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Nanocomposite Materials

Elixir Nanocomposite Materials 59 (2013) 15919-15922

ISSN: 2229-712X

Synthesis and Characterization of TiO_2 Nanopowders and TiO_2 -SiO_2 Nanocomposite by Sol-Gel technique

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ARTICLE INFO

Article history:

Received: 21 April 2013;

Received in revised form: 12 June 2013;

Accepted: 22 June 2013;

Keywords

Synthesis,

Sol- Gel Route,

Nano Composite,

XRD, TEM.

ABSTRACT

TiO_2 and TiO_2-SiO_2 nanocomposite was synthesized by sol-gel method at room temperature using titanium tetraisopropoxide with ethanol and water mixture as Titania source and Silicic acid as Silica source. Characterization of the product was carried out by means of X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive Spectrometry (EDS), Transmission Electron Microscopy (TEM) and Fourier Transform Infrared (FT-IR). An average grain size of ~13nm was obtained for TiO_2 and ~2nm for TiO_2-SiO_2, as estimated by the Debye-Scherrer's equation. From the FTIR results, peaks were observed at 3408 cm^{-1} and 1627 cm^{-1} in both samples due to stretching and bending vibrations of -OH groups.

1. Introduction

Nanostructure materials show lots of promise due primarily to the new and wide spectrum of properties exhibited by them. These are strikingly different from their bulk counterparts [1-6]. Titanium-di-oxide is one of the most attracted materials in Nanoscience and technology because of having a lot of interesting properties from fundamental and practical fact of view [7]. Although many striking results have been succeeded when using nano TiO_2 in the photo catalytic degradation of contaminated compounds or in the photo electrochemical solar-cell fabrication, efforts of scientists to improve performances of this material continuously increase day by day [8]. TiO_2-SiO_2 nanocomposites are very promising in field of heterogeneous photocatalysis, since they could provide simultaneously enhanced photocatalytic and thermal properties compared to pure TiO_2 photocatalyst [9-12]. It has been reported that photocatalytic reactivity of TiO2-SiO2 nanocomposites is highly dependent on the Ti/Si ratios [13-15].

The experimental conditions used in the preparation of these materials play an important role in the particle size of the product. For this reason, a great variety of experimental methods have been used in the production of nanoparticles, such as the hydrothermal method [16], sol–gel technique [17-19] Etc., Sol–gel techniques are among the simplest ones and are much utilized nowadays [20]. In this work, we report novel sol-gel method to synthesis nano sized TiO_2 and TiO_2-SiO_2 Nano composites at room temperature and the obtained powder was analyzed for Grain size by XRD, Surface morphology by SEM, Particle size by TEM, Chemical composition by Energy Dispersive Spectrometry (EDS) and Metal oxide bonds by FTIR.

2. Experimental

2.1 Reagents and Chemicals

The chemicals used in this study were titanium tetraisopropoxide (Ti (O*i*Pr) 4) as titania source, Silicic acid (SiO_2xH_2O) , Tetrahydrofuran (C_4H_8O) as silica source, Nitric acid (HNO_3), anhydrous ethanol (C_2H_5OH) from Merck. Analytical grade reagents were used without further purification.

2.2 Sample Preparation

All the reagents used were of analytical grade and no further purification was done before use. TiO_2 nanopowders were prepared via sol–gel method using titanium tetraisopropoxide (Ti(OiPr)4, sigmal Aldrich), distilled water, and ethyl alcohol (EtOH, Merck) as the starting materials. The sol-gel synthesized TiO_2 was obtained from Titanium tetraisopropoxide was dissolved in absolute ethanol and distilled water was added to the solution in terms of a molar ratio of TTIP: H_2O=1:4. Sodium hydroxide (NaOH) was used to adjust the pH in the range of 10 and for restrain the hydrolysis process of the solution. The obtained solutions were kept under slow-speed constant stirring on a magnetic stirrer for 40 minutes at room temperature. In order to obtain nanoparticles, the gels were dried under 50^{o}C for 1.5 hours to evaporate water and organic material to the maximum extent.

Silica particles were prepared from silicic acid and were stirred with THF for 30 minutes. Then titania gel was slowly added to the silica particles. The mixture was stirred for 2 hours and dried at room temperature. Finally the mixture was heated at 400^{o}C for 1 hour.

2.3 Characterization

Phase identification of the products was carried out by X-ray diffraction (XRD) obtained on Bruker AXS, Germany, at room temperature, operating at 30 kV and 30 mA, using Cu$K\alpha$ radiation (λ = 0.15406 nm). The crystallite size of the samples was determined by Scherrer's equation [21]. Spectroscopic Analysis of the nanocomposite was performed using a Fourier Transform Infrared (FT-IR) AVATAR 370-IR spectrometer (Thermo Nicolet, USA) with a wave number range of 4000 to 400 cm^{-1}, The morphology of the products was studied by Transmission Electron Microscopy (TEM**,** Technai G2 Spirit Twin 120 KV, Netherland).

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3. Results and Discussion

3.1 X-Ray Diffraction (XRD)

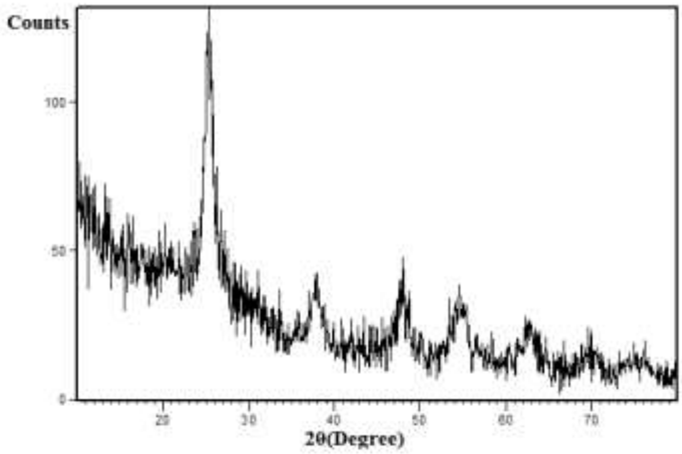

Fig.3.1: (a) XRD patterns of Nano TiO_2

The XRD patterns of the nanoparticles were obtained by sol-gel route as shown in Fig. 3.1.(a) The sample at 50 ºC were largely amorphous. XRD patterns of TiO_2 powders calcinated at 400ºC are shown .Calcination is a common treatment used to improve the crystallinity of TiO_2 powders [22]. It can be obviously seen from fig.3.1 (a) the phase transformation from amorphous to anatase occurred at about 400ºC.Then distinct peaks were noted in the XRD patterns at 25.29°. The peak locations and relative intensities for TiO_2 are cited from the Joint Committee on Powder Diffraction Standards (JCPDS) database.

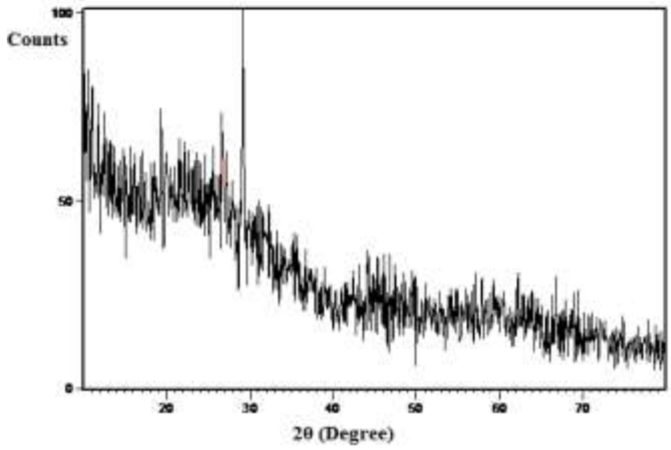

Fig.3.1: (b) XRD patterns of Nano TiO_2-SiO_2

Fig.3.1 (b) shows the XRD patterns of sol-gel derived Nano TiO_2-SiO_2 composite. The crystalline size of Nano composite particles was pure anatase. The most intense reflection at 2θ = 29.16^o is assigned to anatase. Not much dissimilarity has been identified between patterns of TiO_2 and TiO_2–SiO_2. The observed d-spacing value match the reported values for the anatase phase. The intensity of reflections seemed to be decreased for Nano composite as associated to TiO_2 due to presence of amorphous SiO_2.Crystalline size was obtained by Debye-Scherrer's formula given by equation

D=Kλ/ (βcosθ)

Where D is the crystal size, λ is the wavelength of the X-ray radiation (λ=0.15406 nm) for CuKα, K is usually taken as 0.89 and β is the line width at half-maximum height [23]. Where λ is the Cu Kα radiation wavelength and Δ(2θ) is peak width at half-height. The grain sizes were found to be ~13nm for TiO_2 while ~2nm for TiO_2–SiO_2 powders. The weakening and broadening of the XRD peaks may be attributed to the decrease of the sample grain size and the increase of the SiO_2 content. Addition of SiO_2 can meritoriously quash the grain growth of anatase compared with pure TiO_2. Moreover, the dominance is more remarkable with the addition of silica.

3.2 Fourier Transform Infrared Spectroscopy (FT-IR)

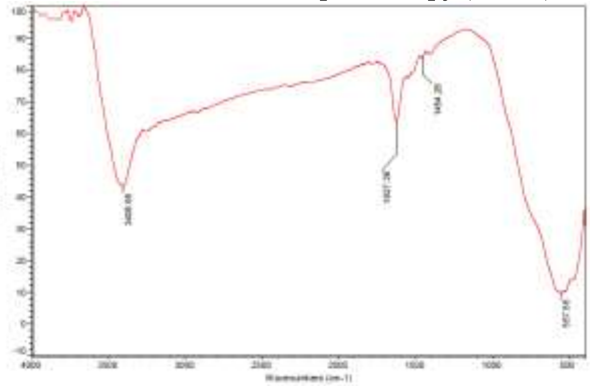

Fig.3.2: FT-IR spectrum of the as-synthesized TiO_2/SiO_2 nanocomposite

FT-IR spectrum of the synthesized composite has three characteristic bands that appeared at around 1627, 1454, and 557 cm−1. The bands at around 557 and 1627 cm^{-1} is representative of TiO_2 and SiO_2 matrixes in nanocomposite. The band at around 1454 cm^{-1} has been consigned to the stretching of the Si-O− species of Si-O-Ti or Si-O defect sites which are formed by the inclusion of Ti^{4+} ions into the SiO_2 matrixes. Thus, the appearance of the band at around 1454 cm^{-1} indicates that the TiO_2 species are embedded into SiO_2 matrixes within TiO_2-SiO_2 nanocomposite. The broad peak seeming at 3408 – 3600 cm^{-1} is dispersed to the fundamental stretching vibration of hydroxyl groups.

3.3 Scanning Electron Microscopy (SEM)

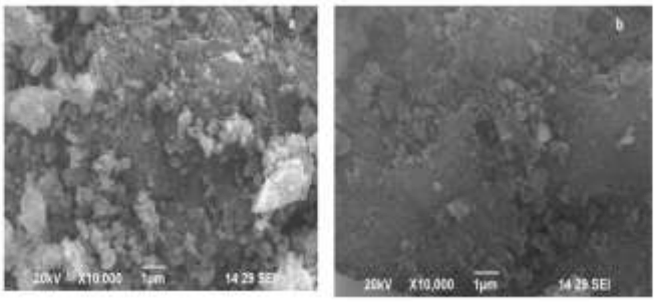

Fig.3.3: SEM Morphology of (a) TiO2 Nano powder (b) TiO_2-SiO_2 Nanocomposite.

The morphology of calcinated nano powders observed by SEM image is shown in fig.3.3 (a) & (b). Surface morphological studies obtained from SEM micrographs showed that the particles with the spherical shapes for TiO_2 nano powder and agglomeration take place due to addition of SiO_2. The Crystalline size of prepared Nano powders was found to be ~13nm for TiO_2 and ~2nm for nanocomposite.

3.4 Transmission Electron Microscopy (TEM)

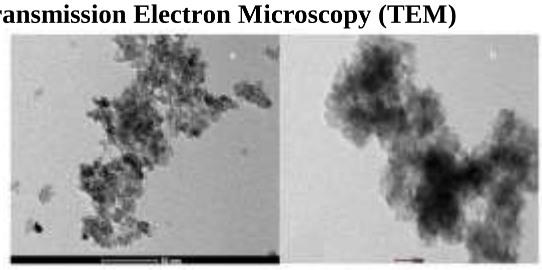

Fig.3.4: TEM Morphology of (a) TiO2 Nano powder (b) TiO_2-SiO_2 Nanocomposite

Fig.3.4 (a) & (b) shows that TEM image of TiO_2 and TiO_2-SiO_2 nanocomposite. It can be observed that the TiO_2 nano powders with the average particle sizes in the range of 13nm and 2nm for TiO_2-SiO_2 nanocomposite. Doping of SiO_2 into TiO_2 could effectively retard the growth of nanoparticles and thus reduce the particle size. This is approximately in conformity to XRD result.

3.5 Energy Dispersive Spectrometry (EDS)

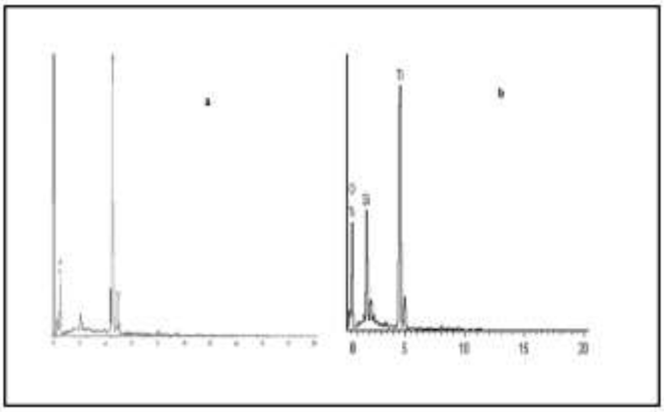

Fig.3.5: EDS of (a) TiO_2 Nano powder (b) TiO_2-SiO_2 Nanocomposite

The Energy Dispersive Spectrometry studies shows the chemical compositions. Fig.3.5 (a) & (b) which indicates the presence of Ti-O and Ti-Si-O.It is supportive study for a Fourier Transform Infrared (FT-IR).

Conclusions

In Summary, TiO_2 nano powders and TiO_2-SiO_2 nanocomposite was prepared by sol-gel route at room temperature. Formation of the Ti-O-Si bond and amorphous SiO_2 in nanocomposite could effectively increase the stability of anatase TiO_2, limits the growth of grain size and escalation the surface area. Surface morphological studies obtain from SEM micrographs showed that the particles with the spherical shapes are anatase in nature and agglomeration take place due to addition of SiO_2. The crystalline sizes were found to be 13nm for TiO_2 while 2nm for nano composite powders. From the FT-IR spectra, all the peaks observed were around 3408 $cm^{-1}$and 1627 cm^{-1} in both samples due to stretching and bending vibrations of -OH groups.

Acknowledgements

The author's thanks the center for Nanoscience and Technology, Tamilnadu Agriculture University, Coimbatore and Karunya University, Tamilnadu, India for use of their characterization facilities.

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Author's Short Biography

Kavitha T is a research Scholar in Nehru Memorial College. She obtained her M.Sc. (Physics) from Nehru Memorial College and she has published papers in various prestigious journals. She has presented several papers in the proceedings of the national and international conferences in the field of Nanomaterials, Thin Films and solar cell.

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