclinic and tetragonal.

3.2 SEM Analysis
Morphological analysis of the samples was done by JEOL make Model JSM 5810 LV scanning electron microscope. SEM images of pure acrylic acid shown in Fig. 2. (a) and two samples of ZrO\(_2\)-polyacrylicacid nanocomposites having ZrO\(_2\) with 0.1% and 0.5% of concentrations are shown in Fig. 2. (b-c) respectively. The nanosized particles can be observed from SEM images. It is clear that the chunks of ZrO\(_2\) material were spread homogeneously throughout whole sample and no change in morphology is observed due to ZrO\(_2\) doping.

![Fig. 2. SEM images of ZrO\(_2\)-polyacrylicacid nanocomposites (a) pure polyacrylicacid (b) 0.1% ZrO\(_2\)-polyacrylicacid & (c) 0.5% ZrO\(_2\)-polyacrylicacid nanocomposites.](image)
3.3 Energy Dispersive X-ray spectroscopy
The Energy Dispersive X-ray (EDX) spectroscopy is an analytical technique used for the elemental analysis of a sample, which identifies the elemental composition of materials imaged in a scanning electron microscope. And Fig. 3 (a-b) reveal that the ZrO$_2$-polyacrylicacid nanocomposites are composed of C, O and Zr elements, which is in good agreement with the used chemicals. The elemental Weight% and Atomic% of C, O and Zr for Fig. 3 (a) is 24.03, 74.49, 1.48 and 29.99, 69.77, 0.24 respectively. And elemental Weight% and Atomic% of C, O and Zr for Fig. 3 (b) is 18.22, 79.44, 2.34 and 23.31, 76.30, 0.39 respectively.

![Fig. 3. EDS spectra of ZrO$_2$-polyacrylicacid nanocomposites (a) 0.1% ZrO$_2$ and (b) 0.5% ZrO$_2$](image-url)

3.4 Fourier transform infrared (FTIR) Spectroscopy
FTIR spectrographs were recorded by a Nicolet IS10 FTIR Spectrometer of Thermo Scientific in the wave number region between 4000–400 cm$^{-1}$ studies the quality and occurrence of functional group in ZrO$_2$-polyacrylicacid nanocomposites. Fig. 4 (a-b) shows the FTIR spectrographs of pure polyacrylicacid and ZrO$_2$-polyacrylicacid nanocomposite, which shows enhanced optical property as the transmittance of ZrO$_2$-polyacrylicacid nanocomposites has higher value with compare to pure polyacrylicacid.

![Fig. 4. FTIR spectrograph of (a) pure polyacrylicacid (b) ZrO$_2$-polyacrylicacid nanocomposite.](image-url)

3.5 Ultraviolet-visible (UV-Vis) Spectroscopy
The absorption spectra were recorded by Evolution 600 UV-Vis Spectrometer of Thermo Scientific. The spectra were taken for the wavelength range of 280nm to 900nm. Fig. 5 (a-b) shows the absorption spectra of ZrO$_2$-polyacrylicacid nanocomposites with different concentration of ZrO$_2$ with 0.1% and 0.5% respectively. A well-defined peak is obtained around 290nm in the absorbance curve. It reveals that the absorbance increases because the amount of ZrO$_2$ increases in the sample [12]. This directly proves that with varying doping concentration we can get a desired energy band gap for ZrO$_2$ nanomaterial.

![Fig. 5. Absorption spectra of ZrO$_2$-polyacrylicacid nanocomposites](image-url)

3.6 Photoluminescence (PL) Spectroscopy
Photoluminescence spectra were obtained by Horiba Jobin Yvon make Fluoromax-4 Spectrofluorometer. Emission spectra for both the samples are shown in Fig. 6 (a-b).
The samples were excited at 300nm, the additional emission peak was obtained at 465nm in both the samples of ZrO₂-polyacrylic acid nanocomposites. This peak may be obtained due to interstellar defect created by ZrO₂ in the polyacrylic acid film [13].

EDX analysis confirmed that the samples were composed of C, O and Zr elements. FTIR spectrographs shows that the transmittance increases in the case of ZrO₂-polyacrylic acid with compare to pure acrylic acid and UV-Vis spectroscopy revealed that a well-defined peak is obtained around 290nm in the absorbance curve, the absorbance increases as the amount of ZrO₂ increases in the samples so we can have desired band gap of material as well. Photoluminescence spectra shows an additional peak obtained around 465nm with good intensity as a significance of ZrO₂ in the samples.

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REFERENCES