

Synthesis and Optical Properties of Rare earth doped Titania-Polyacrylicacid (TiO₂:RE/PAA) Nanocomposites

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Abstract:

Rare earth (RE) doped TiO₂ nanoparticles synthesized by hydrothermal method and RE doped TiO₂-Polyacrylicacid (PAA) nanocomposites were prepared by introducing hydrothermally synthesized TiO₂ to the acrylic acid (monomer) using heating as a conventional polymerization technique. The nanocomposites, thus synthesized had been characterized. X-ray Diffraction (XRD) and Fourier Transform Infrared (FTIR) spectroscopy confirmed the phase and elemental characterisation of TiO₂:RE nanoparticles. Ultraviolet-Visible (UV-Vis) spectroscopy and Photoluminescence (PL) spectroscopy were employed to study the optical properties of TiO₂:RE-PAA nanocomposites. Absorption spectra shows a well-defined peak in absorbance curve.

Keywords: nanocomposites; hydrothermal; optical property; polyacrylicacid (PAA); titania (TiO₂)

I. INTRODUCTION

A 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 titania 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. TiO₂ 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 thermomechanical resistance and high corrosion resistance. These unique properties of TiO₂ have led to their widespread applications in the fields of optical, structural materials, solid-state electrolytes, gas-sensing, thermal barriers coatings, corrosion-resistant, catalytic [5-8].

II. EXPERIMENTAL PART

i. Synthesis of RE doped TiO₂ nanoparticles:

RE (Ce, Dy, Eu, Pr, Tb, Yb) doped TiO₂ nanoparticles were prepared by hydrothermal method. 9.10 ml of titanium isopropoxide was diluted in 90 ml deionized water with stoichiometric amount of rare earth nitrates (0.1 mol%). The solution was stirred for 10 minutes at room temperature. Then it was transferred into stainless steel autoclave, kept in an oven at 200°C for 2 hours and left overnight. The precipitates TiO₂:RE were filtered by Whatmann filter paper, washed with DI water and ethanol many times and dried at room temperature. Dried material was calcined at 400°C for 4 hours in furnace. TiO₂:RE nanoparticles obtained after dried oxide material was powdered with mortar and pestle.

ii. Synthesis of TiO₂:RE-PAA nanocomposites:

Synthesized RE (Ce, Dy, Eu, Pr, Tb, Yb) doped TiO₂ nanoparticles incorporated with polyacrylicacid (PAA) to develop thin films of polyacrylicacid- TiO₂:RE nanocomposites [9]. 1.0 ml acrylicacid was diluted in 10 ml deionized water with (1 mol%) stoichiometric amount of hydrothermally synthesized TiO₂: RE nanoparticles. The solution was ultrasonicated for 20 minutes. Then it was stirred for 25 minutes at 70°C with addition of potassium persulfate (KPS) solution as an activator. The resulted solution was used to prepare thin films of PAA-TiO₂:RE nanocomposites by doctor blade method [10].

III. RESULTS AND DISCUSSION

i. X-ray Diffraction (XRD):

The XRD patterns were recorded on Bruker D8 Advance X-ray diffractometer in 2θ range of 20° to 80° at room temperature with a least count of 0.05°. The 2θ values are mentioned in degrees.

In order to investigate the crystallization process of titania, Fig. 1 shows XRD spectra of as-prepared powder samples. This figure indicates that anatase phase of titania was obtained. The distinguishing characteristic peaks occurred at 2θ values around 25, 38, 47, 54, 62, 70 and 75 degrees for (101), (004), (200), (105), (204), (220) and (301) reflections respectively in all the samples. This is very close to the values in the literature (JCPDS card no. 21-1272).

The crystallite size of the as-prepared $\text{TiO}_2\text{:RE}$ calculated with the Scherer formula and shown in Table 1. XRD results showed that the phase of RE doped TiO_2 nanoparticles was anatase.

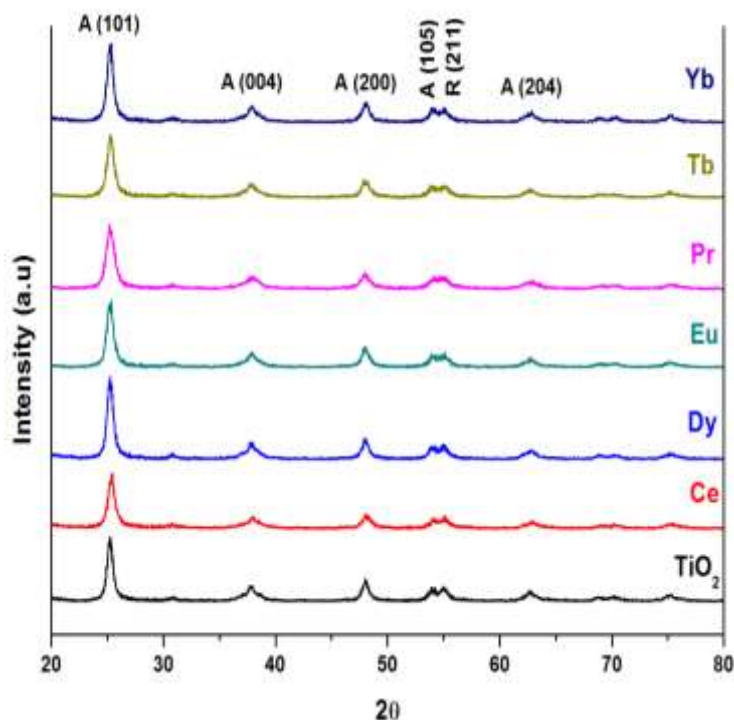


Fig. 1: XRD spectra of RE doped TiO_2 nanoparticles

Table 1: Crystallite size for prepared samples

Sample	Crystallite Size (nm)
TiO_2	7.80
Ce doped TiO_2	7.49
Dy doped TiO_2	7.95
Eu doped TiO_2	9.00
Pr doped TiO_2	6.86
Tb doped TiO_2	8.00
Yb doped TiO_2	8.84

ii. Fourier Transform Infrared (FTIR) Spectroscopy:

FTIR spectrographs were recorded by a Nicolet iS10 FTIR Spectrometer of Thermo Scientific in the wave number region between $400\text{--}4000\text{ cm}^{-1}$ studies the quality and occurrence of functional group in $\text{TiO}_2\text{:RE}$ -polyacrylicacid nanocomposites. Fig. 2 shows the FTIR spectrograph of $\text{TiO}_2\text{:RE}$ -polyacrylicacid nanocomposite. The presence of different functional groups with respective wavenumber is shown in Table 2.

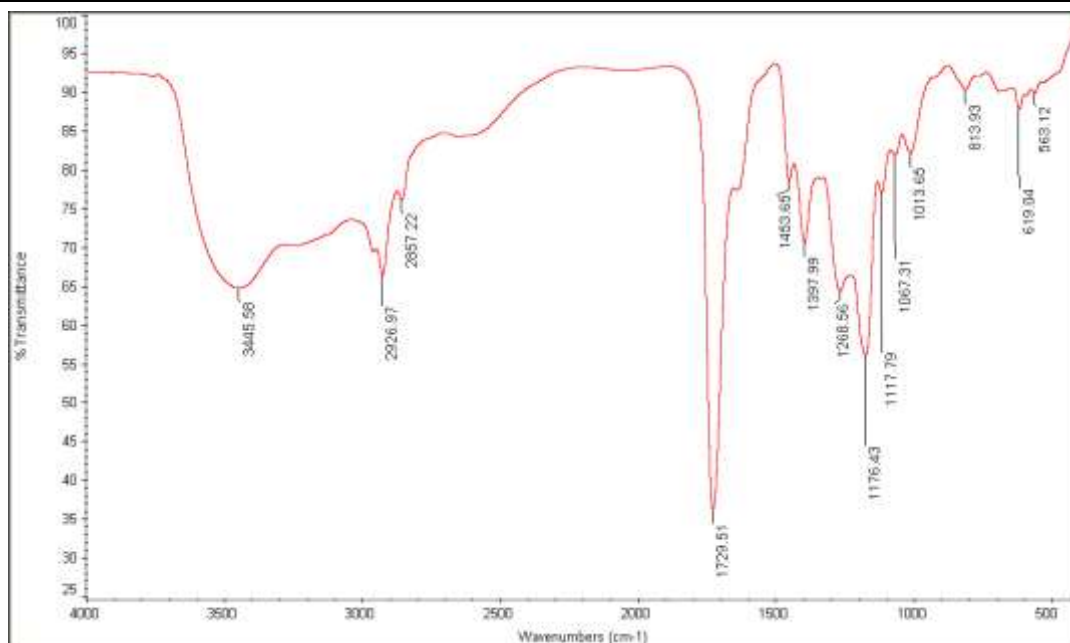
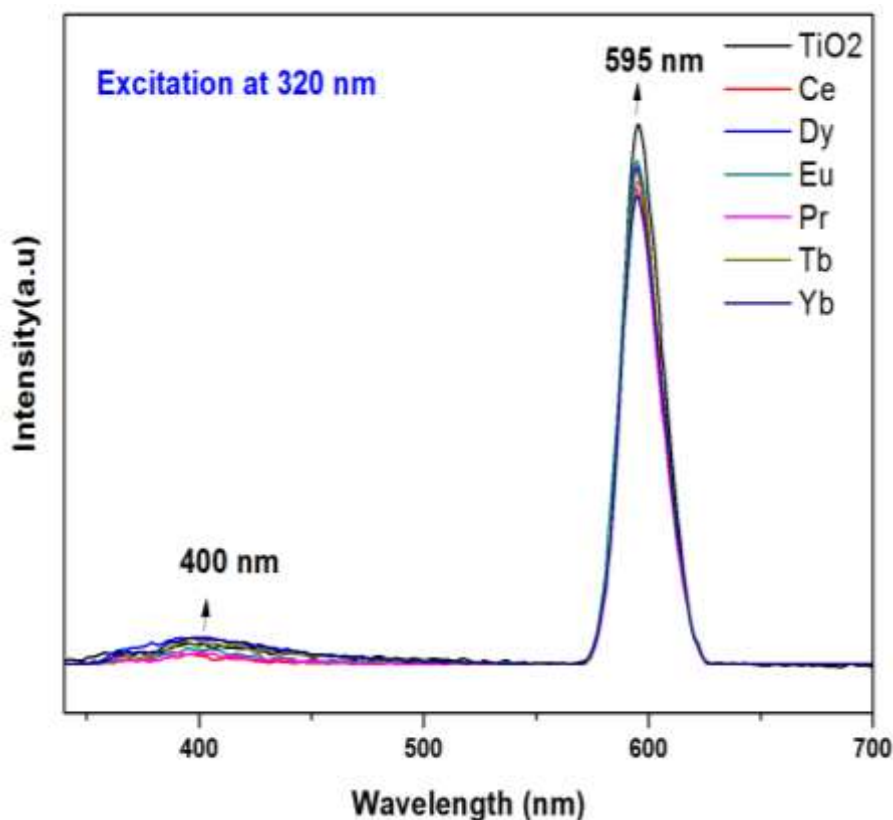
Fig. 2: FTIR spectra of PAA-TiO₂:RE nanocomposites

Table 2: Crystallite size for prepared samples

Wavenumber (cm ⁻¹)	Functional group
~3445	-OH stretching vibration of water associated with the oxide matrix.
~2925	C-H stretching mode of PAA
~2300	CO ₂ linearly adsorbed on the Ti ⁴⁺ ions
~1730	C=O stretching mode of carboxylic group in PAA [11]
~1640	-OH bending mode of hydroxyl groups present on the surface due to moisture
~1450	-COO ⁻ group of PAA [11]
~1400	CH ₂ bonding mode of PAA
~1400 and ~560	Ti-O stretching vibrations of TiO ₂ anatase phase [11]
~1270	Ti-O-Ti bending vibrations
~1170	-(C-O)H stretching mode of PAA [11]
~1060	C-CH ₂ stretching mode of PAA
~810	CH ₂ rocking mode of PAA
The strong peaks in the range 500 to 1500	Ti-O vibration modes [11]

iii. Photoluminescence (PL) Spectroscopy:

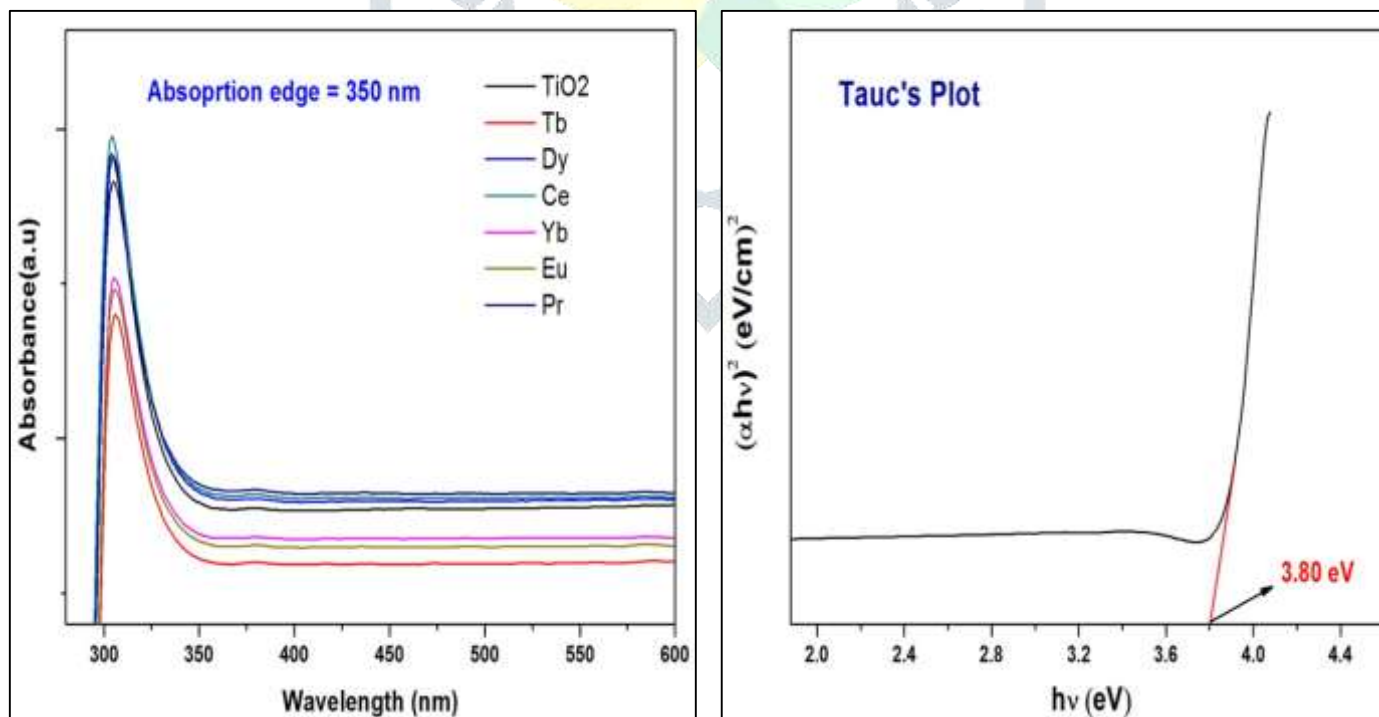
Photoluminescence spectra were obtained by Horiba Jobin Yvon make Fluoromax-4 Spectrofluorometer. Emission spectra for all the samples are shown in Fig. 3. The samples were excited at 320nm, all the samples shows emission at the same wavelength but intensity varies. Strong emission band at 595 nm is observed. the additional small emission peak was obtained around 400nm in all the samples of RE doped TiO₂-polyacrylicacid nanocomposites. This peak may be obtained due to interstellar defect created by RE doped TiO₂ in the polyacrylicacid film [12].

Fig. 3: PL spectra of PAA-TiO₂:RE nanocomposites

iv. 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 600nm. Fig. 4 shows the absorption spectra of RE doped TiO₂-polyacrylicacid nanocomposites and its respective Tauc's Plot. A well-defined peak is obtained around 310nm in the absorbance curve. Figure shows overlay of absorption spectra of all the samples. All the samples have same absorption edge at 350 nm. RE doping does not affect the absorption value. This might be attributed to lower doping concentration.

The optical bandgap was calculated using Tauc's Plot. The bandgap was found to be 3.80 eV. Which is higher than the bandgap of pure TiO₂. The mixing of PAA with TiO₂ could be the reason for higher bandgap value.

Fig. 4: UV-Visible spectra of PAA-TiO₂:RE nanocomposites and respective Tauc's Plot

IV. CONCLUSION

We have successfully synthesized RE doped TiO₂ nanoparticles by hydrothermal technique. Samples of RE doped TiO₂-polyacrylicacid nanocomposites were prepared. With the help of XRD the crystalline size of RE doped TiO₂ nanoparticles calculated with the Scherer formula was found below 10nm and the phase of RE doped TiO₂ nanoparticles were anatase. FTIR spectrographs shows all the expected

elemental groups present in the prepared nanocomposites. Photoluminescence spectra shows a sharp peak obtained around 595nm with good intensity as a significance of TiO₂ in the samples. UV-Vis spectroscopy revealed that a well-defined peak is obtained around 310nm in the absorbance curve. The bandgap was found to be 3.80 eV. Ultimately we got good optical enhancement of polyacrylic acid.

V. ACKNOWLEDGMENT

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