Synthesis of pure and aluminum oxide doped TiO$_2$ nanorods and study of lattice strain and activation energy of crystalline phases

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Synthesis of TiO$_2$ nanorods in anatase, rutile and Ti$_8$O$_{15}$ phases, as well as TiO$_2$ nanorods fabricated with aluminum oxide as dopant by using the sol-gel method is reported. The morphologies and the crystal structures of TiO$_2$ nanorods are characterized by field emission scanning electron microscopy, atomic force microscopy and X-ray diffractometer techniques. The obtained results illustrate an aggregative structure at high calcined temperatures with the formation of spherical particles. The effects of chemical compositions and calcined temperatures on surface topography and crystallization of phases are studied. In addition, the activation energy of nanoparticles formation in pure and doped state are calculated during thermal treatment.

*Keywords:* Nanomaterials, Crystalline phases, Nanorods, Titania, Lattice Strain, Activation energy, Alumina, Dopants, Sol-gel method

TiO$_2$ is an important material that is used in many industrial applications related to photo-splitting of water$^1$, photocatalysis$^2$, photovoltaic devices$^3$, etc. It is known to have three natural polymorphs, i.e., rutile, anatase and brookite. Only the anatase phase is generally accepted to have a significant photocatalytic activity. The photocatalytic performance of this compound depends on characteristics of TiO$_2$ crystallites, such as their sizes and surface areas. Therefore, modification of their physical and chemical property is interesting for researchers$^4$-$^9$. One possible way to modify the property of TiO$_2$ crystallites is by adding a second semiconductor into TiO$_2$ matrix.

Aluminum oxide has been incorporated into the TiO$_2$ matrix to enhance the photocatalytic process because of its high thermal stability and excellent mechanical strength. It can also help to create new catalytic sites due to the interaction between TiO$_2$ and Al$_2$O$_3$ or SiO$_2$$^{10}$ and to obtain a large surface area as well as a suitable porous structure$^{11}$. Due to their high resistance against alkaline solutions Al$_2$O$_3$-TiO$_2$ coatings are attracting the attention of many scientists. Their alkaline resistance is strongly controlled by their surface states.

Characterization of one-dimensional (1D) nanostructures such as nanowires, nanotube and nanorods doped with TiO$_2$ has received considerable attention due to their unique properties and novel applications$^{12}$-$^{15}$. However, detailed investigations focusing on synthesis processes and the effect of dopant on photocatalytic semiconductor surface are needed.

Many methods have been successfully developed for fabricating 1D nanostructures such as vapor-solid, vapor-liquid-solid, solution-liquid-solid, template-based synthetic approaches and laser ablation$^{16}$-$^{25}$. However, most of these methods produce materials with unavoidable contamination. Therefore, one has to explore a new approach to synthesize 1D nanomaterials without using preformed templates or catalysts. Sol-gel process is one such method employed quite often, for synthesizing nanosized catalytic materials. Besides incorporation of an active metal in the sol during the gelation stage, it allows the metal to have a direct interaction with the support, which gives the materials possessing special catalytic properties.

**Materials and Methods**

The precursors, aluminum tri-$s$-butylate (ATSB) (Merck, ≥ 97%), titanium tetraisopropoxide (TTIP) (Ti(OPr$_i$)$_4$, Merck, ≥ 98%), 0.1 $N$ nitric acid (Merck, ≥ 65%), ethanol (Merck, ≥ 97%) and distilled water
were used without further purification. The starting point of the synthesis of a target system was a solution prepared by mixing precursors in the molar ratio TTIP/ EtOH/ H$_2$O = 1:0.022/9.5×10$^{-4}$ and (TTIP/ ATSB = 87.3. ATSB was dissolved in 20 mL deionized water and stirred at room temperature (RT) for 48 hours to get a solution of pH 5. Then, for precipitation, ammonia solution was added dropwise to make the pH 8 and then centrifuged at 1500 rpm to gather the precipitate. The precipitate was heated at 50 °C for 24 hours to yield a powder. Nanorods were obtained by immersing the powder in 10 N NaOH solution in a teflon balloon at 200 °C for 24 h, then once again gathered by centrifugation, and purified with 0.1 N nitric acid and distilled water to eliminate Na ions. Finally, the thus obtained powder was dried at 50 °C for 48 h in air and calcined at three different temperatures, i.e., 300, 600 and 900 °C. The effect of varying calcination temperatures was studied with the as-prepared, 300, 600 and 900 °C samples. XRD patterns were recorded on a GBC-MMA 007 (2000) X-ray diffractometer with Cu-K$_{α}$, 1.54056Å, (0.02° step at 10°/min) radiation over a 2θ range of 10–80°. Transmission electron microscopy (TEM) (CM10 Philips) was used to investigate the structure and morphology of the nanorods. Field-emission electron microscopy (FE-SEM) (S-4160 Hitachi) was used to investigate the morphology of the nanoparticles. For AFM, (Easy Scan 2 Flex Switzerland) measurements, the TiO$_2$ nanorods were first diluted in deionized water to the appropriate concentration (in a ratio of 1: 20 from a 0.04% aqueous suspension) and then ultrasonicated for 30 minutes. The 50 µl of the diluted solution was placed on a cleaned glass substrate (glass was cleaned with ethanol and acetone then dried with a nitrogen steam), incubated for 10 minutes, and then the residual solution was blown by a stream of nitrogen. The measurements were made at 20 °C and relative humidity of 45% using a silicon tip. FT-IR measurements were recorded in KBr on a 1730 infrared fourier transform spectrometer (Perkin-Elmer).

**Results and Discussion**

Crystalline phases of the composite ceramic were investigated by XRD (Fig. 1). Characteristics of the XRD peaks are summarized in Tables S1 and S2 (Supplementary Data). As shown in these figures, different crystalline phases are formed at different calcination temperatures. Amorphous structures are observed for the as-prepared and 300 °C samples due to short range ordering of network$^{15,19,26}$ (Fig. 1), while the samples observed at 600 °C and 900 °C showed a high degree of crystallinity. The peaks observed at 2θ values of anatase, rutile, Ti$_2$O$_3$, Ti$_8$O$_{15}$, Al$_2$O$_3$H and Al$_2$O$_3$ phases were compared with the standard powder diffraction card of Crystal impact AMCSD (99-101-0957), (99-101-0954), (99-100-9833), (99-200-2191), (99-200-3780) and (99-200-0017) respectively (Figs. S1-S9, Supplementary Data). The grain size was calculated

![Fig. 1–XRD patterns of (a) pure TiO$_2$ and (b) doped TiO$_2$ nanorod calcined at 900 °C. [Inset: XRD patterns of as-prepared and samples calcined at 300 °C and 600 °C].](attachment:image.png)
from Scherrer’s equation, \( r = \frac{k\lambda}{2\beta \cos \theta} \), where \( \beta \) is FWHM (full width at half maximum) observed, shape factor \( k \) is assumed to be 0.9 and \( \lambda \) is a wavelength of Cu-K\(_\alpha\) radiation (0.154056 nm). The influence of calcination temperature on grain size of different phases, as seen by the increase in size of grains when the calcination temperature is increased due to the increase in the chemical bond length.

The average crystallite size in pure and doped states was calculated based on the Scherrer’s formula. The crystallite size of rutile increases rapidly from about 31 nm at 600 °C to 145 nm at 900 °C, while crystallite size of anatase increases slowly (from 54 nm to 60 nm). Phase transformation occurs due to two main effects: surface energy and precursor chemistry. At very small particle dimensions, the surface energy is an important part of the total energy and it has been found that surface energy of anatase is lower than those of rutile and brookite. Further, crystal structure stability has been explained on the basis of a molecular picture, where nucleation and growth of different polymorphs of TiO\(_2\) are determined by precursor chemistry, which depends on the reactants used. Rutile crystals are known to grow much faster than anatase. So, generally, with increasing calcination temperature, rutile nanocrystals exhibit larger diameters.

The particle growth kinetics under hydrothermal conditions are determined by coarsening and aggregation–recrystallization processes, allowing control over average nanoparticle size. Phase transformation of TiO\(_2\) may be affected by aluminum oxide doping, which improves the thermal stability of anatase, suppress particle aggregation and grain growth of anatase and increase specific area of rutile phase. The effect of the dopants demonstrates stabilizing effect on anatase since coverage of TiO\(_2\) surface by dopant species can protect TiO\(_2\) nanoparticles from agglomeration during calcinations temperatures. Incorporation of dopants into TiO\(_2\) network may also enhance straining force in anatase lattice due to structural distortion, which could further affect the growth of crystallite size in rutile phase.

The crystallite size of TiO\(_2\) and Ti\(_3\)O\(_{15}\) increases rapidly from about 13 and 12 nm at 600 °C to 24 nm at 900 °C. This is directly related to the crystallization of nanoparticles. Similar to the pure state, the crystallite size increases by increasing calcination temperature in doped state also. Prominent peaks of TiO\(_2\) phases change from 2\( \theta \) = 23° in pure state to 2\( \theta \) = 24° in the doped state.

Linear plots of \( \ln D \) against 1/\( T \) were obtained according to Scott’s equation (Supplementary Data, Figs S10 & S11). Under the condition of homogeneous nanocrystallite growth describing approximately the crystal growth during annealing, the activation energy \( E \), was calculated accordingly to Scott’s equation, \( D = C\exp(-E/RT) \) where \( C \) is a constant, \( E \) is activation energy, \( R \) is gas constant and \( T \) is absolute temperature. The values of \( E \) for pure and doped TiO\(_2\) nanorod phases are shown in Table 1.

It is seen that the calcination temperature has a remarkable effect on nanocrystallites growth. The activation energies of anatase, rutile and TiO\(_2\) phases in doped state are higher than those in pure state.

Lattice strain (\( \varepsilon \)) of nanocrystallites in pure and doped TiO\(_2\) nanorods were determined for dependence of FWHM on diffraction lines observed in 2\( \theta \) range of 10-80° on sin \( \theta \) according to Williamson-Hall’s equation:

\[
\beta \cos \theta = (k\lambda/L) + 4\sin \theta \varepsilon
\]

where \( \beta \) is FWHM, shape factor \( k \) is assumed to be 0.9, similar to Scherrer equation and \( \lambda \) (wavelength of K\(_{\alpha}\)(Cu)). Lattice strain was determined from the slope of the linear plots of \( \beta \cos \theta \) against 4sin\( \theta \). Due to poorly crystallized powder samples, the linearity between \( \beta \cos \theta \) and 4sin\( \theta \) is not very good. The plots of \( \beta \cos \theta \) against 4sin\( \theta \) for different diffraction lines are illustrated in Fig. 2. For low calcination temperatures, experimental points for diffraction lines are scattered because the peaks are weak and broad, therefore, their FWHMs are difficult to measure. It can be seen that in the pure state, lattice strain decreases by increasing the calcination temperature. By increasing the calcination temperature up to 600 °C, lattice strain decreases from 0.8048 to 0.1019 and by further increase from 600 °C to 900 °C, the strain decreases by increasing the calcination temperature.

<table>
<thead>
<tr>
<th>Table 1—The activation energy of nanoparticles formation in pure and doped state</th>
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<tr>
<td><strong>Crystallite phase</strong></td>
</tr>
<tr>
<td>------------------------</td>
</tr>
<tr>
<td>Anatase</td>
</tr>
<tr>
<td>Rutile</td>
</tr>
<tr>
<td>TiO(_2)</td>
</tr>
<tr>
<td>Ti(<em>3)O(</em>{15})</td>
</tr>
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It is seen that the calcination temperature has a remarkable effect on nanocrystallites growth. The activation energies of anatase, rutile and TiO\(_2\) phases in doped state are higher than those in pure state.
lattice strain increases from –0.2783 to –0.0991. This implies that by increasing the calcination temperature, the form of lattice strain varies from external to internal strain. Similar to the pure state, the lattice strain decreases on increasing the calcination temperature in doped state.

Figure 3 shows nanorod structure of the pure sample calcined at 900 °C. As shown in this figure, the diameter is 43 nm and the length is 400 nm. The FE-SEM images of TiO$_2$ nanorods are shown in Figs 4 and 5. The as-prepared sample has spherical coverage, but contains many rods. It seems that the nanoparticles are formed in a thin rope shape. The particles with spherical coverage with diameter about 560 nm are observed only in pure state. This is due to the suppressive effect of dopants on crystallite growth of TiO$_2$. Figures 4 and 5 show that the rods are formed at high temperature, viz., 600 °C and 900 °C. FE-SEM of TiO$_2$ nanorods doped with aluminum oxide show that particles in rope-shape exist in discrete regions in as-prepared state and form nanorods on increasing calcination temperature. The shapes of the particles in the samples with higher calcination temperatures are similar to each other and likely to become rods in general at calcination temperatures of 300, 600 and 900 °C. It is seen that both pure and doped sample particles agglomerate when calcined at 300, 600 and 900 °C. Agglomeration may result from the calcination treatment conditions. However, size distribution of the particles has not been determined. Dopants affect the length and shape in such a way that they enlarge length and separate the nanorods, due to dopants, which exist as discrete particles at the nanocrystallite interfaces and "pins" the grain boundaries in place by restricting surface diffusion and reducing radius of the curvature of the nanocrystals.

The surface morphology of TiO$_2$ nanorods and TiO$_2$ nanorods doped with aluminum oxide are shown in Figs 6 and 7. As shown in these figures, the islands have a considerably compacted shape with length of 2–3.5 µm in pure state and about 10 µm in doped state, when the islands are changed into arm-like shapes. The growth reflects continuous presentation of dendritic or irregular pattern while maintaining an arm width of about 6 µm. Two factors affect the rod structures: (i) Diffusion of adatoms into the matrix at higher concentration and a larger fraction of deposited TiO$_2$ or dopants impinging onto the existing islands. These adatoms can diffuse off of the first island and condense at the step edge, thereby, thickening the structure. (ii) Similar to some fractal design, where
nanoaggregates shapes have been formed. As the linear size of islands increases a higher percentage of TiO$_2$ or dopants occupy the fractal regions between the arms. TiO$_2$ or dopant atoms in these regions tend to fill in and do not contribute to further radial growth. Radial growth, on the other hand, is slowed to the extent that islands are not coalesced and can still be identified as individual entities. The dendritic shapes are due to kinetic limitation existing at room temperature, which can be concluded from their thermal instability.$^{37}$
The surface morphologies are characterized by average thickness of the sheets, intervals between the sheet and the roughness parameters such as \( S_a \), \( S_m \) and \( S_q \) (Table 2). It can be seen from Figs 6 and 7, that roughness of pure TiO\(_2\) nanorods surface is greater than that of doped TiO\(_2\) nanorods. Also, the maximum height (\( h_{\text{max}} \)) of 3-dimension view of pure TiO\(_2\) nanorods structure is greater than that of the doped TiO\(_2\) nanorods.

The FTIR spectra of TiO\(_2\) nanorods calcined at different temperatures were recorded (Fig. S12, Supplementary Data). In the as-prepared gel, the

<table>
<thead>
<tr>
<th>Sample</th>
<th>( S_a ) (nm)(^a)</th>
<th>( S_q ) (nm)(^b)</th>
<th>( S_m ) (pm)(^c)</th>
<th>( h_{\text{max}} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure TiO(_2) (congestion state)</td>
<td>34.979</td>
<td>54.599</td>
<td>45.987</td>
<td>219</td>
</tr>
<tr>
<td>Pure TiO(_2) nanorods (single nanoaggregate state)</td>
<td>37.021</td>
<td>49.139</td>
<td>45.898</td>
<td>169</td>
</tr>
<tr>
<td>Doped TiO(_2)</td>
<td>10.191</td>
<td>14.612</td>
<td>46.00</td>
<td>40.4</td>
</tr>
</tbody>
</table>

\( a = \frac{1}{N} \sum_{i=1}^{N} x_i \) \\
\( b = \frac{1}{N} \sum_{i=1}^{N} (Z(x_i))^2 \) \\
\( c = \frac{1}{N} \sum_{i=1}^{N} x_i \)
3200 cm\(^{-1}\) band is attributed to hydroxyl groups from water and ethanol occluded in the titania pore. Besides, the OH bending band of water in gel is observed at 1650 cm\(^{-1}\) and low energy interval Ti-O band are found at 1061 and below 1000 cm\(^{-1}\). The IR spectra show characteristic peaks of Ti-O-Ti (495-436 cm\(^{-1}\)). When the composite is calcined at 900 °C, the high-energy stretching band almost vanishes and 1650 and 3200 cm\(^{-1}\) bending vibration band intensity decreases due to vaporization of the liquid. By comparison between pure nanorods and doped nanorods, the bands at 780 and 570 cm\(^{-1}\) are attributed to Al-O vibration bond.

The present study shows that, the homogeneous hydrolysis of metal alkoxide provides an excellent technique for preparation of TiO\(_2\) nanorod materials. The results indicate that homogeneous hydrolysis of tetraisopropyl-orthotitanate via sol-gel route is a promising technique for preparing photosensitive material by uniform nanoparticles. The influence of calcination temperatures and addition of other oxides such as aluminum oxide can affect structural properties such as size, strain and activation energy. Average crystallite size increases with an increase in calcination temperatures.

**Supplementary Data**

Supplementary data associated with this article i.e., Figs S1–S12, and, Tables S1 and S2, are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_53A(11)1377-1383_SupplData.pdf.

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**References**