International Journal of Latest Research in Engineering and Technology (IJLRET)
ISSN: 2454-5031
www.ijlret.com ǁ PP.39-42

Surfactant free solvothermal synthesis of TiO_2 nanococoons and its optical properties

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Abstract: An aqueous solvothermal method was used to synthesise anatase TiO_2 nanococoons using titanium isopropoxide and ammonium hydroxide (25%) as solvent. The X-ray diffraction pattern was used to confirm the highly crystalline nature of the anatase TiO_2. High resolution transmission electron microscopy (HRTEM) reveals nanococoons with diameter of about 15nm and length of about 50 nm with few rhombohedral particles. The HRTEM along the length of the rod shows the fringe spacing of 0.35 nm corresponding to (101) planes of anatase TiO_2. The UV visible diffuse reflectance spectrum shows a blue shift in the band gap (3.4 eV) . Room temperature PL spectrum shows a sharp luminescence peak in the green region of the visible spectrum.
Keywords: Nanococoons, blue shift, solvothermal method

1.0 Introduction

Research activities in the field of nanoscience and nanotechnology to synthesise nanomaterials with different morphology and size has increased exponentially in the past two decades. This is because new physical, chemical and optical properties emerge by tailoring the morphology of nanoparticles and thus produce flexibility and options for the design of new materials to satisfy unique requirements. TiO_2 particles is one of the most widely investigated oxide semiconductor due to its unique physicochemical properties and applications as gassensors, catalysis, photocatalysts, photovoltaics, optics, environmental and energy storage materials [1-3]. Nanosized titanium dioxide (TiO_2) is a very interesting transparent conducting metal oxide because of its excellent optical transmittance, high refractive index, UV absorbing material, and good stability in diverse environments makes it a potential candidate in the field of photocatalysis and photo electrochemistry[1] In titanium dioxide, the valence band consists of oxygen 2p orbitals and the conduction band is made up from the titanium 3d orbitals. The band gap of TiO_2 anatase is 3.2 eV and rutile is 3.0eV corresponding to an absorbance threshold, λ = 388 and 415 nm respectively [7,8]. The studies on the optical properties of nanocrystalline TiO_2 in the recent years have shown interesting results .Solution based techniques like sol-gel ,hydrothermal, solvothermal have been reported for synthesising crystalline anatase/rutileTiO_2 nanoparticles of various morphologies like nanospheres, nanosheets, snowflakes, nanoflowers .nanorods , nanowires etc [4-6]. TiO_2 nanorods are usually synthesized by hydrothermal method by adding several grams of TiO_2 powder to concentrated NaOH or KOH solution and heated at moderately high temperatures for long hours in an autoclave. Ti-O-Ti bonds will be replaced Ti-O-Na bonds resulting in the formation of sodium titanate or potassium titanate rods.TiO_2 nanotubes are obtained after the products are washed with a dilute HCl aqueous solution and distilled water. New Ti-O-Ti bonds were formed after the Ti-O-Na and Ti-OH bonds reacted with acid and water[4].Although enormous work on the synthesis of TiO_2 nanorods are reported as it is one of the most important quantum semiconductor particle, there are no reports on the preparation of crystalline TiO_2 nanococoons without the use of templates and surfactants. Here we report the preparation of TiO_2 nanoparticles using ammonium hydroxide as a solvent.
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2.0 Experimental :

All the precursor chemicals were of analytical grade and used without any further purification. Typically 6ml of titanium isopropoxide was slowly dropped into 150ml of ammonia solution (25%). A white precipitate was formed. It was stirred for 1 hour and then transferred into a teflon lined autoclave and heated at 200°C for 30 hours. The autoclave was cooled naturally to room temperature. A white precipitate was obtained. The precipitate was filtered, washed with distilled water and ethanol several times and dried at 50°C for 12 hours for further characterization.

2.1 Characterization

XRD studies to analyse the crystalline nature was made using X PANanalytical X'pert PRO diffractometer with Cu-Kα λ = 1.54060 Å. The lattice constants of the unit cell are calculated from the XRD pattern. Optical absorption studies were carried out using aUV-ViS-NIR spectrometer (Varian, Cary 5000) by

diffuse reflectance spectroscopy, operated in the spectral range of 175-3300nm.The High Resolution Transmission Electron Microscopy (HRTEM) were obtained on a Jeol/JEM 2100 operated at a voltage of 200kV. Room temperature PL was recorded on a Cary Eclip spectrophotometer with a Xenon flash lamp at an excitation wavelength of 259nm.

3.0 Results and discussion

3.1 XRD

The XRD pattern of the sample is given in fig (1).The peaks present in the spectra confirm the polycrystalline nature of the nanostructures, corresponding to that of tetragonal TiO_2 crystal structure with lattice constants a=3.785A˚ and c=9.513 A˚ . The peak positions matched well with the standard data for TiO_2: JCPDS card no. 21-1272. No other crystalline by-products are found in the pattern, indicating that the prepared sample has a pure anatatase nature. The average particle size D was calculated using Scherrer equation $D=0.9\lambda/\beta\cos\theta$. The average particle size was about 20 nm.

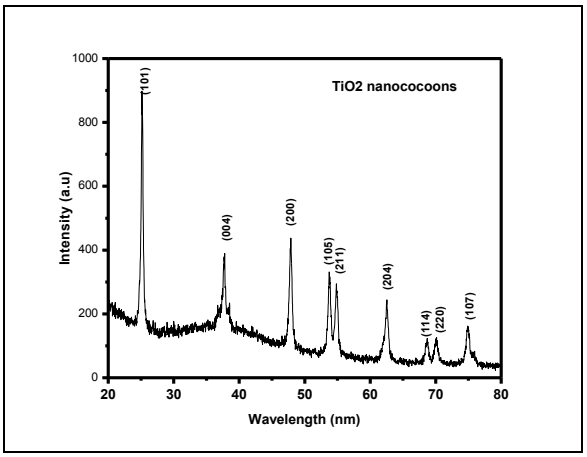

Fig 1: XRD pattern of TiO_2 nano structure. Matched with JCPDS No. 21-1272

3.2 High Resolution Transmission Electron Microscopy

The morphology of the samples was investigated by means of bright-field HRTEM images. Fig 2 (a) , (b) & (c) gives the HRTEM micrographs of synthesized TiO_2 nanoparticles. The samples show almost uniform nanococoon shaped particles with around 20 nm diameter and 30-50 nm length without much agglomeration. The figures shows two types of particle morphologies mainly cocoon shaped and few bipyramidal or rhombohedral nanoparticles. The lattice resolved images taken by HRTEM in fig.(2d) reveals a fringe width of 0.35nm corresponding to the (101) planes of anatase TiO_2 [11].

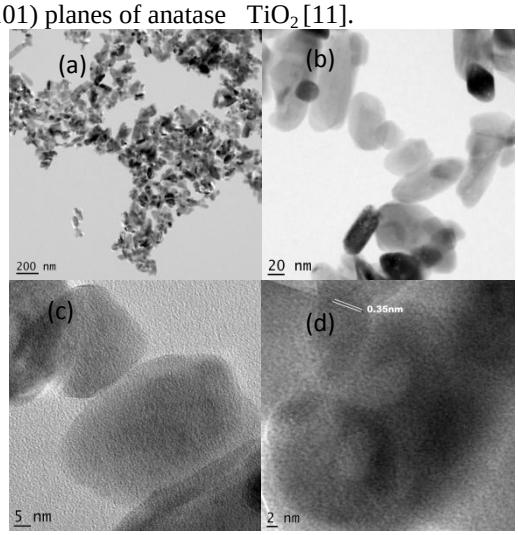

Fig 2 HRTEM micrograph of TiO_2 nanoparticles.

3.3 UV-Vis spectroscopy

UV-Vis spectroscopy was used to characterize the optical absorptions of TiO_2 nanoparticles. The absorption spectra of the sample is shown in fig (3a) with a rising absorption edge at 352nm. To determine the optical band gap of the synthesised TiO_2 the reflectance spectra was taken (fig 3b) and for determining the exact band gap value of TiO_2,the reflectance values were converted to absorbance by applying Kubelka-Munk function. The relationship between the absorption co-efficient α and the photon energy hν for direct allowed transition is given as $(\alpha h\nu)^2 = B(h\nu - Eg)$ where hν is the photon energy Eg is the apparent optical band gap. The band gap of the sample is calculated by drawing a line on the linear part of the curve, [F(R)hν] vs hν and extrapolating it to intersect the energy axis at α =0. The band gap value is found to be 3.4eV. A blue shift of 0.2eV is seen in the optical transitions. Since the nanomaterial are not quantum dots the blue shift cannot be explained on the basis of quantum confinement effect. Therefore it might be due to the reduced ionicity of the TiO_2 phase synthesized, which results from mixing of the O^{2-} p-orbitals and Ti^{3+} d-orbitals [8,9]. Serpone et al has also reported similar absorption features in his work [10]

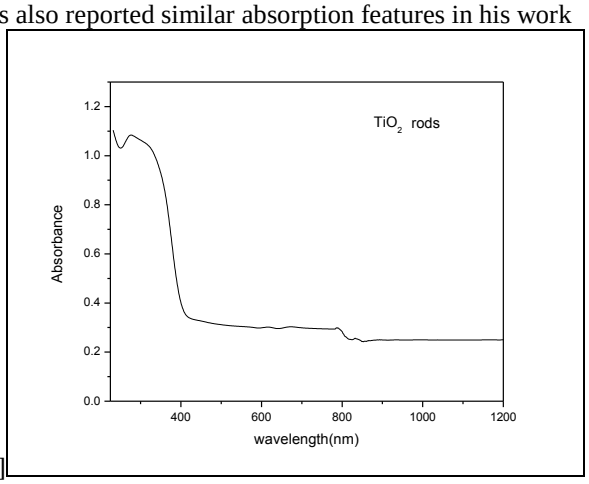

Fig 3a : UV-Vis absorption of TiO_2 nanoparticles

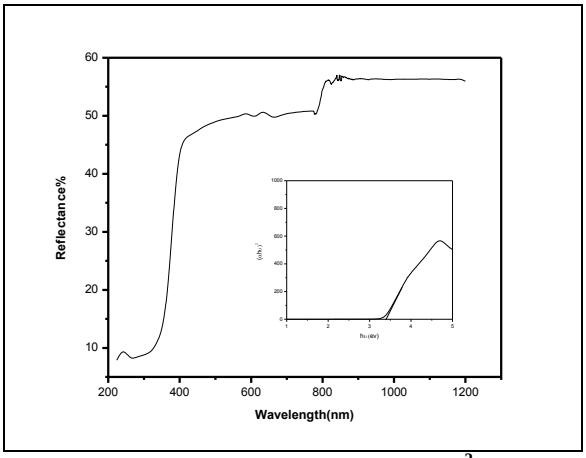

Fig 3b: UV visible reflectance spectrum . The inlet shows the (□h □)^2 vs photon energy plot for TiO_2 nano particles.

3.4 Photoluminescence studies

Fig 4 shows the photoluminescence spectra of TiO_2 cocoons. Photoluminescence (PL) is an effective tool to study the optical properties and also about the defect levels in semiconductor materials. The emission spectra was obtained at an excitation wavelength of 259nm, using a Xe flash lamp. The spectra shows a sharp emission peak in the green region with few low intensity emission peaks centered at 378nm and 420nm and 483nm respectively. The surface state emissions are due to the shallow- trap state near the absorption band edge, the deep-trap band far below the band edge, and a combination of these effects [9]. The emission peaks occurring at 387 nm are attributed to the excitonic emission or quasi-free recombination at the absorption band edge. The sharp emission in the green region is due to the oxygen vacancies and surface hydroxyl groups as the

samples are annealed at low temperatures [9,10].The origin of luminescence centers are investigated as it finds application in the field of optoelectronics.

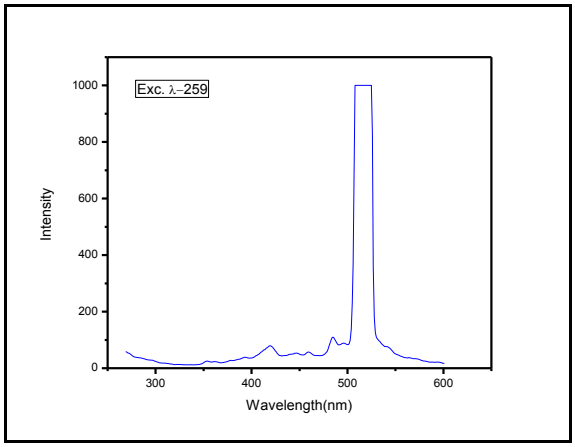

Fig 4 PL spectrum of TiO_2 nanoscocoon

4. Conclusions

TiO_2 nanoparticles were synthesized by a simple solvothermal method using ammonia as the solvent.The UV-DRS spectra shows a blue shift in the band gap value. HRTEM micrographs show almost uniformly distributed cocoon shaped nanoparticles of varied size as a surfactant free synthesis is performed. The photoluminescence spectra of TiO_2 nanocoons was found to be dominated by a strong and sharp emission in the green region and the exciton emission in the UV region, with two very low intensity peaks in the blue region. The excitonic emissions and shallow trap emissions in the blue region could be due to broad size distribution as there is no capping agent is used in this preparation.

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