Synopsis of the Thesis entitled

Study of Optical Properties of Transition/RE Oxide- Polymer Nanocomposites

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by

Dhaval P. Hirani

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Dr. Bishwajit S. Chakrabarty

Applied Physics Department

Faculty of Technology & Engineering

The M. S. University of Baroda

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The background

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.

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. Because of their nanometer sizes, filler dispersion nanocomposites exhibit markedly improved properties when compared to the pure polymers or their traditional composites. There is increasing research interest in polymeric nanocomposites owing to improvements in electrical, thermal, optical, and mechanical properties and their great potential for highly functional materials (Geethu Krishnan, P.M., *et al*., 2014). Synthesis and optical properties of polyacrylicacid capped lanthanide-doped BaFCl nanocrystals were studied (Qiang Ju, Wenqin Luo, *et al*., 2010). In particular, nanoparticles embedded in a transparent matrix have attracted attention as advanced technological materials because of their high transparency, high refractive index, and attractive optoelectronic properties. High refractive index polymers have many applications ranging from antireflection coatings for solar cells to high RI lenses.

Acrylic acid undergoes the typical reactions of a carboxylic acid. When reacted with an alcohol, it forms the corresponding ester. The esters and salts of acrylic acid are collectively known as acrylates (or propenoates). The most common alkyl esters of acrylic acid are methyl, butyl, ethyl, and 2-ethylhexyl acrylate. Acrylic acid and its esters readily combine with themselves (to form polyacrylic acid) or other monomers (e.g. acrylamides, acrylonitrile, vinyl compounds, styrene, and butadiene) by reacting at their double bond, forming homopolymers or copolymers, which are used in the manufacture of various plastics, coatings, adhesives, membranes, packaging materials, elastomers, as well as floor polishes, metal polish, glass replacement and paints (Wasan Al-Taa'y, *et al.*, 2014). Acrylic acid is a compound, which is used in many industries like the diaper industry, the water treatment industry or the textiles industry. On a worldwide scale the consumption rate of acrylic acid is projected to reach more than an estimated 8,000 kilo tons, by 2020. This increase is expected to occur because of using this product in new applications, including personal care products, detergents and products that are used for adult incontinence.

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. Applied in various fields like light emitting displays, ceramic, glass replacement, paint, optical fibers, clothing, packaging, etc.

ZrO_2 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 ZrO_2 have led to their widespread applications in the fields of optical, structural materials, solid-state electrolytes, gas-sensing, thermal barriers coatings, corrosion-resistant, catalytic. ZrO_2 exists in three different polymorphs namely Monoclinic, Tetragonal and Cubic. At room temperature it remains in monoclinic phase. As temperature increases, it transforms into Tetragonal and then Cubic phase. It has been reported that ZrO_2 exhibits low phonon energy, increasing the number and probability of radiative transitions in the rare earth (RE)-doped samples. This fact has increased the interest in developing rare earth doped of zirconium oxide, which is suitable for making optical waveguides. Doping rare earth elements into zirconia results in structural modification, which influences the electronic structure of the lattice, thereby emerging a change in the optical properties. Hence, it is of interest to follow the spectroscopic consequences accompanying the structural modifications.

Titanium dioxide (TiO_2) is a wide band gap semiconducting material. TiO_2 is chemically inert, cheap and easy to synthesize. It is a naturally occurring mineral. TiO_2 exists in three different crystal structures namely Anatase, Rutile and Brookite. Among these, the Anatase and Rutile phase has major applications as they can be synthesized easily. The bandgap of material can be varied by either changing particle size or by adding impurities. Transition and rare earth metal ions shift the absorption edge towards visible region and increase photo reactivity of TiO_2 in the visible region.

Titanium dioxide (TiO_2) is an extensively used material for optical and protective applications because of its high transparency in the visible region, excellent mechanical durability and chemical stability in aqueous solution. TiO_2 films are valuable for such applications as catalysis, optical coatings, gas sensors, and other electronic devices. The physical and chemical properties of TiO_2 are such that it becomes suitable for a wide spectrum of applications. Two of the most important optical properties, namely the refractive index and the extinction coefficient are generally called optical constants. The amount of light that transmits through thin film material depends on the amount of the reflection and the absorption that take place along the light path. It has been used mostly as a pigment in paints, sunscreens, ointments, toothpaste etc. For instance, TiO_2 has high corrosion resistance and chemical stability and an excellent optical transparency in the visible and near infrared regions hence applicable in metal polish, replacement of glass and packaging. It also has high refractive index that makes it suitable for anti-reflection coatings in optical devices like solar cells and others.

Major objectives of the study are:

- To synthesize novel and relatively less investigated rare earth doped transition metal oxide- polyacrylicacid nanocomposites.
- To authenticate the preparation of material using standard characterization techniques.
- To study the optical properties such as fluorescence emission, absorption, optical bandgap, variation of absorption co-efficient, variation of extinction co-efficient, refractive index and variation of refractive index of the composites.
- To explore the material from application point of view.

Chapter 1: Introduction

The first chapter of the thesis deals with the introduction of rare earth doped transition metal oxide- polyacrylicacid nanocomposites. The chapter also gives details regarding the applications of synthesized nanocomposite materials and deals with the general properties of materials used for the study like polyacrylicacid (PAA), Titania (TiO_2), Zirconia (ZrO_2), rare earth elements.

Chapter 2: Instrumentation/ Characterization Techniques

The second chapter is on instrumentation. The chapter gives details of the various instrumentation techniques, like X-ray diffraction (XRD) and Fourier-Transform Infrared Spectroscopy (FTIR). The instrumentation techniques used for investigating the optical characteristics of synthesized nanocomposites like UV-Vis spectroscopy (UV-Vis) and Photoluminescence spectroscopy (PL) has been also discussed in the chapter.

Chapter 3: TiO_2:RE- Polyacrylicacid Nanocomposites

This chapter deals synthesis as well as characterization of nanocomposites. This chapter gives the process of synthesizing rare earth RE (Ce, Dy, Er, Eu, Pr, Tb, Tm) doped Titania (TiO_2) by hydrothermal technique with 0.1mol% & 2mol% doping concentration of rare earth elements. Fourteen such samples were synthesized and incorporated with polyacrylicacid (PAA) with 1mol% & 2mol% respectively to develop thin films of polyacrylicacid- TiO_2:RE nanocomposites by spin coating.

In order to investigate the crystalline phase of TiO_2:RE nanostructures, X-ray diffraction (XRD) studies were carried out. The XRD results of powder samples of TiO_2:RE confirm the presence of the material in anatase phase with high degree of crystallinity and match with JCPDS file no. 21 – 1272. Some peaks of RE dopants were also observed. The crystallite size calculated by Scherer's formula using XRD data puts the crystalline size in the order of nanometers (< 10nm).

The phase formation and purity of the TiO_2:RE-polyacrylicacid nanocomposites are further confirmed by FTIR spectroscopy. FT-IR studies the quality and occurrence of functional group in TiO_2:RE-polyacrylicacid nanocomposites.

Study of optical properties of TiO_2:RE-polyacrylicacid nanocomposites such as absorption, optical bandgap, variation of absorption co-efficient, variation of extinction co-efficient, refractive index and variation of refractive index carried out by UV-Vis spectroscopy. Initially the Tauc plot was made, which gives the band gap of the nanocomposites. High transparency and high refractive index has been observed.

To study of fluorescence emission of TiO_2:RE-polyacrylicacid nanocomposites photoluminescence (PL) spectroscopy was carried out. The emission spectra reflects quite good emission of TiO_2:RE-polyacrylicacid nanocomposites in comparison to pure polyacrylicacid in several samples.

Chapter 4: ZrO_2:RE- Polyacrylicacid Nanocomposites

The chapter describes the synthesis and characterization of Zirconia based composites. It gives the process of synthesizing rare earth RE (Ce, Dy, Er, Eu, Pr, Tb, Tm) doped Zirconia (ZrO_2) by hydrothermal technique with 0.1mol% & 2mol% doping concentration of rare earth elements. Fourteen such samples were synthesized and incorporated with polyacrylicacid (PAA) with 1mol% & 2mol% respectively to develop thin films of polyacrylicacid- ZrO_2:RE nanocomposites by spin coating.

In order to investigate the crystalline phase of ZrO_2:RE nanostructures, X-ray diffraction (XRD) studies were carried out. The XRD results of powder samples of ZrO_2:RE confirms that the samples have monoclinic structure with high degree of crystallinity and matching with JCPDS file no. 83–0944. One peak corresponding to plane (101) belongs to tetragonal structure with highest intensity matching with JCPDS file no. 79-1770. The tetragonal phase is not thermodynamically stable at room temperature, though it can be stabilized when doping ZrO_2 with the rare earths. Some peaks of RE were also observed. The crystallite size calculated by Scherer's formula using XRD data puts the crystalline size in the order of nanometers (< 10nm).

The phase formation and purity of the ZrO_2:RE-polyacrylicacid nanocomposites are further confirmed by FTIR spectroscopy. FT-IR studies further confirms the formation of pure ZrO_2 with no other impurities or secondary phases and studies the quality and occurrence of functional group in ZrO_2:RE-polyacrylicacid nanocomposites.

Study of optical properties of ZrO_2:RE-polyacrylicacid nanocomposites such as absorption, optical bandgap, variation of absorption co-efficient, variation of extinction co-efficient, refractive index and variation of refractive index carried out by UV-Vis spectroscopy. The Tauc plot gives the band gap of nanocomposites. High transparency and high refractive index has been observed.

To study of fluorescence emission of ZrO_2:RE-polyacrylicacid samples, photoluminescence (PL) spectroscopy was carried out. The emission spectra reflects quite good emission of ZrO_2:RE-polyacrylicacid nanocomposites in comparison to pure polyacrylicacid in several samples.

Chapter 5: Application

This chapter is devoted to investigate the potential applications of the synthesized nanocomposites. Exploration of the material from application point of view is discussed. As mentioned earlier, because of their high transparency, high refractive index, and attractive optical properties, polyacrycacid-rare earth doped transition metal oxide nanocomposites applied in various field like packaging, glass replacement and anti-reflection coatings in solar cells. The results of the optical studies are correlated to the applications.

Chapter 6: Summary and Future Scope

The final chapter concludes the work undertaken in the thesis and also future perspectives on different hybridization combinations. It also mentions some of the lacunae of the researcher’s study, its scope for future prospects.

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Publications:

[1] ***Synthesis And Optical Properties Of Zirconia (ZrO_2)-Polyacrylicacid (PAA) Nanocomposites*, Dhaval Hirani, Kevil Shah, B. S. Chakrabarty, (International Journal of Scientific & Technology Research (2019), Vol. 8, Issue 12, pp. 4001-4004).**

Seminars/Conferences/Workshops Attended:

- Attended a Conference on **"Innovation in Collegiate Science Education and Research"** organized at V.P. & R.P.T.P. Science College, Vallabh Vidyanagar on 8th January, 2011.
- Attended and gave Oral presentation on **"Study of Nanotechnology and its Applications"** in the meeting held at Gujarat Technological University, Ahmedabad for developing a centre for the study of nanotechnology and its applications on 11th February, 2011.
- Attended an International Symposium on **"Advanced Ceramics, Composites & Nano Structured Materials"** on 17-18 February, 2011 at Department of Material Science, S.P. University, Vallabh Vidyanagar.
- Attended the UGC sponsored **"National Conference on Recent Trends in Theoretical and Experimental Physics (NCRTTEP-2011)"** during 18-19 February, 2011 at V.P. & R.P.T.P. Science College, Vallabh Vidyanagar.
- Attended a Seminar on **"Wireless Communication & FPGA Debugging"** organized at Ele. Engg. Dept., Feculty of Tech. & Engg., The Maharaja Sayajirao University of Baroda, Vadodara on 18th August, 2011.

- Attended and Poster presented in the **"International Conference on Nanomaterials & Nanotechnology (ICNANO-2011)"** during 18-21 December, 2011 at University of Delhi, India.
- Attended and Poster presented in the **"International Symposium On Semiconductor Materials And Devices (ISSMD-3)"** during 2-5 February, 2015 at crystal growth centre, Anna University, Chennai.
- Attended and Poster presented in the national seminar on **"Recent Scenario in Science and Technology (RSST-2016)"** on 27th February, 2016 at Faculty of Technology and Engineering, The Maharaja Sayajirao University of Baroda, Vadodara.
- Attended and gave Oral presentation in "International Seminar on Luminescence and Materials (ISLM-2017)" during 16-17 July, 2017 at Nenyang Technological University, Singapore.

Research Student

(Dhaval Hirani)

Guide	Head	Dean
Dr. B.S.Chakrabarty Applied Physics Dept. The M.S. University Of Baroda	Dr. B.S. Chakrabarty Applied Physics Dert. The M.S. University Of Baroda	Prof. Arun Pratap Faculty of Tech. and Engg. The M.S. University Of Baroda