Microwave plasma assisted sol-gel technique for synthesis of TiO$_2$ nanoparticles

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Abstract. Titanium dioxide (TiO$_2$) nanoparticles have attracted the attention of research community due to their novel functionalities as compared to the bulk material. TiO$_2$ is an excellent photocatalyst due to its high photosensitivity, nontoxicity, high refractive index, strong oxidizing ability, high stability, wide band gap and high resistance to photocatalytic. The main objective of this study was to investigate the influence of microwave (MW) plasma treatment on TiO$_2$ nanoparticles synthesized using sol-gel method. TiO$_2$ nanoparticles were obtained through sol-gel method at ambient temperature. The suspension was heated at 300 °C for 2 hours to evaporate the organic content. The obtained nanoparticles were placed in partially vacuumized chamber for MW plasma treatment. The plasma treatment is a promising technique for oxidation of nanomaterials. Both plasma treated and untreated samples were evaluated with X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV-Visible spectroscopy for crystallite size, crystal phases, band gap energy and surface morphology. The obtained results confirmed the existence of anatase and rutile phases of TiO$_2$ with smaller particle size within the range of 0.2 to 14 nm. The particles were of aggregated and trigonal shapes. The MW Plasma treatment improved the photocatalytic activity of TiO$_2$ nanoparticles by raising their band gap energy and reducing the grain size.

1. Introduction

Titanium dioxide (TiO$_2$) is a white inorganic material. It is environmental friendly, cheap, easy to handle [1], resistive to photochemical and anti-chemical erosion and has high photocatalytic activity [2]. Due to unique electronic structure and light reduced redox phenomenon to act as sensitizers, TiO$_2$ and ZnO have attracted the great attention of the researchers. Among all the semiconductors, TiO$_2$ is widely used as n-type semiconductor [3]. TiO$_2$ nanopowders are also used in cosmetics, glazes, toothpaste, enamels, plastics, paper, fibers, pharmaceuticals, paints [4], antibacterial agents [5-7], foods, friction reducing agent, etc. [8].

TiO$_2$ is found in nature in polymorphs crystalline form, such as stable rutile, brookite and anatase [9]. Brookite phase is rarely synthesized in the laboratory, whereas the other two are widely synthesized in the laboratory. Anatase is a low temperature and chemically stable phase whereas rutile is a thermodynamically substantial form of TiO$_2$. Anatase can be converted in rutile at higher temperatures through phase transformation. This transformation from anatase to rutile happens at high temperatures higher than 400 °C [10]. However, this phase transformation can happen at ambient temperature under optimized synthesis parameters [11].
Physical and chemical properties of TiO$_2$ are related to its crystalline phase, size, and morphology [12]. TiO$_2$ nanoparticles adsorb enough dye molecules, consequently, produce large number of photons for current conversion efficiency. The photo-electrodes, coated with TiO$_2$, usually have higher transparency [13, 14]. Enough visible light can be transmitted through these materials. The smaller particle size results in only negligible scattering of light [15, 16]. Single phase TiO$_2$ has fewer application as compare to the mixed phase TiO$_2$ consisting of anatase and brookite phases.

Numerous methods have been reported during last few years to synthesize TiO$_2$. These methods include atomic layer deposition, chloride process, sol-gel route [17], direct oxidation of TiCl$_4$ [18, 19], chemical vapor deposition, hydrothermal method [20], liquid flame spray [21-23], sulfate process [24], and electrospinning method [25, 26]. Each technique has some merits and demerits [27]. Comparatively, sol-gel is a low cost and most commonly used method for synthesis of TiO$_2$ nanoparticles [28]. Different morphology of TiO$_2$ nanoparticles can be obtained with this technique. The morphologies include nanosheets, nanoparticles, nanowires, nanotubes, nanorods, mesoporous and aerogel [29]. The plasmas discharges are also being used to tailor the surface chemistry of such materials. A survey of the published literature shows scant information about the effect of plasma assisted calcination on the structural and optical properties of the metal oxide nanoparticles. Therefore, this research was carried out with the following objectives: (i) to synthesize the titanium dioxide nanoparticles through a sol-gel technique, (ii) to remove the dried gel, oxides and other impurities from the nanoparticles through MW plasma exposure and (iii) to study the effect of plasma treatment on the surface morphology, chemical composition and size distribution of the nanoparticles.

2. Materials and methods

2.1. Chemicals

The chemicals, used to prepare TiO$_2$ nanoparticles, were titanium tetra iso-propoxide (TTIP) C$_{12}$H$_{28}$O$_4$Ti (98.0%, company Dae-Jung, Korea) as precursor, Isopropanol (C$_3$H$_7$OH, Riedel-deHaen, extra pure) as solvent, Nitric acid (HNO$_3$ 68%, Huchems fine chemical corp. Korea) as stabilizers and deionized water as dispersing media [10, 30].

2.2. Synthesis of TiO$_2$ nanoparticles

TiO$_2$ nanoparticles were obtained by sol gel method in the presence of nitric acid (HNO$_3$) as a stabilizer. Titanium tetra isopropoxide (TTIP) and 2-propanol were used as starting materials. Solution A was prepared by mixing 24 mL of deionized water and 20 mL of iso-propanol [30, 31]. Solution B was obtained by dripping titanium tetra-isopropoxide in solution A and was continuously stirred on a magnetic hot plate at ambient temperature. After 1 hour of stirring, 0.5 ml of HNO$_3$ was added to the solution B and stirred continuously for 6 hours. During first 3 hours, a milky white solution was transformed into a transparent white solution known as sol. In next 3 hours, the viscous solution (sol) transformed into viscous gel. The obtained gel was subjected to continuous heating for 2 hours at 300°C. The organic content evaporates from gel during heating. Finally, TiO$_2$ was obtained in the form of nanocrystals, which were grinded using pestle mortar. The dried TiO$_2$ powder was placed inside a partially vacuumized chamber to perform MW plasma treatment. The plasma of oxygen gas was sustained with a 2.45 GHz microwave source. The TiO$_2$ sample was exposed to the plasma for fixed time of 5 minutes. The flowchart for the preparation of TiO$_2$ nanoparticles is shown in figure 1.

2.3. Characterization

SEM, XRD and UV-Visible techniques were used to evaluate the surface morphology, composition, structures, phases and size of MW plasma treated TiO$_2$ nanoparticles. The particle size was calculated using Scherrer formula:

$$D = \frac{\lambda K}{\beta \cos \theta}$$  \hspace{1cm} (1)
where $D$ is grain size, $K$ is the constant of shape factor ($K=0.89$), $\beta$ is full width half maximum (FWHM) in radian and $\lambda$ is the X-ray wavelength for Cu target K$\alpha$ radiations and $\theta$ is the Bragg's diffraction angle.

UV-Visible analysis was carried out to study the effect of different stabilizers on optical properties of TiO$_2$ nanoparticles. The band gap energy ($E_g$) was determined from the optical absorption spectra by using the equation (2).

$$E_g = \frac{1240}{\lambda} \text{eV}$$  

where $E_g$ represents the band gap energy electron volts (eV) and $\lambda$ is the wavelength of absorption edge obtained from the spectrum.

![Flowchart of synthesis of TiO$_2$ nanoparticles through plasma assisted sol-gel method.](image)

**Figure 1.** Flowchart of synthesis of TiO$_2$ nanoparticles through plasma assisted sol-gel method.

3. Results and discussion

### 3.1. Structural analysis

XRD spectra of TiO$_2$ samples was generated to study the particle size and crystalline phases. XRD spectra confirmed the formation of different phases of TiO$_2$. The major phases were anatase and rutile [32]. Figure 2 Shows XRD pattern of TiO$_2$ sample with peaks at 2\(\theta\) = 25.28°, 27.19°, 36.06°, 36.94°, 37.66°, 38.60°, 41.33°, 47.94°, 54.30° and 56.70°. These peaks correspond to (011), (110), (101), (013), (004), (112), (111), (020), (211) and (220) planes of TiO$_2$. The peaks corresponding to planes (011), (013), (004), (112) and (200) indicates the anatase phase whereas (110), (101), (111), (211) and (220) planes represent the rutile phase of TiO$_2$. The observed peaks and planes were in good match with the
standard (JCPDS no: 21-1272 and 21-1276) [33]. XRD analysis revealed 68% anatase phase and 32% rutile phase of TiO$_2$ [34].

The particle size was calculated using Scherrer’s formula. The size was remained in the range of 0.2 nm to 14 nm, which is much smaller as compared to conventional sol-gel method. The conventional sol-gel approach produced the particle sizes almost 2 times larger than the plasma assisted sol-gel approach. The particle size distribution of plasma treated, and untreated nanoparticles is given in table 1.

![Figure 2. XRD spectrum of MW plasma treated TiO$_2$ nanoparticles.](image)

| $2\theta$ (deg.) | Particle size of untreated sample (nm) | Particle size of plasma treated sample (nm) |
|------------------|----------------------------------------|-------------------------------------------|
| 25.28            | 3.99                                   | 7.18                                      |
| 27.19            | 5.32                                   | 9.57                                      |
| 36.06            | 0.23                                   | 0.41                                      |
| 36.94            | 14.21                                  | 25.57                                     |
| 37.66            | 5.47                                   | 9.84                                      |
| 38.60            | 3.98                                   | 7.16                                      |
| 41.33            | 10.49                                  | 18.82                                     |
| 47.94            | 4.41                                   | 7.98                                      |
| 54.30            | 6.61                                   | 11.98                                     |
| 56.70            | 8.84                                   | 15.12                                     |
3.2. **SEM analysis**

Figure 3 shows SEM micrographs of untreated and plasma treated TiO$_2$ nanoparticles. Most of the nanoparticles in untreated sample exist in the form of nano-rocks. On plasma treatment, these nano-rocks break into nanoparticles. The size of nanoparticles almost reduces by half after plasma treatment. SEM Images clearly reveal a change in the surface morphology of plasma treated TiO$_2$ nanoparticles.

![Figure 3. SEM micrographs of; (a) untreated and (b) plasma treated TiO$_2$ nanoparticles.](image)

3.3. **UV-Visible analysis**

Figure 4 shows a typical absorption spectrum of plasma treated TiO$_2$ nanoparticles. UV-Visible study was conducted to evaluate the opto-electric properties of plasma treated TiO$_2$ nanoparticles. The band gap energy ($E_g$) was computed using equation (2) [35]. The plasma treated TiO$_2$ exhibited UV-resistance up to absorption edge wavelength of 200.55 nm. The band gap energy, corresponding to this wavelength, was calculated about 6.18 eV. This energy was almost 1.8 times higher than the band gap energy of untreated nanoparticles. The photocatalytic activity of nanomaterial semiconductors depends on the band gap energy, which is governed by the particle size. These results reveal that plasma treated TiO$_2$ nanoparticles have higher photocatalytic activity due to larger band gap energy and smaller grain size.

![Figure 4. Typical UV-Visible spectrum of plasma treated TiO$_2$ nanoparticles.](image)
4. Conclusion
Plasma assisted sol-gel is a promising technique for production of nanoparticles of controlled sizes. The size of nanoparticles, synthesized through plasma assisted sol-gel, remained in the range of 0.2 nm to 14 nm. The particle sizes obtained through conventional sol-gel method were two times larger than those obtained through plasma assisted sol-gel technique. Most of the nanoparticles in untreated sample existed in the form of nano-rocks. On plasma treatment, these nano-rocks broke into smaller nanoparticles. The size of nanoparticles almost reduces by half after plasma treatment. The band gap energy of plasma treated nanoparticles was calculated about 6.18 eV. This energy was almost 1.8 times higher than the band gap energy of untreated nanoparticles. The plasma treated TiO$_2$ nanoparticles showed higher photocatalytic activity due to larger band gap energy and smaller grain size.

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