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Synthesis of TiO_2 Nanoparticles by Ultrasonic Assisted Sol-Gel Method

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Abstract: **N**anoparticles of titania (TiO_2) were synthesized by sol-gel method under the assistance of ultrsonication. The structural and morphological studies were carried out for the sample using X-ray diffraction (XRD) and Field emission scanning microscopic image (FESEM) respectively. The optical properties were determined by UV-Vis absorbance and Photoluminescence (PL) spectroscopes. The XRD pattern shows the anatase TiO_2 structure and crystallite size around 25 nm. The FESEM image shows the particle nature of the synthesized TiO_2. The purity of the sample was verified by EDAX spectrum. The synthesized TiO_2 has the wide band gap of energy 3.12 eV.
Keywords: Titania, titanium dioxide, nanopartcicles, nanocrystals, sol-gel, ultrasonication.

Introduction

In the last century, titanium dioxide has been widely used as pigment[1], in sunscreens[2], paints[3], ointments, toothpaste[4], etc. Now it has been used as photocatalyst in splitting of water under ultra violet radiation[5]. Integration of nanostructured TiO_2 materials in the photo voltaic cells can open up the possibilities of developing low cost solar cells[6]. TiO_2 in the anatase form appears to be the most photoactive and stable material under UV radiation. By doping or sensitization, it is possible to improve the photoactivity of TiO_2 nanomaterials in the visible region[7]. Nanosized TiO_2 has been synthesized by sol-gel[8], reverse micelle[9], solvothermal[10], hydrothermal[11], microwave radiation[12], sonochemical[13], Anodizing[14], CVD[15] and PVD[16] methods. Sol-gel method is a simple process that allows us to get different structural and shape which can be obtained by varying precursor concentration, pH, temperature, sol-gel formation time and aging time[17]. Sug-moto et al. have formed TiO_2 nanoparticles of different sizes and shapes by tuning reaction parameters using the sol-gel method[18]. In this work, TiO_2 nanocrystal was prepared by sol-gel method under ultrasonication. Sonication improves the quality of the TiO_2 nanoparticle compared to the conventional method and reduces the time of making the nanocrystal[19]. The structural, morphological and optical properties of the TiO_2 nanoparticles were studied and discussed.

Materials and method

Titanium (IV) isopropoxide $Ti(OC_3H_7)$ (Aldrich, 97%), acetone (Merck, GR), isopropyl alcohol (IPA) (Merck, GR), ethanol (Merck , GR), and ammonia liquid (Merck, 25% GR) were used. The 18.2 ohm cm (Millipore Direct-Q3 UV) purified water was used in the synthesis.

IPA and water mixture (1:1) of 40 ml solution was prepared in a 100 ml beaker. Sol-gel was prepared by drop wise addition of 15 ml of Titanium (IV) isopropoxide in the solution under sonication for 10 minute. 5 ml of liquid ammonia was added drop by drop in the sol-gel solution under sonication for 30 minute and the pH was measured as 9. The precipitated Titanium hydroxide $Ti(OH)_4$ was allowed for 24 h aging which remove any particulates. The precipitate was washed 5 times by ethanol and acetone to remove the organic components. It was dried in oven at 373 K for 5 h to remove the solvent. Titanium oxide was obtained by the calcination of $Ti(OH)_4$ for 3 h at 500°C.

The synthesized TiO_2 nanoparticles was characterized by a X-ray Diffractometer RAYOS-X with monochromatic $CuK_\propto$ (λ=1.5406 Å) radiation and taken over the 2θ range 10° – 80° by step scanning with a step size of 0.05°. The UV-Vis absorption spectrum of the sample was recorded in the range 200-800 nm, employing a double beam Varian Cary 5E spectrometer. The photoluminance study was done on the TiO_2 nanopowder using Jobin Yvong flurolog-3-11 spectroflurometer. Field Emission Scanning Electron Microscope (FESEM) image of TiO_2 nanocrystals was obtained from (SUPRA 55)-CARL ZEISS FESEM.

Result and discussion

The X-ray diffraction pattern of the synthesized TiO_2 nanopowder which has the planes (1 0 1), (0 0 4), (2 0 0), (2 1 1), (2 0 4), (2 2 0) and (2 1 5) corresponding to the angles 2θ in the Fig. 1 indicates the anatase structure of TiO_2 (JCPDS 73-1764). The average crystallite size was calculated as 25 nm using Sherrer's formula[20]. The FESEM image of the prepared sample in the Fig. 2 has the particle nature and its average size was around 25 nm and some particles have the size around 40 nm that is due to the two different sides of the tetragonal phase. The EDAX spectrum in the Fig. 3 shows the purity of the TiO_2.

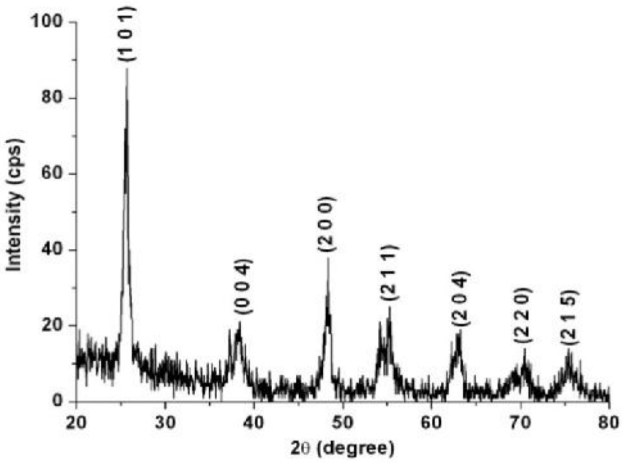

Fig. 1 XRD pattern of TiO_2 nanoparticles

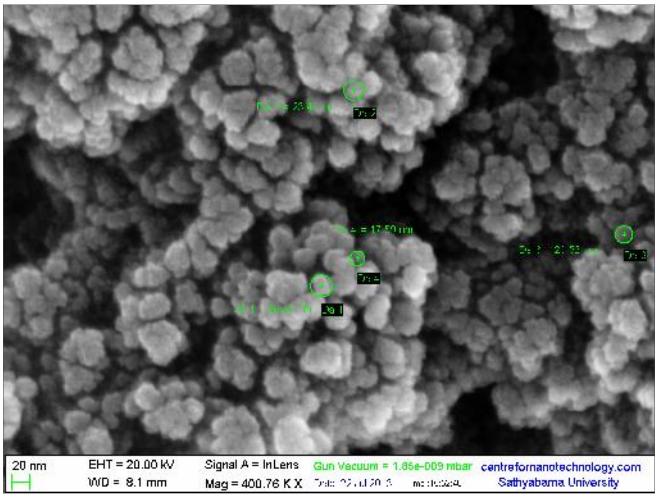

Fig. 2 FESEM image of TiO_2 nanoparticles

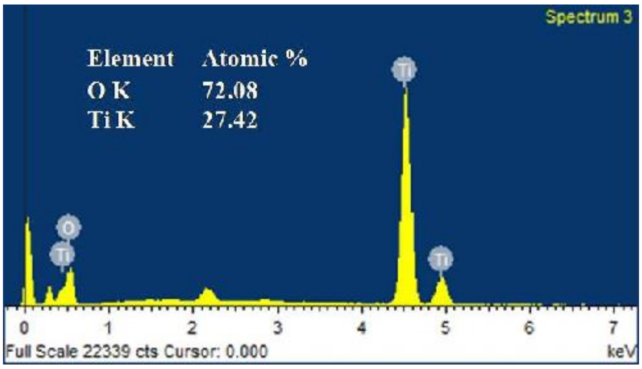

Fig. 3 EDAX image of TiO_2 nanoparticles

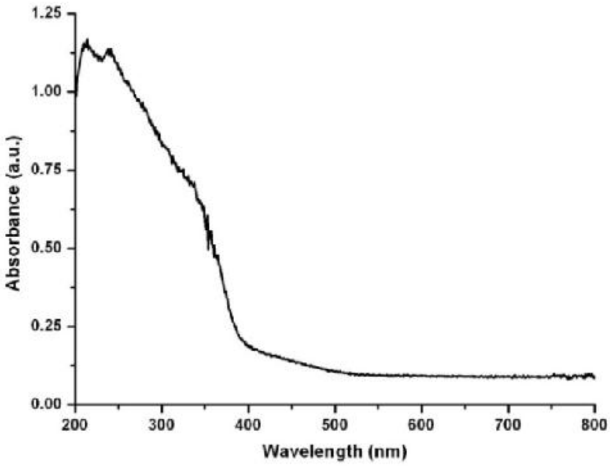

Fig. 4 UV-Vis absorption spectra of TiO_2 nanocrystals

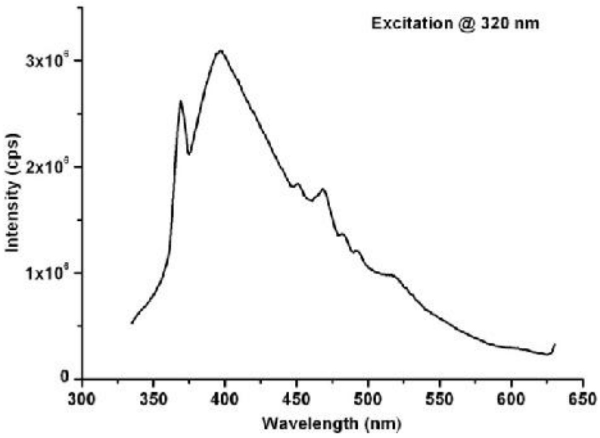

Fig. 5 PL spectra of TiO_2 nanocrystals

The absorption spectrum in the Fig. 4 shows the prepared TiO_2 has the absorption in the ultra violet region and first excitation maximum was absorbed at the wave length 338 nm. The photoluminescence emission spectra of TiO_2 in the fig. 5 shows the luminescence maximum at the wavelength 397 nm for the excitation wavelength 320 nm. The band gap energy of the synthesized TiO_2 nanopatricles is 3.12 eV which is corresponding to the wavelength of the photoluminescence emission maximum 397 nm.

In the synthesis the sol was formed from the hydrolysis of $Ti(OC_3H_7)$ in the IPA water mixture and loss of solvent lead to the polymerization that produced gel. Both the processes were accelerated by ultrasonication. The mixed oxide gel was produced by increasing the pH by drop wise addition of ammonia solution. Sonication produces acoustic cavitations that reduces the viscosity and increases the dispersibility which induce hydrolysis process and condensation to form gel. It also favors for the formation well dispersed nanoparticles and reduce the synthesis time. The aging process could promote the formation of anatase TiO_2[6]. The formation of $Ti(OH)_4$ is favored with high hydrolysis rates for medium amount of water. A prolonged heating time below 373 K for the as prepared gel can be used to avoid the agglomeration of the TiO_2 nanoparticle during the crystallization process[17]. During the calcinations process $Ti(OH)_4$ was converted into anatase TiO_2 nanocrystals.

Conclusion

The anatase form of nano structured pure TiO_2 particles were synthesized by ultrasonic assisted sol-gel method from hydrolysis of a titanium precursor Titanium (IV) isopropoxide. The time to form sol-gel was reduced by ultrasonication. From the XRD and FESEM image the nanocrystal structure, size and surface morphology were discussed. Optical properties show the prepared material has the wide band gap of TiO_2 as 3.12 eV. The surface area and pore size of the TiO_2 particles were determined.

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