Advance Physics Letter

Surfactant Assisted Hydrothermal Synthesis of TiO_2 Nano-spindle and their Characterizations

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Abstract: Crystalline TiO_2 nano-spindle were prepared by hydrothermal process of titanium isopropoxide stabilized in acidic/ethanol/water solution in presence of PEG 20000 surfactant. FESEM analysis shows the Nano-spindle structure of as-prepared TiO_2 materials using surfactant. An XRD result indicates the anatase phase structure and crystalline nature, which is well supported to the SAED obtained from pattern HRTEM studies. Morphological analysis is well indicated to the synthesis and sintering reaction of prepared materials, which is a formed different sized TiO_2 based material. A wormhole-like mesostructure without long-range order of HRTEM images of TiO2 were shown. The optical (direct) band gap was estimated to be 3.15 eV for TiO_2 (without surfactant) and 2.65 eV for TiO_2 (with surfactant).

Keywords: Crystalline, Anatase phase, Nano-spindle, and Surfactant

I. INTRODUCTION.

Titanium dioxide (TiO_2) is an attractive semiconducting material that has been widely utilized in various fields, and has attracted tremendous interest due to its unique optical and electrical properties, good chemical stability, high photoactivity, strong oxidizing power and low cost [**1-4**]. These characteristics have been applied it to control environmental pollution, photocatalysis, solar energy conversion and storage, photovoltaic cells, photonic crystals, molecular sensors, gas sensors, medical applications and cosmetics [**5-8**].

TiO_2 is a polymorphous compound which exists in three types of rutile, anatase and brookite. All the types have the octahedral structure, but the arrangements of octahedral units are different. Anatase TiO_2 is more stable and also shows a better photocatalytic activity than the rutile due to its wide-band gap [**7, 9**]. Various methods and techniques have been developed to synthesize TiO_2 nano crystals, including sol-gel method, chemical vapour decomposition, hydrothermal technique, and reversed micelle method [**4, 10-12**]. Since photocatalytic activity of TiO_2 is directly related to its morphology [**4**], all the oxidation reactions and photocatalysis take place on the surface of TiO_2**.** Additionally, the degradation rate of organic materials depends on the amount of catalytic surface active sites, surface area of the catalyst, light utilization, and other structural properties [**6**]. Since the mentioned properties can be improved by tailoring the shape and dimensionality, [**13**] the size and shape control of this material is a very important factor for accessing to the most application**s** of this semiconductor oxide.

The synthesis of TiO_2 particles in different sized in solution phase would be one of the best routes for controlling both the size of individual particles and the stabilized colloidal suspensions. These materials have been synthesized from the hydrolysis of various precursors such as $TiCl_4$, titanium isopropoxide, or titanyl sulfate-based precursors in acidic condition [**14-21**]. In addition, the reverse micelle methods in non-polar solvent with surfactants have been used [**22-25**]. So far considerable progress has been achieved in the synthesis of Titania nanoparticles, but further studies still have to be exerted for the control of particle size, crystallization in the form of primary particle, and the inhibition of inter-particular aggregation.

We report the synthesis of anatase TiO_2 with different shapes by simple and inexpensive method such as hydrothermal. The objective of this paper is to compare the properties of the products with each other. We also investigate the role of the temperature and surfactant in the morphology of the samples. The goal is to discuss on the relationship between TiO_2 structure, UV-Visible, and optical band gap.

II. EXPERIMENTAL SECTION

2.1. Materials and Method. Titanium iso-propoxide was purchased from Aldrich Chemical Co. (97 %), whereas other chemicals like iso-propanol and Diethylene Triamine was bought from Merk India. Distilled water was used throughout the synthesis process.

2.2. Synthesis of Nano-spindle TiO_2. In a typical synthesis, we are slightly modified the synthetic procedure [**26**]. In this route, 1.00 mL of deionized water was added to 30 mL of isopropyl alcohol (IPA) with 10 min of stirring to prepare **solution 1**. 0.15 mL of diethylenetriamine (DETA) was added slowly to the

solution 1 and stirred 5 min to form **solution 2**. In this acidic iso-propanol/water environment, 0.75 mL of titanium-(IV) iso-propoxide was added on **solution 2** and stirred continuously for 30 min, to form white precipitate. It is continued the stirring into in an oil bath and maintained temperature at 50 °C for 2 h. After that, obtained products were separated by centrifugation and washed with deionized water/ethanol followed by drying in a vacuum at 50 °C for 2 h. Finally, the products were calcined at 400 °C for 2 h.

2.3. Characterization techniques

The obtained samples were characterized by XRD pattern, and they were collected on a Phillips PW-1710 advance wide angle X-ray diffractometer, Phillips PW-1729 X-ray generator with CuK_α radiation (λ = 1.5417 Å) in the range of 10-70º. The field emission scanning electron microscope (FESEM) analysis was carried out on the samples on a using Carl Zeiss Supra 40 scanning electron microscope. The high resolution transmission electron microscopy (HRTEM) and Energy dispersive X-ray spectrum analysis (EDX) were carried out on the samples on a JEM-2100 HRTEM, JEOL, and Japan. The UV-Vis absorption spectra of the samples were recorded by using the Micropack UV-VIS-NIR, DH 2000 in the wave length region 200-1000 cm^{-1}. The thermogravimetric (TG) analysis were recorded by the NETZSCH TG-209 F1 analyzer at a heating rate of 10 °C/min in nitrogen environment.

2.4. Results and Discussion

Fig.1 shows the XRD patterns of the TiO_2 nanoparticles and nano-spindle calcined at 400 ºC. All the diffraction peaks can be indexed as the tetragonal anatase structure [26].

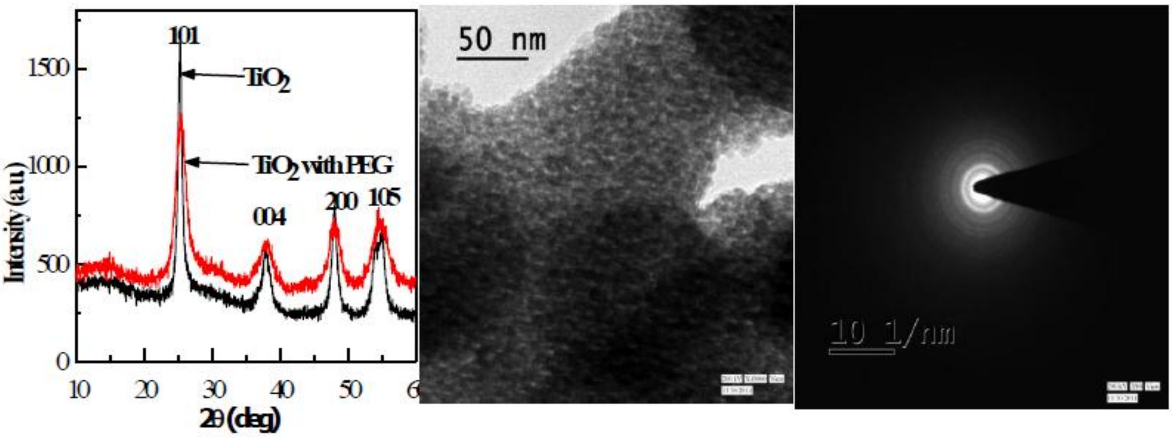

Figure 1 XRD pattern (left one), HRTEM images (middle one), and SAED pattern (right one) of indicated anatase TiO_2

The surface morphology and EDS of the samples are examined by FESEM is shown in **Fig. 2**. Uniform spherical-like morphologies were observed in **Fig.2** (left one, without surfactant). The nano-spindle like morphologies was observed in **Fig. 2** (middle one, with surfactant) with an average length and diameter of 1.4 μm and 56 nm, whereas a spherical particles were observed in **Fig.2** (**left one**, without surfactant) with an average particle size of ~ 185 nm, which is consistent with FESEM. The nano-spindle-like morphology was observed in the PEG assisted sample (**Fig. 2, middle one**, with surfactant)) [**26**]. The surfactant not only provides a favourable site for the growth of the particulate assemblies, but also influences the formation process, including nucleation, growth, coagulation and flocculation.

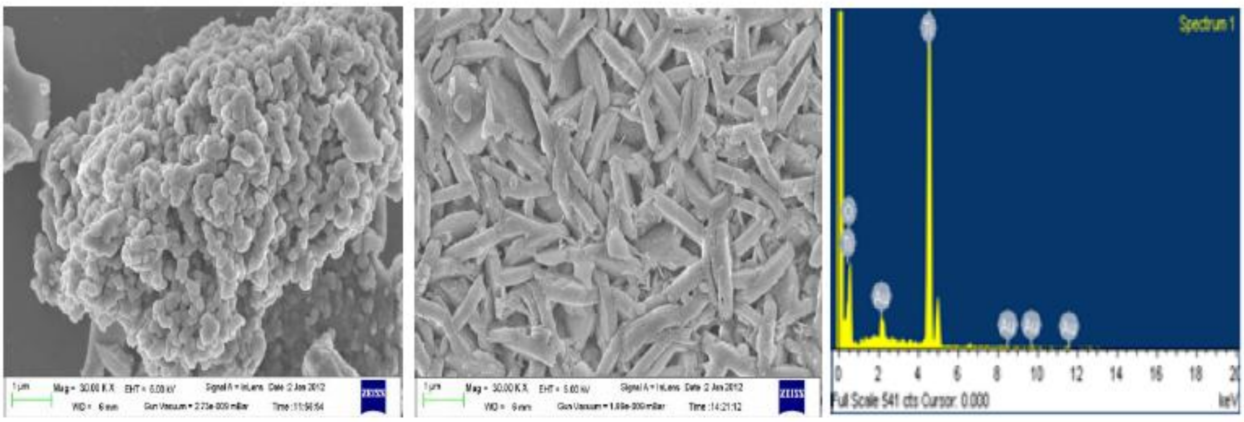

Figure 2 FESEM images of TiO_2 nanomaterials with (**left one**) and without (**middle one**) used surfactant and EDX (**right**) of TiO_2 (used surfactant)

Fig. 2 (**right one**) shows the EDX pattern of the PEG 20000 assisted TiO_2 nanoparticles. Ti and O are present in the spectrum, which clearly indicates that the synthesized sample is TiO_2. It exhibits that Ti and O are the only main elements with an atomic percentage of O 73.33% and Ti 25.99%. The HRTEM image of TiO_2 shows a wormhole-like mesostructure without long-range order calcined at 400 ºC **Fig.1** (**middle one**) [**27**]. The selected area electron diffraction (SAED) pattern of PEG 20000 assisted-TiO_2 sample is shown in the inset of **Fig.1** (**right one**). All the ring patterns exhibit different lattice planes which have the poly crystalline nature of the anatase structure of TiO_2 nano spindle, which is in good agreement with the XRD patterns [**28**]. **Fig. 3** (left one) represents the UV absorption spectra of TiO_2 nanoparticles; absorbance edges were observed at 341 and 299 and 340 nm for the TiO_2 with and without surfactant (PEG 20000). Considering the red shift of the absorption onsets to the present samples can be assigned to the indirect transition of the electrons in the TiO_2 nanoparticles [**29**]. The optical band-gap energy (**E_g**) of the semiconductor is given by an equation as [**29**]: $(\alpha h\nu)^2 = A(h\nu - E_g)$. The extrapolation curve of $(\alpha h\nu)^2$ vs hν is in the inset of **Fig.3 (**right one**)**. The estimated band gap energy can be calculated to be 2.65 eV (PEG 20000 assist TiO_2) and 3.15 eV (TiO_2 for without surfactant); The former one has larger band gap than the later one [**29**]. The optical property test indicates that the absorption peak of the nanoparticles shifts towards the short wavelength by changing the PEG 20000 surfactant. And the red shift phenomenon might be ascribed to the quantum confinement effect [**30**].

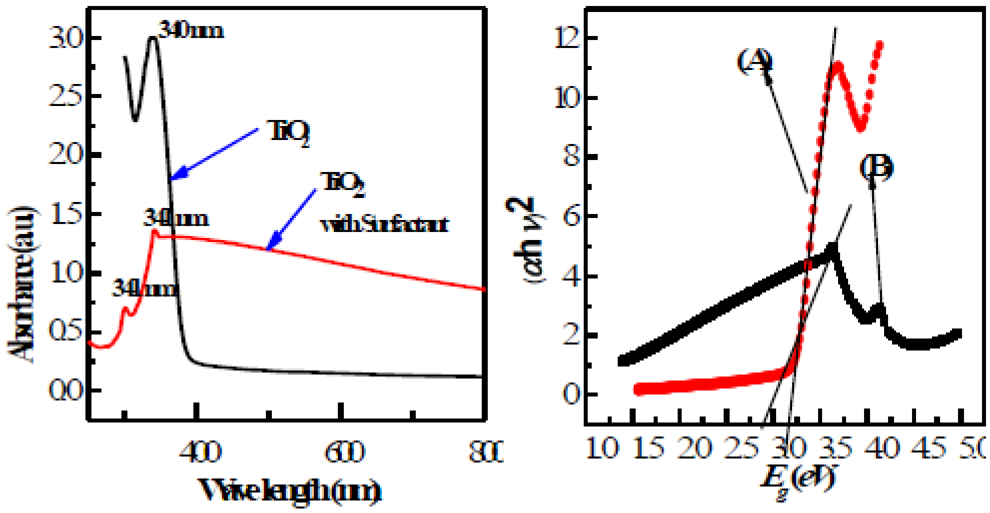

Figure 4 Absorption spectra (first one) and band gap (second one) of prepared TiO_2 nanomaterials

III. CONCLUSION.

A simple hydrothermal method has been presented to create TiO_2 nanospnidel on the PEG 20000 surfactants. The characterization of TiO_2 nanomaterials were studied by the XRD, FESEM, HRTEM, UV-Visible, optical band gap and TGA. The SEM and TEM analyses showed that the TiO_2 nanoparticles have nanospnidel structure which was obtained by using surfactant (PEG 20000). Our investigations indicated that the PEG 20000 assisted TiO_2 nanoparticles are the best, in terms of size, morphology, structure and optical properties. This method may prove to be applicable for the synthesis of other kinds of metal oxides.

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