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Synthesis and Studies of PANI/Cerium dioxide Nanocomposites

E. Kumar[1,3], **P. Selvarajan**[2*]

[1]Department of Physics, Infant Jesus College of Engineering and Technology, Keela vallanadu, Tuticorin- 628851, Tamilnadu, India; [2]Department of Physics, Aditanar College of Arts and Science, Tiruchendur-628216, Tamil Nadu, India; [3]PRIST University, Thanjavur, - 613 403, Tamil Nadu, India

Abstract

Nanomaterials possess unique and interesting mechanical, optical, electrical, magnetic, thermal and other properties. These materials range from inorganic to organic, crystalline to amorphous, which can be found as single particles, aggregates, powders, nanowires, quantum dots, nanofilms, nanofibres, nanotubes. Nanocomposites are also possessing unique properties like pure nanomaterials. In this work, We report the synthesis of nanocomposite of polymer added cerium dioxide (CeO_2) by microwave-assisted solution method and it was fabricated via in situ polymerization of the monomer in the presence of cerium dioxide (ceria) nanoparticles. The as-synthesized ceria nanoparticles and PANI/ceria nanocomposite materials were subjected to various studies like XRD, SEM, FT-IR, TEM and UV-Visible Spectroscopic studies.

Keywords: Cerium dioxide; nanoparticles; microwave-assisted method; Characterization; XRD; SEM; FTIR; TG/DTA

Introduction

Conducting electro-active polymers have attracted considerable attention in recent years because of their potential applications in new technologies, such as electrochemical displays, sensors, catalysis, redox capacitors, antistatic coatings, electromagnetic shielding, optical, photoelectrical properties, and secondary batteries[1,2] and these polymers are usually used to prepare organic-inorganic hybrid materials due to their good stability and controllable thickness and they can be chemically bonded to inorganic materials by method of polysorption. This method is limited to inorganic materials that have active groups (such as hydroxyl group) on their surface. [3-5]. Among organic conducting polymers, polyaniline(PANI) has attracted intense interest because of its high conductivity, excellent stability and relatively high transparency to visible light. These properties make it one of the most applied conducting polymers [6]. For application in optoelectronics, normally the polymeric matrices are the most desirous as the film of the nanoparticles/polymer composite can be cast easily and thus offer direct use in devices. The re-dispersed nanoparticles when loaded in polymer by dissolution of the as-synthesized particles can not be guaranteed and this leads to difficulties in knowing the concentration of nanoparticles within the polymer. If the nanoparticles are synthesized in polymeric reaction medium, such issues can be tackled with much ease[7]. The use of polymers is a prominent method for the synthesis of nanoparticles. The reason for using the polymers to prepare nanocomposites is to control the growth and morphology of the nanoparticles. Inorganic nanoparticles stand for a class of new materials having promising applications in broad fields. To obtain the materials with synergetic or complementary behavior between polymer and inorganic nanoparticles, various composites of polymer with inorganic nanoparticles have been synthesized in recent years [8-13]. Among those inorganic nanoparticles, cerium dioxide (CeO_2) nanoparticles have been intensively studied due to their unique catalytic, electrical and optic properties, as well as their extensive applications in diverse areas [14-19]. A variety of methods based on wet chemical routes have been extensively employed to synthesize of ceria (CeO_2) nanoparticles like co-precipitation, hydrothermal, sol-gel method] microemulsion method and other methods[20-24]. In this work, polianiline(PANI) was mixed with cerium dioxide to prepare nanocomposite material by microwave-assisted solution method and the prepared pure ceria and PANI/ceria nanomaterials were characterized by various studies.

Experimental

Materials

The aniline (AR grade MERCK) was distilled twice under reduced pressure. Ammonium persulphate[$(NH_4)_2S_2O_8$] (Analytical regant, RANBAXY fine chemicals Limited, india), Hydrochloric acid (AR grade MERCK) and ammounium Ce(IV) nitrate, [$(NH_4)_2Ce(NO_3)_6$] (AR grade MERCK) and Sodium hydroxide [NaOH] (AR grade MERCK) were used to prepare the nanocomposites of this work. Water used in this investigation was de-ionized water.

Synthesis

Initially, Ceria (CeO_2) nanoparticles was prepared as follows: the precursors like ammounium Ce(IV) nitrate ($(NH_4)_2Ce(NO_3)_6$) and Sodium hydroxide (NaOH) were taken in 1:4 molar ratio and dissolved completely in de-ionized water. Here the pH value of the solution was adjusted to be 12. The mixture solution was stirred well using a magnetic stirrer for about 1 hour with a stirring rate of 1000 rpm. Then the prepared mixture solution was kept in the microwave oven (900 W, 2450 MHz., Onida, India) at a temperature of 50^0C for about for 30 minutes. When ammounium ceric nitrate is treated with sodium hydroxide, the hydrolysis process takes place and the products like sodium nitrate, ammonium hydroxide and cerium hydroxide are formed. During the reaction, one proton(H^+) is removed from cerium hydroxide due to polar nature of water and this leads to the formation of hydrated cerium dioxide. Synthesized pale-yellow precipitate was filtered and washed with de-ionized water twice. Annealing of the synthesized powder at 130 °C in air for 2 hours results in the formation of CeO_2 nanoparticles. The following chemical reaction takes place in the formation of ceria nanoparticles.

$y\ ((NH_4)_2Ce(NO_3)_6)\ +\ x\ (NaOH) \rightarrow x\ (NaOH)\ +\ y\ (NH_4OH)\ +\ CeO_2\ nH_2O\ +\ H_3O^+$

Polyaniline / CeO_2 nanocomposite was prepared as follows: 4.5 ml aniline was injected to 70 ml of 2 M HCl containing 2 g of CeO_2 nanoparticles under ultrasonic action to reduce the aggregation of nanoparticles. After 12 h, 4.5 g Ammonium Persulphate(APS) (dissolved in 20 ml de-ionized water) was dropped into solution with constant stirring for about 10 minutes. The polymerization was allowed to proceed for 3 h at 30^0 C. Reaction mixture was filtered under gravity, and washed with 2 M HCL and de-ionized water, afterwards dried at 90^0 C for 12 h in vacuum to obtain a fine tint green powder.

Instrumentation

Powder X-ray diffraction pattern of the nanoparticles was obtained using a powder X-ray diffractometer (PANalytical Model, Nickel filtered Cu K_α radiations with $\lambda = 1.54056$ Å at 35 KV, 10 mA). The sample was scanned over the required range for 2Θ values(10-70°). The powder XRD pattern of the sample was recorded at RRL, Trivandrum. The FTIR spectrum of the sample was recorded at M.K.University, Madurai using a Shimadzu 8400S spectrometer by the KBr pellet technique in the range 400-4500 cm^{-1}. The optical spectra of nanocomposites have been recorded in the region 190-1100 nm using a Perkin Elmer (Model:Lambda 35) UV-vis-NIR spectrometer at M.K.University, Madurai. The SEM image of the synthesized cerium dioxide nanoparticles was recorded using a Hitachi Scanning Electron Microscope at IIT, Chennai. The size and shape of nanoparticles were obtained by transmission electron microscopy (TEM). TEM measurements were carried out on a HITACHI H-7500 TEM. Sample for TEM was prepared on 300 mesh

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* Corresponding Author, Email: pselvarajanphy@yahoo.co.in

copper grid coated with carbon. A drop of the nanoparticle solution was carefully placed on the copper grid surface and dried. The size distribution of the particles was measured from enlarged photograph of the TEM image.

Results and Discussiosn

X-ray diffraction (XRD) studies

The powder XRD pattern for the as-prepared pure CeO_2 nanoparticles is presented in the figure 1. It is observed that the XRD reflection peaks for pure CeO_2 sample are in a perfect match with the diffraction pattern of CeO_2 published in the (JCPDS File No. 34-0394). All the reflections of powder XRD patterns of this work were indexed using the TREOR and INDEXINg software packages. The lattice parameters from powder XRD data were found using the UNITCELL software package and the obtained values were found to be a = b=c= 5.416 Å, □□□□□□ 90^o. Thus phase of CeO_2 was observed to be cubic. The powder XRD pattern of CeO_2 nanoparticles shows broad peaks, which confirmed the formation of small-sized nanoparticles. The particle size of nanoparticles was determined using the Scherrer's relation d= $(0.9\lambda)/(\beta\cos\theta)$ where β is the full width at half maximum in radians, λ is the wavelength of X-rays used and θ is the Bragg's angle[25]. For the various reflection peaks of the XRD pattern, the particle size was estimated and the average size of nanoparticles of the sample was found to be around 27 nm. The figure 2 shows the powder XRD pattern for PANI/CeO_2 nanocomposite and this figure contains the reflection peaks belonging to both CeO_2 and PANI. The XRD line diagram in the figure 2 belongs to polyaniline(PANI) and it is noticed that the reflection peaks of PANI are overlapped with the XRD pattern of CeO_2.

Fig.1: The powder XRD pattern for pure CeO_2 nanoparticles

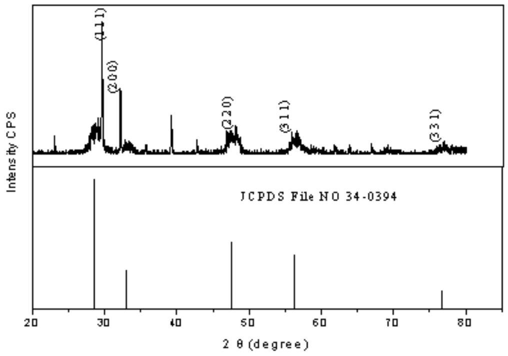
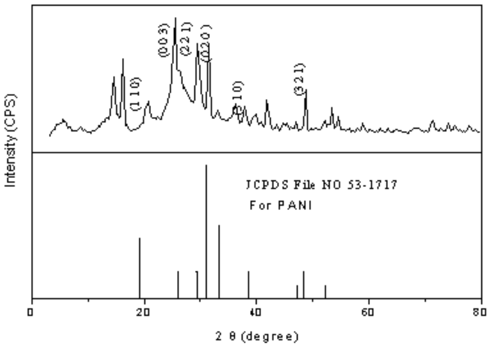


Fig.2: The powder XRD pattern for PANI/CeO_2 nanocompostie



Fourier Transform Infrared (FTIR) spectral studies

The Infrared spectroscopy is effectively used to identify the functional groups of the synthesized compounds. The FT-IR spectra of the samples were recorded using Shimadzu 8400S spectrometer by KBr pellet technique. The figure 3 shows the absorption peaks/bands in the FTIR spectrum of CeO_2 nanoparticles. The broad absorption band located around 3400 cm^{-1} corresponds to the O–H stretching vibration of residual water and hydroxyl groups, while the absorption band at 1630 cm^{-1} is due to the scissor bending mode of associated water. The complex bands observed at about 1518, 1350 , 1053 cm^{-1} are due to unwanted residues in the sample. The band at 848 cm^{-1} corresponds to metal–oxygen bond. The figure 4 presents the FTIR spectrum for PANI/CeO_2 nanocomposite. In this figure, it is observed that there are no peaks belonging to residual water and hydroxyl groups as in the FTIR spectrum of pure CeO_2 nanoparticles. The peaks/bands at 1475, 1280, 1202, 725, 633 and 499 cm^{-1} are corresponding to the functional groups of polyaniline(PANI) and the peak at 840 cm^{-1} belongs to metal-oxygen bond. The peaks/bands of FTIR spectra are given assignments in accordance with the data reported in the literature[26].

Fig.3: FTIR spectrum of pure CeO_2 nanoparticles

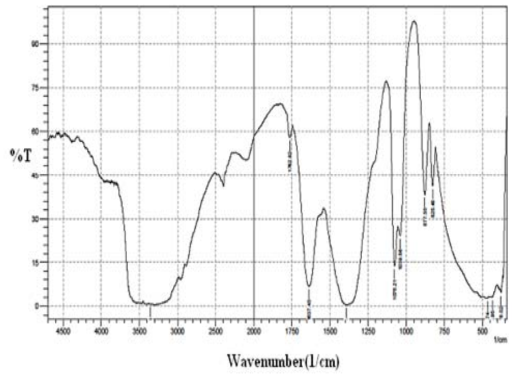
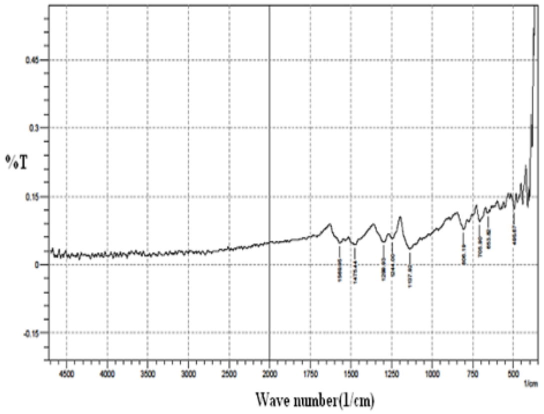


Fig.4: FTIR spectrum of PANI/CeO_2 nanocompostie



SEM and TEM studies

The morphology and size of nanoparticles are found using a Scanning Electron Microscope(SEM) and Transmission Electron Microscope(TEM). The SEM images of the as-prepared cerium dioxide and PANI/CeO_2 nanosamples are shown in the figures 5 and 6. From the figure 5, it is noticed that most of particles are spherical, flower-like and some are elongated in shape and these particles are observed to be agglomerated. The figure 6 shows impregnation of PANI in the CeO_2 material. It is observed that some grains are spherical and some are irregular shapes and they are agglomerated. The morphology and distribution of CeO_2 nanoparticles in the Polyaniline nanocomposite were also investigated using TEM. The figures 7 and 8 show the TEM images of pure CeO_2 and polyaniline/CeO_2 nanosamples. It is observed that the CeO_2 nanoparticles are spherical in shape and they are varying in size (Fig.7). The figure 8 clearly shows that CeO_2 nanoparticles are loosely distributed and impregnated within the polyaniline medium.

Fig.5: SEM image for pure CeO_2 nanoparticles

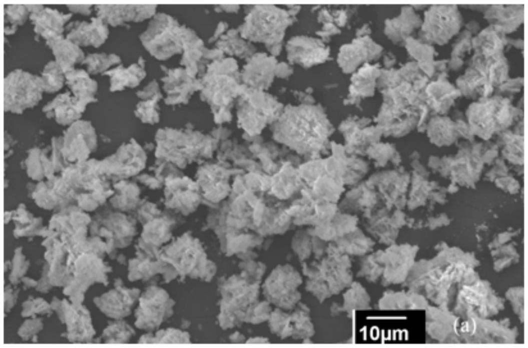


Fig.6: SEM image for PANI/CeO_2 nanocompostie

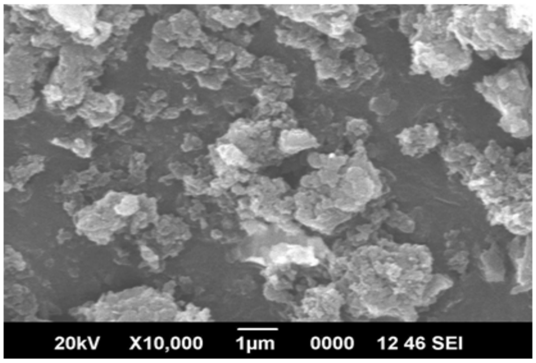


Fig.7: TEM image of CeO_2 nanoparticles

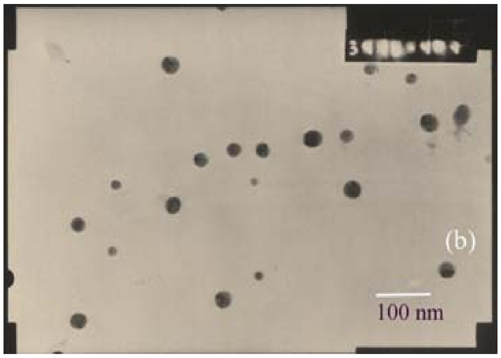
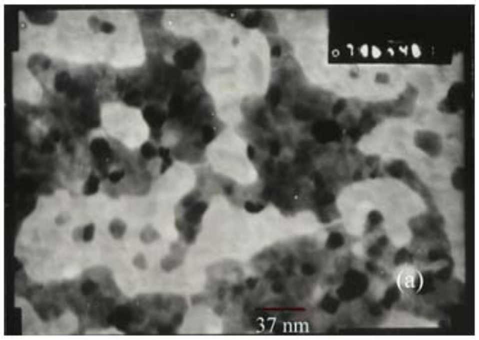


Fig.8: TEM image of polyaniline/CeO_2 nanocomposite



UV-visible absorption studies

UV-visible absorption spectral study may be assisted in understanding electronic structure of the optical band gap of the material. Absorption in the near ultraviolet region arises from electronic transitions associated within the sample. UV–visible absorption spectra of pure cerium dioxide nanoparticles and polyaniline/CeO_2 nanocomposite dispersed in ethanol solution were recorded and they are presented in the figures 9 and 10. The spectrum in the figure 9 shows a strong absorption band in the UV region due to the charge transfer transitions between the energy states. In the wavelength range 700-500 nm, no absorption was detected. The broadness of the absorption shoulder in UV region is attributed to the self-assembly of the nanoparticles and this is confirmed from SEM study. In the figure 10, the absorption peak around 845 nm is due to the presence of polyaniline in the nanocomposite sample. As the size of semiconductor particles decreases to the nanoscale, the band gap of the semiconductor increases, causing a blue shift in the UV–visible absorption spectra. When CeO_2 nanoparticles are impregnated in polyaniline(PANI) medium, it is observed that the peak at 320 nm in fig. 10 is blue shifted compared to the shoulder peak in the figure 9.

Fig. 9: UV-visible absorption spectrum for CeO_2 nanoparticles

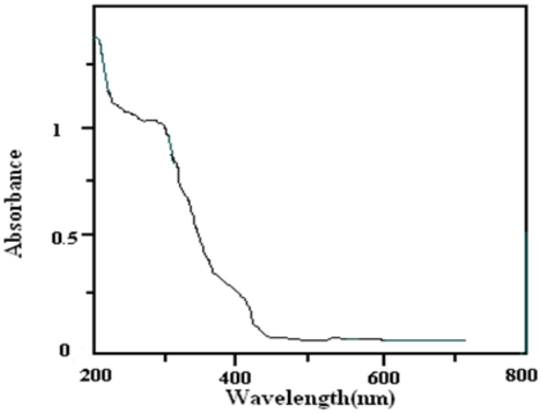
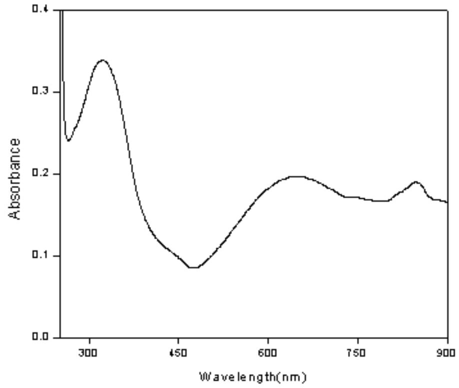


Fig. 10: UV-visible absorption spectrum for PANI/CeO_2 nanocomposite



Conclusion

The nanomaterials like pure CeO_2 nanoparticles and PANI/CeO_2 nanocomposites have been synthesized by microwave-assisted solution method and they were characterized by various studies. X-ray diffraction (XRD) patterns showed that the obtained CeO_2 nanoparticles were of cubic phase. The blue-shift phenomenon of the UV absorption threshold has been found and this is attributable to the size quantization effect. The morphology of the synthesized particles were found by SEM and TEM studies. The functional groups of the samples were identified from FTIR spectra. The synthesized PANI/CeO_2 nanocomposites can be used for fabrication of films or coatings, or even in further polymer blending.

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