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Facile synthesis of single-crystalline rutile TiO_2 nano-rods by solution method

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Abstract: A convenient and scalable technique for the synthesis of rutile titanium dioxide (TiO_2) nano-rods was presented by using bulk TiO_2 powder, sodium hydroxide (NaOH) and distilled water as raw materials. X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM) studies indicate that the prepared sample is crystalline and free from any impurities, however, it has no distinct shape and possesses a huge degree of agglomeration, and the average crystal size is around 40 nm. After annealing the sample at 600 °C for 2 h, it is observed through FESEM that nano-rods are formed. And XRD analysis shows that the nano-rods are single crystalline with distinct and smooth surfaces in different sizes with average length of about 1 μm and diameter of about 80 nm. Further UV-visible spectroscopy and Raman studies were conducted for the prepared sample and the band gap of the final product is found to be 3.40 eV.

Key words: TiO_2; nanorods; solution method; crystal growth; rutile

1 Introduction

Nano-scale structures are of great interest due to their unique properties and the possibility of their application in the field of nano-electronics [1] and several other possible applications [2−10], because this 1D metal-oxide nano-structures have been center of interest of many academic and industrial research groups. Among these metal-oxide nanostructures TiO_2 is one of the most studied materials because of its unique application in photo-voltaic devices and dye sensitized solar cells [11−13] owing to a wide band gap of about 3.0−3.2 eV [14]. And we know as a matter of fact that there are three distinct structural polymorphs of TiO_2 anatase, rutile and brookite, brookite however is the least characterized among three, and rutile has proven to be comparable to anatase in its properties only with an additional advantage of being more stable chemically and thermally and has a high refractive index [15]. Over the last forty years TiO_2 synthesis has been intensely investigated and there have been various methods employed for the synthesis of nanostructures, e.g. physical/chemical vapor deposition, sol-gel, hydrothermal, electro-templating methods have been widely used as synthesis techniques and there are various reports that discuss the effects of synthesis techniques on the nano-structures [16−19]. Compared to vapor deposition methods, solution methods are more suitable for inexpensive mass production however the hydrothermal technique requires specialized equipment and a variable pressure gradient control which makes it a little expensive over the simple solution method and it is time intensive. KOLEN'KO et al [18] used hydrothermal synthesis for nanorods of titanium oxide; TSAI et al [16] demonstrated and explained the formation of Nanorods using hydrothermal method. KASUGA et al [20] also demonstrated the formation of nano-tubes by similar kind of method and the only drawback of these techniques being time intensive. In this work, an easy and scalable and a very less time demanding approach for synthesis of rutile TiO_2 nano-rods using solution method and the effect of annealing on the structural and morphological properties were reported.

2 Experimental

All the reagents involved in the experiments were of analytical grade and utilized as-received without further purification. In the experimental arrangement, 1:6 molar

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ratio of bulk TiO_2 powder (<5 μm, 99.99% from Sigma Aldrich; 0.05 mol/L) to sodium hydroxide (NaOH, 99.99%, Sigma Aldrich; 1.0 mol/L) solution was made by dissolving in DI water 250 mL with mild stirring at room temperature in a 250 mL capacity glass beaker and the setup was placed over a hot plate at the temperature of 100 °C for 90 min under vigorous stirring. After 90 min the precipitate was collected and centrifuged at 3000 r/min for 5 min. This process was repeated 3 times using ethanol. The remainder was dried in a furnace at 80 °C for 12 h. Later after drying the substance was hand grinded in agate mortar with a pastel to make it into a powder form and was used for characterization. Half of the powder was subjected to annealing at 600 °C for 2 h and then it was characterized.

The phase purity of the obtained product was characterized using Phillips X'pert (MPD−3040) X-ray diffractometer with Cu K_α radiations (λ=0.15406 nm) operated at voltage of 40 kV and current of 30 mA. The XRD pattern was recorded within the scan range of 20°−80°. Field emission scanning electron microscopy (FESEM) images were obtained using a MIRA II LMH microscope with an operating voltage of 15 kV. The elemental composition of TiO_2 nano-rods was determined by energy dispersive X-ray spectroscopy (EDX, Inca Oxford, attached to the FESEM) with an operating voltage of 15 kV within the energy range of 0−10 keV. In order to get the phonon vibration study of the TiO_2 nano-rods, micro-Raman spectrometer (NRS−3100) was used with a 532 nm solid-state primary laser as an excitation source in the backscattering configuration at room temperature. Room temperature optical absorption spectrum was recorded in the range of 200−800 nm using a UV-Vis spectrophotometer (Agilent 8453).

3 Results and discussion

3.1 Structural studies

Figure 1 shows the XRD patterns of the as-prepared sample and the sample annealed at 600 °C for 2 h. The presence of (110) peak indicates that the obtained powder is rutile TiO_2. Comparing the XRD pattern with the standard JCPDS (89−4920) it can be observed that the prepared sample is free from any others phases of TiO_2 (anatase and brookite), and also there are no characteristic peaks depicting any impurities. The standard lattice parameters are a=b=0.4584 nm and c=0.2953, which are in agreement with the calculated values for our samples a=b=0.4582 nm and c=0.2953. The average crystallite size was calculated from the Scherrer equation [10].

$$\tau = K\lambda/(\beta\cos\theta) \quad (1)$$

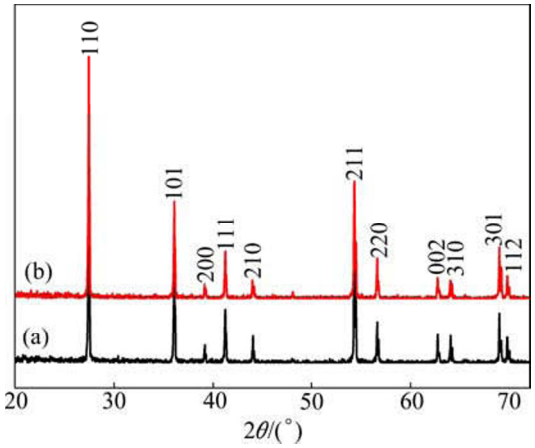

Fig. 1 XRD patterns of rutile TiO_2 as-prepared (a) and annealed at 600 °C for 2 h (b)

where τ is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size; K is a dimensionless shape factor, with a value close to unity. The shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite. λ is the X-ray wavelength, in this case it was Cu K_α radiation that has λ=0.15406 nm. β is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radians. This quantity is also sometimes denoted as $\Delta(2\theta)$. θ is the Bragg angle.

The crystallite size calculated from the Scherrer equation for the as-prepared sample was found to be about 40 nm and for the sample annealed at 600 °C for 2 h was found to be 52 nm.

Figure 2 shows the laser Raman spectra of TiO_2 taken at room temperature with a green (532 nm) laser in a back scattering mode for as prepared sample and the sample annealed at 600 °C for 2 h. The thermodynamically stable rutile phase TiO_2 exhibits major peaks at 242 cm^{-1}, 446 cm^{-1} and 610 $cm^{-1}$and minor peaks at 818 cm^{-1}, 707 cm^{-1}, and 319 cm^{-1} [21−28]. Based on the space group D_{4h}^{14} for rutile and assumed site symmetries for the Ti and O atoms within the unit cell, group-theoretical analysis shows four Raman-active "lattice vibrations" assigned as follows: A_{1g}(610 cm^{-1})+B_{1g}(144 cm^{-1})+B_{2g}(827 cm^{-1})+E_g (446 cm^{-1}) [22]. The peaks that are at 448 cm^{-1}(E_g), and 619 cm^{-1}(A_{1g}) in the as-prepared sample and the peaks at 447 cm^{-1}(E_g) and 609 cm^{-1}(A_{1g}) in the sample that is annealed at 600 °C for 2 h are attributed to Ti—O—Ti vibrations [21] and are the characteristic peaks of a rutile TiO_2 crystal system. The broad Raman peak at 242 cm^{-1} and 234 cm^{-1} in both the as-prepared and annealed samples are attributed either to the second order scattering or disorder effects. The Raman mode at 826 cm^{-1} (B_{2g}) cannot be recorded due to its weak intensity. There is a blue-shift of the E_g mode between the