Nonhazardous Process for Extracting Pure Titanium Dioxide Nanorods from Geogenic Ilmenite

Tharindu P. B. Rajakaruna, Chandana P. Udawatte, Rohana Chandrajith, and R. M. Gamini Rajapakse

ABSTRACT: The current rate of industrial production of titanium dioxide, from natural ilmenite, is around 6500 kT per annum. The two main processes used, namely, sulfate and chloride processes, require concentrated corrosive acids and drastic conditions, such as 1000 °C, in open processes, thus contributing to considerable costs and environmental pollution. To reduce the cost and impact to the environment, a closed process involving a rotatory autoclaving followed by refluxing and stationary solvothermal treatment of ilmenite, below 170 °C, was developed. The as-synthesized product is 100% pure titanium dioxide in its amorphous state (24% crystallinity), which has nanorods arranged in a flowerlike morphology. This can be converted to over 99% pure anatase phase with 90% crystallinity and 100% pure rutile phase nanorods with 98% crystallinity by calcining at 350 and 650 °C, respectively. The direct band gaps of the three materials are 3.40, 3.60, and 3.15 eV, respectively.

1. INTRODUCTION

Conversion of the naturally occurring ilmenite, present in mineral sands, to pure titanium dioxide nanomaterials is highly desirable due to its numerous industrial and technological applications in paints, varnishes, lacquer, paper, paperboard, printing inks, rubber, floor covering, ceramics, food, and pharmaceuticals.1−4 As the entire world is moving toward greener and sustainable energy, TiO2 is a material of choice for fabricating some solar cells and in photocatalytic hydrogen generation from water. TiO2 is also used in the photocatalytic degradation of pollutants in the environmental segments.1−4 The currently used processes demand drastic conditions such as temperatures over 1000 °C and high concentrations of corrosive acids such as sulfuric or hydrochloric. Although the sulfate process involving concentrated sulfuric acid tolerates low-grade ilmenite with a feedstock comprising a finely ground ilmenite concentrate of a minimum 44% TiO2 or a sulfatable titanium slag of 78% TiO2, the process is environmentally hazardous and the byproduct iron sulfate is considered as a waste.5 On the other hand, the chloride process is comparatively less hazardous; although it gives chlorine gas to the environment and uses high concentrations of hydrochloric acid (>12 M), it demands high-grade ilmenite produced by smelting and roasting of natural ilmenite. This process requires over 1000 °C of temperature, and making it also highly expensive.6 As of now, only these two processes are used worldwide to produce pure titanium dioxide from natural ilmenite, and fine-tuning conditions to improve the processes are being attempted as exemplified by some literature including several patents.7−12

The process developed in our research also uses hydrochloric acid in a minimal volume, at a comparatively low concentration (350 mL of 6 M HCl for 25 g of ilmenite), and a much lower temperature of 170 °C, making it a very low cost process. Since the reactions occur in the closed system of an autoclave, the escape of chemicals to the environment is also minimal. The used hydrochloric acid containing leached iron component is separated and used for synthesizing iron-based nanomaterials, such as magnetite and zero-valent iron nanoparticles. Therefore, the byproduct formed is also converted to useful products. During the latter stages of the process, hydrochloric acid is neutralized with a base to form environmentally nonhazardous salts such as sodium chloride that can be recovered in a saltern. In the novel process developed here, it is used a closed hydrothermal system utilizing a revolving autoclave to maintain the desired pressure and temperature conditions within the closed system. This is the first time of use of an autoclave to break the crystalline...
structure of hard inorganic solids at considerably lower temperatures. This process can be extended to extract pure compounds from other natural minerals also. The process is, therefore, of low cost, environmentally nonhazardous, and universally adaptable for the large-scale synthesis of the phase-specific pure titanium dioxide from natural ilmenite.

The products prepared in this process were duly characterized by several independent analytical techniques. Material and phase identification were done by powder X-ray diffractometry, which was also used to calculate the crystallinity percentages of the products. The morphology and dimensions of the particles of the products are revealed by their scanning electron microscopy (SEM) images. Energy-dispersive X-ray analysis was performed to get the atomic percentages of the products. Fourier transform infrared spectra of the samples showed characteristic vibrations, while the UV–vis–near-infrared spectra were used to calculate direct band gaps of the products. The purity of the as-prepared amorphous titanium dioxide is confirmed by its energy-dispersive X-ray (EDX) spectrum of the SEM image, which gives 33.33% titanium and 66.67% oxygen atomic percentages, thus confirming the 1:2 stoichiometry of the compound (Figure 4). It shows the area of the image scanned as a square in pink color (a), the pattern of peaks (b), and a table showing the corresponding data.

This is a clear indication for the formation of 100% pure titanium dioxide from natural ilmenite from this process. This is the first report of obtaining 100% pure, phase-specific titanium dioxide nanomaterials at different magnifications.

Figure 3d are the calculations of rod diameters and lengths of (i) anatase phase and (ii) rutile phase titanium dioxide produced. The diameters of anatase and rutile nanorods are 32 and 67 nm, respectively, and ~350 nm long as calculated from the SEM images given in Figure 3d. Comparing these data with those obtained for the crystallite size from the XRD indicate that each nanorod is composed of a large number of crystallites arranged in a rodlike structure to form nanorods.

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However, the development of the rutile phase is apparent due to the peak shown at 27.45°, which is due to the diffraction from the (110) plane of the rutile phase of titanium dioxide. However, if the calcination temperature is from 300 to 350 °C, then the sample becomes purely anatase. As shown in Figure 1c, the P-XRD pattern of the samples calcined at 650 °C contains peaks at 27.45, 36.16, 41.26, 54.40, and 56.70°, respectively. These peaks correspond to diffractions from the (110), (101), (111), (211), and (220) planes of the pure rutile phase of titanium dioxide (JCPDS Card No. 29-1360). These results clearly show that the novel, low-cost process developed here can be used to prepare phase-specific titanium dioxide from natural ilmenite. The crystallinity calculated from the XRD peak areas shows that amorphous, anatase, and rutile phases have, respectively, 24, 90, and 98% crystallinity percentages. The crystallite sizes of the anatase and rutile phases, calculated using the Scherrer’s equation, are 0.8 and 1.2 nm, respectively.

The scanning electron microscopy (SEM) images of the as-prepared samples calcined at 350 °C and 650 °C are shown in Figure 2a–c, respectively. These images indicate that the as-prepared sample has a flowerlike morphology (Figure 2a), which develops into a network of nanorods in the anatase phase due to the heat treatment at 350 °C (Figure 2b). Upon heat treatment at 650 °C, the rutile phase obtained has individual TiO2 nanorods (Figure 2c).

Figure 3 shows the scanning electron microscopy images of (a) amorphous, (b) anatase phase, and (c) rutile phase titanium dioxide nanomaterials at different magnifications.

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The Fourier transform infrared (FT-IR) spectra of the amorphous titanium dioxide nanorods arranged in the flowerlike structures show typical Ti–O stretching and bending in the wavenumber range 700–1000 cm−1, broad O–H bending vibration centered at 1600 cm−1, and O–H stretching vibrations of the absorbed water appearing in the range 2600–3000 cm−1. When the sample is calcined at 350 °C to make anatase, the typical water absorption bands disappear and the bands responsible for Ti–O vibrations become prominent.

The Ti–O bands are further sharpened in the spectrum of the rutile sample, indicating that the material becomes more and more crystalline due to high-temperature calcination. The FT-IR spectra of the as-prepared amorphous titanium dioxide,

Figure 1. Powder X-ray diffraction patterns of (a) the as-prepared sample, (b) the as-prepared sample calcined at 350 °C, and (c) the as-prepared sample calcined at 650 °C.
Figure 2. Scanning electron microscopy images of (a) the as-prepared sample, (b) the as-prepared sample calcined at 350 °C, and (c) the as-prepared sample calcined at 650 °C.

Figure 3. Scanning electron microscopy images of (a) amorphous, (b) anatase phase, and (c) rutile phase titanium dioxide nanomaterials (d) showing the calculation of rod diameters and lengths of (i) anatase phase and (ii) rutile phase titanium dioxide produced.

Figure 4. Energy-dispersive X-ray (EDX) spectrum of the as-prepared sample: (a) area scanned and (b) EDX spectrum.
its anatase phase obtained by calcining at 350 °C, and the rutile phase obtained by calcining at 650 °C are shown in Figure 5.

The UV–vis–NIR spectra of amorphous, anatase, and rutile phases of titanium dioxide nanomaterials obtained in this process are shown in Figure 6a–c, respectively.

The Tauc plots (shown as an inset in each spectrum) obtained from the UV–vis–NIR spectra for amorphous, anatase, and rutile samples give the direct band gaps of 3.40, 3.60, and 3.15 eV, respectively. These values of direct band gaps of anatase and rutile phases of titanium dioxide match exactly with those in the literature.14,15

Interestingly, these results indicate the possibility of the breakage of the well-crystalline ilmenite lattice at a significantly lower temperature of 170 °C, which is applied to the autoclaving system. This is the first report in which ilmenite is totally converted to pure titanium dioxide nanomaterials below 1000 °C. It is possible that the inside pressure is much higher in the close system of an autoclave, thus facilitating the breakage of the lattice. This process also eliminates the usual problem associated with the chloride process where both titanium and iron are dissolved in high concentrations of hydrochloric acid particularly at low temperatures. To eliminate titanium dissolution, a low concentration of hydrochloric acid and high-temperature conditions are preferred.16,17

However, in an open system, these conditions do not favor the breakage of ilmenite lattice. As such, usually chloride process utilizes high temperature of 1000 °C and high HCl concentration of over 12 M. This will result in the complete dissolution of iron and the dissolution of titanium as TiOCl2\(^{2-}\)(aq) and TiOCl\(_2\)(aq) to some extent, as shown in eqs 1 and 2.

\[
\begin{align*}
\text{FeTiO}_3(s) \rightarrow \text{Fe}^{2+}(aq) + \text{TiOCl}_2^{2-}(aq) + 2\text{H}_2\text{O(l)} & \quad (1) \\
\text{FeTiO}_3(s) + 4\text{HCl}(aq) \rightarrow \text{FeCl}_2(aq) + \text{TiOCl}_2(aq) + 2\text{H}_2\text{O(l)} & \quad (2)
\end{align*}
\]

This is a noteworthy problem in the usual chloride process where the wastage due to titanium leaching, recovery of titanium from the leachate, which demands a high cost, and the inability to convert the leachate to pure iron byproducts are difficult to overcome. Titanium dioxide can be precipitated in its polymer form as shown in eqs 3 and 4.

\[
\begin{align*}
\text{TiOCl}_2^{2-}(aq) + (1 + n)\text{H}_2\text{O(aq)} \rightarrow \text{TiO}_2\cdot n\text{H}_2\text{O(s)} + 2\text{H}^+(aq) + 2\text{Cl}^-(aq) & \quad (3) \\
\text{TiOCl}_2(aq) + \text{H}_2\text{O(l)} \rightarrow 2\text{HCl(aq)} + \text{H}_2\text{TiO}_3(s) & \quad (4)
\end{align*}
\]

To rapidly achieve the critical polymerization concentration of Ti(IV), a low concentration of HCl and high temperatures are required. The required high temperature can be maintained in the closed system of an autoclave by maintaining the external temperature at a considerably lower value of 170 °C. Ideally, if ilmenite is composed of pure iron titanite, the above reactions guarantee the separation of pure titanium products by the complete removal of iron from the solid precipitate of Ti(IV) products. However, this situation is far from the reality since natural ilmenite invariably contains other impurities such as silica-trapped inside the ilmenite crystals. Magnetic separation does not completely remove these silica impurities. Therefore, our product also contains these trapped silica impurities, thus giving discoloration instead of pure white TiO\(_2\). To remove these silica impurities, a refluxing process was used in a mild basic medium (0.5 M NaOH) together with

Figure 5. Fourier transform infrared spectra of (a) amorphous, (b) anatase, and (c) rutile phases of titanium dioxide nanomaterials.

Figure 6. UV–vis–NIR spectra of (a) amorphous, (b) anatase, and (c) rutile phase of titanium dioxide nanomaterials obtained in this process. The insets shown in each figure give the Tauc plots for calculating the direct band gaps of the materials.
hydrogen peroxide. Then, the titanium residues react with H2O2 in alkaline condition maintained with NaOH according to eqs 5 and 6 dissolving as titanium sol containing Na2Ti(O2)(OH)2. Under these conditions, silica impurities remain undissolved.

\[
\text{TiO}_2 + n\text{H}_2\text{O}(s) + \text{H}_2\text{O}_2(l) + \text{NaOH}(aq) \\
\rightarrow \text{Na}_2\text{Ti(O}_2\text{)_(OH)_(aq)} + n\text{H}_2\text{O}(l)
\]

(5)

\[
\text{H}_2\text{TiO}_3(s) + \text{H}_2\text{O}_2(l) + \text{NaOH}(aq) \\
\rightarrow \text{Na}_2\text{Ti(O}_2\text{)_(OH)_(aq)} + \text{H}_2\text{O}(l)
\]

(6)

The separated titanium sol is mixed with the surfactant hexadecyltrimethylammonium bromide (HDTMA) at a concentration above its critical micelle concentration and subjected to hydrothermal treatment in a closed system of an autoclave. This will result in the formation of a disordered phase of Na2Ti3O7, which is present in the form of a layered structure. These particles are formed within the micelle structure, leading to a flowerlike morphology of rods emerging in all directions starting from one point as shown in Figure 7.

**Figure 7.** Schematic illustrations of (a) nanorod formation within soft templated micelle structure and (b) surfactant molecule.

The medium is now made acidic and sonicated to result in the formation of H2Ti3O7(s) (eq 7). The surfactant is then removed by washing with copious amounts of ethanol.

\[
\text{Na}_2\text{Ti}_3\text{O}_7(s) + 2\text{H}^+(aq) \rightarrow \text{H}_2\text{Ti}_3\text{O}_7(s) + 2\text{Na}^+(aq)
\]

(7)

The product is then heated at 150 °C to give an amorphous TiO2 (eq 8). Calcination of the amorphous TiO2 at 350 °C gives an anatase nanorod network and at 650 °C gives rutile nanorods.

\[
\text{H}_2\text{Ti}_3\text{O}_7(s) \rightarrow 3\text{TiO}_2(s) + \text{H}_2\text{O}(l)
\]

(8)

It is important to note that this study reveals the use of a closed autoclaving system to break down well-crystalline inorganic mineral structures such as ilmenite under much milder conditions. This method can be easily upscaled for the mass production of pure titanium dioxide from impure natural ilmenite. The byproducts obtained are also useful nanomaterials such as magnetite and zero-valent iron, which are also in their 100% pure form. These results will be presented in a subsequent publication. This simple yet powerful technique can be used to prepare pure nanomaterials from many other natural minerals, enabling low-cost production of technologically and industrially important nanomaterials. Figure 7 gives a schematic representation of the bunches of nanorods formation when a soft template of HDTMA-water is used at the critical micelle concentration of the surfactant HDTMA. TiO2 particles arrange in the spaces provided within the spherical micelle structure. Since they originate from a common base, the nanorods formed are connected at this point, giving rise to flowerlike structure of nanorods when the soft template is removed with ethanol and heat treatment. Further heat treatment leads to the breakage of petals of the flowerlike structure, forming individual nanorods, as clearly shown by the SEM images of the three phases of TiO2. This is the first report of using autoclave under much lower temperatures to make phase-specific TiO2 nanorods from natural ilmenite. Considering the zero emission to the atmosphere and nonpollution of the aquatic resources and enormously reduced cost of the process carried out at 170 °C, this process warrants high feasibility for the industrial-scale production of TiO2 nanorods from natural ilmenite.

**3. CONCLUSIONS**

Simple, low-cost, and environmentally nonhazardous process developed to extract titanium dioxide nanorods in their amorphous state under mild conditions has been presented. Characterization of the material using various analytical techniques showed that the nanorods contain 100% pure TiO2. When calcined at 350 °C for 2 h, the amorphous phase changes to the anatase phase. It can be converted to 100% pure rutile by calcining at 650 °C for 2 h. The byproducts were converted to magnetite and zero-valent iron nanoparticles, and the effluent contains only sodium chloride aqueous solution. Sodium chloride thus produced could be recovered in a saltern when the process is upscaled for industrial production.

**4. EXPERIMENTAL METHODS**

The ilmenite sample provided by the Sri Lanka Mineral Sands Ltd. was run through a magnetic separator (FRANTZ L-1 Isodynamic Magnetic Separator) with a 19° forward angle, a 15° side angle, an applied voltage in the range 17.7 V, and a current of 0.3 A to separate pure ilmenite from mineral sands. Then, the separated pure ilmenite sample was powdered using a dry ball mill to reduce the size to around 100 μm. The powdered ilmenite sample (25 g) was treated in a 70% HCl(aq) (350 mL) at 170 °C for 3 h in a closed system (500 mL total internal volume) to leach out iron using a revolving (horizontal rotation at a rate of 10 rpm) autoclave. It was then filtered using a cellulose nitrate membrane filter (Whatman with 0.2 μm pore size for 20 min), and the sedimented residue was washed by distilled water and then dried at 70 °C overnight in a vacuum oven. The solid residue thus formed was placed in a round-bottom flask and 250 mL of 0.5 M NaOH(aq) was added. Then, 2.0 mL of 30% H2O2(aq) was added to the solution as an oxidizing reagent and the solution was allowed to condense at 40 °C for 1 h under reflux.

Afterward, the resultant mixture was centrifuged for 20 min at 5000 rpm and the supernatant collected. Then, a mixture of hexadecyltrimethylammonium bromide (HDTMA, surfactant 5 g)—water (150 mL)—ethanol (25 mL) at the critical micelle
concentration of the surfactant was added to the supernatant and hydrothermal treatment was reintroduced at 150 °C for 2 h in a closed system using an autoclave. Then, the resultant white powder was filtered using a cellulose nitrate membrane filter (Whatman with 0.2 μm pore size) using distilled water and ethanol. Finally, the resultant dried white powder was ultrasonicated (ROCKET SONER 206H) using acetic acid and distilled water and calcined at 350 °C for 3 h to get the anatase phase and 650 °C for 3 h to get the rutile phase of titanium dioxide nanomaterials.

Figure 8 depicts the (a) complete setup and (b) autoclave used.

The process flowchart involving the entire process containing revolving autoclaving, followed by refluxing and steady autoclaving for obtaining pure titanium dioxide in its amorphous phase and calcining them at 350 °C for obtaining the pure anatase phase material and at 650 °C for obtaining over 99% pure rutile phase is shown in Figure 9.

The products were characterized by powder X-ray diffraction (XRD) using a Bruker D8 Advanced Eco X-ray diffraction system (Cu Kα1 radiation, λ = 1.540598 Å). The morphology was studied by scanning electron microscopy (SEM) using field emission gun (FEG) Quanta 450 FEG microscope operating at 30 kV with Oxford systems nanoanalysis EDX mounted on a FEG electron microscope using Aztec 2.1 as the analyzing software. Fourier transform infrared (FT-IR) spectrophotometer (NICOLET ISS50) was used for the FT-IR transmission spectrum of the powder samples. Also, the samples were characterized by UV–vis–NIR spectrophotometer (SHIMADZU UV-1650 PC) for wavelength-dependent transmittance spectrum and using that spectrum to calculate the direct band gap of each product using the Tauc plot.

Figure 9. Process flow diagram for the conversion of raw ilmenite present in mineral sands to pure titanium dioxide nanomaterials of the desired phases.

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