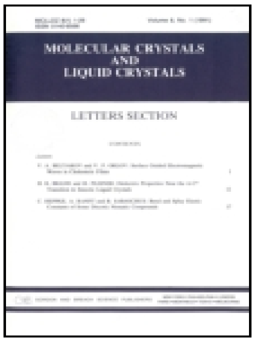

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Synthesis of nanosized TiO_2 powder by sol gel method at low temperature

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ABSTRACT

Nanotechnology is all about making products from very small constituents, components or subsystems to gain greatly enhanced material properties and functionality. Nanocrystalline anatase TiO_2 was prepared by a facile sol–gel route at a temperature of 50°C under mild conditions. Titanium tetraisopropoxide (TTIP) was used as a titanium precursor, and 2-propanol was used as a solvent. XRD, TEM, SEM, FT-IR and BET were applied to characterize the crystal phase. The Crystalline size of TiO_2 powder has been obtained with diameter < 30 nm for anatase at 500°C using an acid.

KEYWORDS
Titanium dioxide; sol-gel; nanocristallites; Anatase

1. Introduction

Nanotechnology is the understanding and control of matter at dimensions between approximately 1 and 100 nanometers. Nanocrystalline Titanium dioxide (TiO_2) or titania is one of the most successful modern functional [1] for a number of technologically important applications, such as catalysis, white pigment for paints or cosmetics, dye-sensitized solar cells [2], photocatalyst [3], and electrodes in lithium batteries [4].

Titania presents three crystalline phases, rutile (tetragonal structure), anatase (tetragonal structure) and brookite (orthorhombic structure).

In general, TiO_2 is preferred in anatase form because of its high photocatalytic activity, since it has a more negative conduction band edge potential (higher potential energy of photogenerated electrons), high specific area, non-toxic, photochemically stable and relatively inexpensive[5].

Several methods for the preparation of nanocrystalline TiO_2 have been developed and they are electrochemical reaction [6], continuous reaction [7], supercritical carbon dioxide [8], precipitation [9], multi-gelation [10], chemical solvent and chemical vapor decomposition [11, 12], ultrasonic irradiation [13], RF sputtering [14], sol–gel [15], Aerogel and Xerogel [16, 17].

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Comparing these methods, sol gel process is regarded as a good method to synthesize ultra-fine metallic oxide [18], and it has been widely employed for preparing titanium dioxide nanoparticles [19].

The sol gel process, as the name implies, involves the evolution of inorganic networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel). A sol is a dispersion of the solid particles, with diameter of 1–1000 nm, in a liquid where only the Brownian motions kept particles in suspension. While a gel is a state where both liquid and solid are dispersed in each other, which presents a solid network filled with liquid components [20]. The wet gel is converted into a dense ceramic with further drying and heat treatment. In this method, the precursors are usually inorganic metal salts or metal organic compounds such as metal alkoxides.

The reaction scheme is usually written as follows:

a) Hydrolysis

$$\text{Ti-OR} + H_2O \rightarrow \text{Ti-OH} + \text{R-OH}$$

b) Condensation

$$\text{Ti-OH} + \text{RO-Ti} \rightarrow \text{Ti-O-Ti} + \text{R-OH}$$

$$\text{Ti-OH} + \text{HO-Ti} \rightarrow \text{Ti-O-Ti} + H_2O$$

Depending on the chemical conditions under which such compounds are synthesized very different structures can be obtained ranging from colloidal particles to precipitation or gels [21]. The resulting product is strongly affected by the kinetics of hydrolysis and condensation reactions of the alkoxide precursor. Experimental parameters such as the hydrolysis ratio $H = n_{H2O}/ n_{alcoxide}$ and the nature of the alkoxy groups (R) are important factors influencing the kinetics of the hydrolysis and condensation reactions [22, 23].

In this work, Nanostructured TiO_2 has been synthesized with the sol-gel method from hydrolysis of a titanium precursor. This process normally proceeds via an acid-catalyzed hydrolysis step of titanium (IV) alkoxide followed by condensation [24]. The phase, structure, morphology, size distribution and surface area were examined by X-ray diffraction (XRD), Transmission Electron Microscopy (TEM). Scanning Electron Microscopy (SEM), Fourier Transformed Infrared spectroscopy (FTIR) and Brunauer Emmett-Teller adsorption (BET).

2. Experimental methods

2.1. *Sample preparation*

The sample of TiO_2 nanopowder was prepared via the sol–gel method using titanium tetraisopropoxide (TTIP), distilled water, and alcohol (2-propanol) as the starting materials.

The sample is prepared by adding hydrochloric acid (HCl) to 10 mL of 2–propanol to adjust the pH to 1.88 and to restrain the hydrolysis process of the solution. 11.7 mL of TTIP was slowly added, followed by refluxing at 50°C in order to obtain the sol. The 11.5 mL of distilled water was added to the solution and left a few minutes under heating.

In order to obtain nanoparticles, the gel was dried under 70°C for 15 hr to have the solvent evaporated, then calcinated in oven at 500°C to give TiO_2 nanopowder.

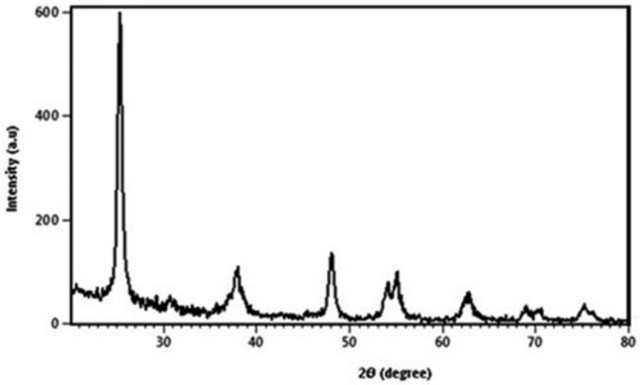

Figure 1. XRD patterns of Titania particles calcined at 500°C.

2.2. *Characterization*

The titania sample was characterized by PR-XPERT diffractometer (PW3064) using CuKα radiation ($\lambda = 1.5406$ Å), operating at 45 kV and 40 mA. RDX patterns were obtained in the range of 20–80°. The Morphology and particle size were examined by Transmission Electron Microscope (TEM, Detector : SUTW-Sapphire) and Scannig Electron Microscope (SEM, Hitachi S3500). The FT-IR spectra were measured by the KBr pellet method on infrared spectrophotometer (Shimadzu-FTIR 8400S) in the wavenumber range of 4000–400 cm^{-1}. The BET surface area was measured using a Micromeritics FlowSorb III, while pore size distributions (pore diameter and pore volume) were measured by adsorption of the N_2/He.

3. Results and discussions

The XRD patterns of the nanoparticles were obtained by sol-gel method and calcinated at 500°C as it is shown in Fig. 1.

It is clear that a peak was recorded at 2θ value of 25.33°, which corresponds to crystalline Anatase phase of TiO_2. The preferred orientation corresponding to the plane (101) is observed in both the samples.

The diffraction angles (2θ) of 25.33° 37.78°, 48.07°, 53.92°, 55.12°, 63.80°, 68.59°, 70.36° and 75.09° represent respectively the (101), (103), (004), (112), (200), (105), (116), (220), (215) crystal face of Anatase.

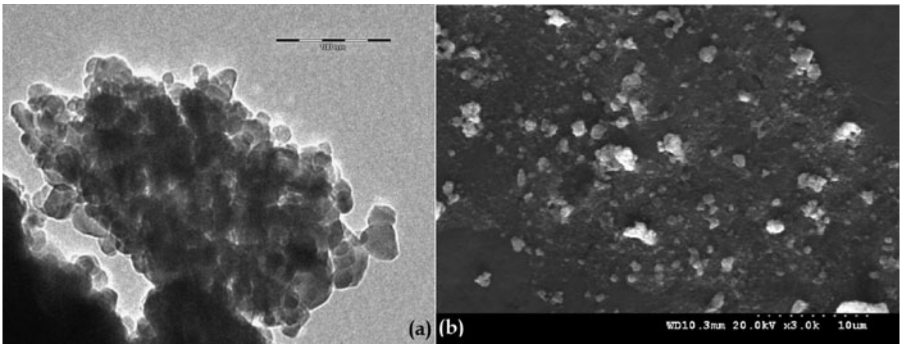

Figure 2. (a) TEM image, (b) SEM image.

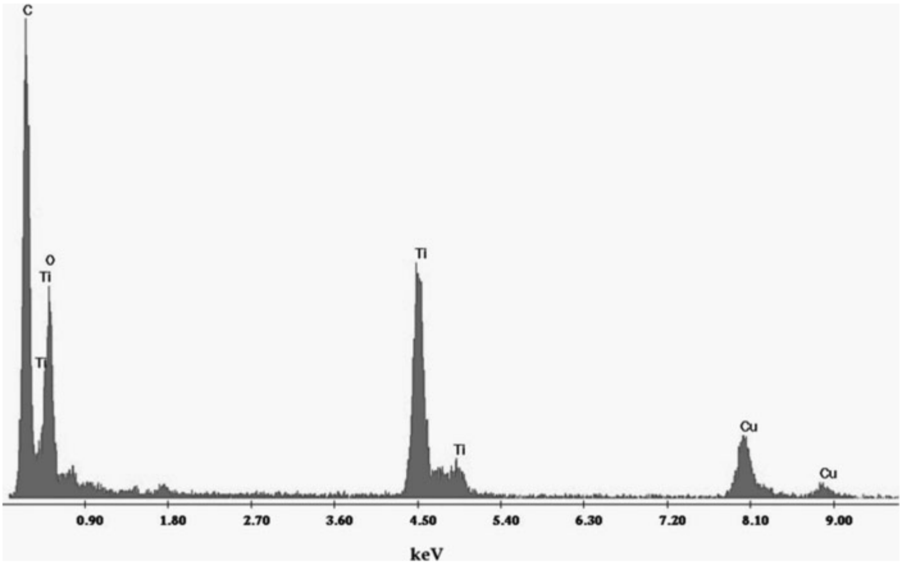

Figure 3. Energy dispersive X-ray spectrometry (EDX) of TiO2 nanoparticles.

Crystallite size was obtained by Debye-Scherrer's formula given by equation $\mathbf{D} = \mathbf{K\lambda/(\beta\cos\theta)}$. Where **D** is the crystal size; $\boldsymbol{\lambda}$ is the wavelength of the X-ray radiation ($\boldsymbol{\lambda} =$ 0.15406 nm) for CuKα; K is usually taken as 0.89; and $\boldsymbol{\beta}$**(=0,4689)** is the line width at half-maximum height [25]. The crystallite size was obtained using this formula is 29.8 nm.

The SEM and TEM pictures were used to fully understand the dispersion properties and size of nanocrystalline TiO_2, it is important to investigate their microstructure.

As seen in Fig. 2(b),The SEM image of the sample shows the formation of irregular clusters composed of spherical nanomeric primary particles. The clusters are about 200 nm. The TEM image of the sample is shown in Fig. 2(a). It can be seen that the clusters observed in the SEM images are mainly composed of grains of about 20 nm in diameter.

Energy dispersive X-ray spectrometry (EDX) analysis of TiO_2 nanoparticle shows peaks for Ti element and oxygen. The spectra always show the presence of C and Cu, which is from the C support film as well as the Cu TEM grid.

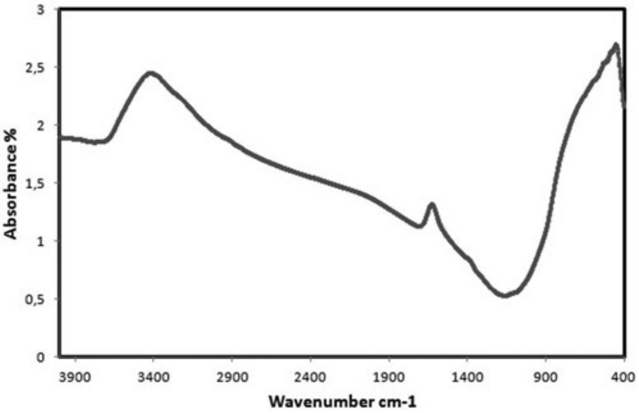

Figure 4. FTIR spectra of TiO_2.

Table 1. Characteristics anatase structure.

Space group	$I4_1/amd$
Density (g/cm^3)	3,90
a(Å)	3.7830
c(Å)	9.5100
Volume (Å^3)	136,10

The specific surface area of the TiO_2 powder was measured by adsorption/desorption of nitrogen/helium (30–70%) using the Brunauer Emmett-Teller adsorption (BET). The BET apparatus measures the equilibrium volume of nitrogen/helium physically adsorbed on the TiO_2 particles. The BET surface area is about 53.73 m^2/g. The average particle size was estimated by assuming all the particles to have the same spherical shape and size [26].

The particle size, **D** is given by equation : $D_{\mathbf{BET}} = \frac{6}{\mathbf{SBET}.\,\rho.}$

Where $\mathbf{S_{BET}}$ is the BET-specific surface area $\boldsymbol{\rho}$ is theoretical density and 6 is an experimental number calculated and assumed to spherical shape particles. The size of particles is 26.39 nm.

FT-IR spectra provide information of surface functional groups, the peak at about 3417 cm^{-1} was attributed to the O–H stretching of physisorbed water on the TiO_2 surface, and a band at 1636 cm^{-1} was attributed to the bending vibration of bonds, which is assigned to the chemisorbed water. The peak at about 454 cm^{-1} is due to the stretching vibrations of Ti-O-Ti and Ti-O bonds [27].

4. Conclusion

Nanocrystalline anatase TiO_2 has been successfully synthesized at a temperature as low as 50°C by a facile sol gel method. The size of nanocrystal particles was between 16 and 30 nm and the surface area was 53.73 m^2/g. The applications of nanosized anatase TiO_2 are primarily determined by its physicochemical properties such as crystalline structure, particle size, surface area, porosity and thermal stability.

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