Effects of pure and mixed stabilizers on opto-electrical properties and morphology of TiO$_2$ nanoparticles synthesized by sol-gel method

M Ayyaz$^1$,*, N U Huda$^1$, F Rasool$^1$, H Sami-ur-Rehman$^1$, A Mehmood$^2$, M Y Naz$^1$, S Shukrullah$^1$ and A Ghaffar$^1$

$^1$Department of Physics, University of Agriculture Faisalabad, 38040 Faisalabad, Pakistan.
$^2$Department of Chemistry, Government College University Faisalabad, Punjab 38000, Pakistan.

*E-mail: muhammadayyaz333@yahoo.com

Abstract. Titanium dioxide (TiO$_2$) is acknowledged as the most advanced nanomaterial. It has been used in certain application, such as semiconductor, photocatalyst, dye solar cells, paints, dyes, cosmetics, antifogging coatings, self-cleaning windows, etc. Although TiO$_2$ nanoparticles occur naturally in mineral form, but the particles are also being synthesized through different well-known techniques. The past literature reveals that sol-gel methodology is considered as the most attractive and suitable technique for the preparation of such kind of nanoparticles. This article reports the effects of three different stabilizers (HCl, HNO$_3$ and mixture of HCl+HNO$_3$) on the morphological and opto-electrical properties of TiO$_2$ nanoparticles. The nanoparticles of TiO$_2$ were synthesized through sol-gel process by using titanium tetra isopropoxide (TTIP) as precursor in a solution of deionized water and isopropanol at 80 °C under constant stirring. The synthesized TiO$_2$ nanoparticles were characterized through X-ray Diffractometry (XRD), Scanning electron microscopy (SEM) and UV-Visible spectrophotometry. The grain size with perfect crystallinity obtained through XRD were in good agreement with SEM results. The grain size of the prepared TiO$_2$ nanoparticles using HCl, HNO$_3$ and (HCl+HNO$_3$) were 3 nm, 2.8 nm and 3.3 nm, respectively. The optical characterization of TiO$_2$ revealed band gap energy values of 4.10 eV, 6.16 eV and 6.14 eV corresponding to absorption edges at 302 nm, 201.2 nm and 201.73 nm, respectively. The smaller grain sizes were having larger band gaps.

1. Introduction

TiO$_2$ is known as an inert and safest material and has been utilized for various applications in optical, electrical, magnetic and chemical fields [1, 2]. The particles of TiO$_2$ also known as ultrafine powder of titanium dioxide, are the particles with diameter lower than 100 nm [3]. This ultrafine powder of TiO$_2$ is also utilized as part of sunscreens due to its ability of blocking UV radiations coming from sun and it remains transparent to the skin. Its properties of photocatalytic sanitizing and applications in dye solar cells, paints, dyes, cosmetics, medicates, varnishes and nano fabrics make it more suitable for antifogging coatings and self-cleaning windows [3-5]. It known as the second most advanced nanomaterial in extremely using products after introduction of silver nanoparticles. Owing to its immense usage in commercial and technological applications, TiO$_2$ is known as “legacy nanomaterial”
[5-7]. The nanoparticles of TiO$_2$ are used on large scale for catalytical degradation of organic materials as catalyst, sensor technology and for chemical conversions in solar cells as photo catalyst [8-10].

A variety of techniques has been used to synthesize TiO$_2$ nanoparticles, such as wet chemical method, precursor method, coprecipitation method, solution route, microemulsion technique, sol-gel method and solvothermal method [11, 12]. Comparison of these methods shows that sol-gel approach is the most attractive and suitable technique for the preparation of nanoparticles due to its convenient features such as it is versatile in processing, it has extended composition ranges, stability, better homogeneity and low energy consumption for processing [13-15].

Sol gel technique is also termed as polymerization process because of its intrinsic nature [16], which involves conversion of monomers into a transparent colloidal solution known as “Sol”. The sol is converted into viscous gel after further processing [17, 18] as shown in figure 1. A metal-oxo-polymer network (gel) is obtained from molecular precursors, such as metal salts or metal alkoxides [19]. Recently, Mahshid et al. [20] analysed the effects of pH on the particle size of TiO$_2$ nanoparticles prepared by the hydrolysis of TTIP. They observed that the particle shape was totally spherical because of the poor agglomeration due to acidic condition. Behnajady et al. studied the effect of different precursors and different solvents under different synthesis conditions utilizing the sol gel approach [21]. It was revealed that the grain size and rutile phase increase and anatase decreases with the change of solvent type along with increased photo-catalytical activities of TiO$_2$. They used TTIP instead of TBOT (Titanium butoxide). Nadzirah et al. [22] studied the role of three different stabilizers in preparation of TiO$_2$ films via sol gel method. It was predicted that Acetic acid stabilized TiO$_2$ films are more suitable for biosensor applications due to their surface roughness and electrical stability while HCl stabilized films were suggested to be used in photosensor applications due to their smooth surface. However, monoethalmine acid (MEA) stabilized TiO$_2$ films were suggested to be useless in electrical applications due to their low stability of electrical properties.

![Figure 1. Schematic of sol-gel approach.](image)

Although, the effect of some stabilizers on TiO$_2$ in sol gel method has been studied [22, 23] but the comparative study of the effects of pure and mixed stabilizers on TiO$_2$ nanoparticles under the sol gel method is still unclear. The main objective of this work was to synthesize the TiO$_2$ nanoparticles through sol gel approach by using three different stabilizers (HCL, HNO$_3$ and mixture of HCL and HNO$_3$) and titanium tetra isopropoxide as precursor.

2. Materials and methods

2.1. Chemicals

Chemicals used to prepare TiO$_2$ nanoparticles, were titanium tetra iso-propoxide (TTIP) C$_{12}$H$_{26}$O$_4$Ti (98.0%, from Dae-Jung, Korea) as precursor, Isopropanol (C$_3$H$_6$OH, Riedel-deHaen, extra pure) as solvent, Hydrochloric acid fuming (HCL, Merck Germany, 37% extra pure) Nitric acid (HNO$_3$ 68%, Huchems fine Chemical Corp. Korea) as stabilizers and deionized water as dispersing media [18, 24].

2.2. Synthesis of TiO$_2$ powder

To prepare TiO$_2$ using HCl as stabilizer, firstly, a 45 mL solution was prepared by mixing 30 mL of isopropanol as solvent with 15 mL of deionized water as dispersing media. The solution was kept under constant stirring at the temperature of 80 °C and 30 mL of TTIP was dissolved as a precursor drop wise
to the solution \[18\]. After 1 hour, the temperature was reduced from 80 °C to 60 °C and a water-acid mixture (1.5 mL of HCL diluted with 50 mL deionized water) was mixed up with the TTIP dissolved solution. White thick precipitates were formed, which on continuous stirring turned into a transparent and stabilized white sol after 3 hours. The resulting sol was stirred continuously for 150 minutes to complete the process of hydrolysis and condensation. The obtained gel was annealed at 300 °C in open atmosphere for 2 hours to obtain TiO$_2$ nanocrystals. Finally, the resulted nanocrystals of TiO$_2$ were grinded for 45 minutes to obtain the fine powder of TiO$_2$ nanoparticles.

For synthesis of TiO$_2$ nanoparticles with HNO$_3$ as a stabilizer, 40 mL solution was prepared from 25 mL Isopropanol and 15 mL deionized water under constant stirring at 80 °C. Thereafter, 25 mL solution of TTIP was added drop wise to the prepared solution under continuous stirring. After 1 hour, the temperature was reduced from 80 °C to 60 °C and a water-acid mixture consisting of 1.5 mL of HNO$_3$ diluted with 60 mL deionized water, was added to the TTIP mixed solution under continuous stirring \[22\]. After 90 minutes of processing, the solution turned into a transparent white sol. The resulted sol was stirred continuously for 150 minutes to convert it into a viscous sol-gel. The obtained gel was dried at 300 °C in open atmosphere to obtain TiO$_2$ nanoparticles. The obtained nanoparticles were grinded using piston mortal for 45 minutes to obtain fine powder of TiO$_2$ nanoparticles.

Similarly, to obtain TiO$_2$ nanoparticles with a mixture of HCL and HNO$_3$ as stabilizer, 40 ml solution was prepared from 25 mL of Isopropanol and 15 mL of deionized water at 80 °C under continuous stirring. Thereafter 30 mL of TTIP was added drop wise to the solution under continuous stirring. After 1 hour of processing, the temperature was decreased from 80 °C to 60 °C and 61.4 mL of water acid mixture (0.6 mL HCL + 0.8 mL HNO$_3$) diluted with 60 mL of deionized water was added to TTIP mixed solution under continuous stirring. The solution turned into a transparent white sol after 90 minutes. The obtained sol was stirred continuously until it converts into a viscous gel after 2 hours. The resulted sol-gel was annealed at 300 °C for 2 hours in open air and nanocrystals of TiO$_2$ were obtained, which were grinded for 45 minutes to obtain fine powdered TiO$_2$ nanoparticles \[25\]. A flowchart of synthesis of TiO$_2$ nanoparticles is given in figure 2.

![Flowchart of synthesis of TiO$_2$ nanoparticles](image_url)

**Figure 2.** Flowchart of preparation of TiO$_2$ nanoparticles using sol-gel method.
3. Results and discussion

3.1. Structural properties

XRD was used to analyze TiO$_2$ samples synthesized with three different stabilizers. In figure 3, XRD spectra confirmed the formation of TiO$_2$. The diffraction peaks were observed in the angle range of $18^\circ \leq 2\theta \leq 60^\circ$. TiO$_2$ samples were crystalline in nature and composed of anatase and rutile phases. The HCl stabilized nanoparticles produced XRD peaks at 25.23°, 36.78°, 37.48°, 38.49°, 48.03°, 53.70° and 54.96° with corresponding anatase phases as (011), (013), (004), (112), (111), (020), (015) and (121), respectively. Similarly, XRD peaks at 27.29°, 35.80°, 38.97°, 40.91°, 43.68°, 53.68°, and 56.27° produced rutile phases as (110), (101), (200), (111), (120), (211) and (220), respectively.

The HNO$_3$ stabilized nanoparticles produced XRD peaks at 25.24°, 36.77°, 37.63°, 38.53°, 40.88°, 47.95°, 53.77°, and 55.00° with corresponding anatase (h k l) values of (011), (013), (004), (112), (111), (020), (015) and (121), respectively. The XRD peaks at 27.22°, 35.81°, 38.94°, 40.88°, 43.73°, 53.89° and 56.24° represented (110), (101), (200), (111), (120), (211) and (220) phases of rutile TiO$_2$.

Similarly, (HCl+HNO$_3$) stabilized nanoparticles produced XRD peaks at 25.18°, 36.83°, 37.74°, 38.57° and 48.00° with corresponding (h k l) values (011), (013), (004), (112) and (020), respectively.

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**Figure 3.** XRD spectra of TiO$_2$ synthesized with different stabilizers.

The HNO$_3$ stabilized nanoparticles produced XRD peaks at 25.24°, 36.77°, 37.63°, 38.53°, 40.88°, 47.95°, 53.77°, and 55.00° with corresponding anatase (h k l) values of (011), (013), (004), (112), (111), (020), (015) and (121), respectively. The XRD peaks at 27.22°, 35.81°, 38.94°, 40.88°, 43.73°, 53.89° and 56.24° represented (110), (101), (200), (111), (120), (211) and (220) phases of rutile TiO$_2$.
which belong to anatase phase. The XRD peaks at 27.26°, 35.77°, 38.91°, 40.92°, and 43.71° presented the (110), (101), (200), (111) and (120) phases of rutile TiO$_2$. The most intense XRD peak was observed at 25.24°, which was used to calculate the particle size. This peak belongs to tetragonal anatase and rutile phase. The lowest peak intensity was observed at 25.18° by using mixed stabilizer. The particle size was calculated using Scherrer formula [24, 26]:

$$D = \frac{\lambda K}{\beta \cos \theta}$$  \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. Using above equation (1), the determined particle sizes are given in table 1.

Table 1. Influence of different stabilizers on crystallite size of TiO$_2$.

| Stabilizer   | Solvent    | Precursor | Annealing Temperature | 2\(\theta\) (Deg.) | Particle size (nm) |
|--------------|------------|-----------|-----------------------|---------------------|--------------------|
| HCl          | Isopropanol| TTIP      | 300°C                 | 37.48°              | 3.0                |
| HNO$_3$      | Isopropanol| TTIP      | 300°C                 | 37.63°              | 2.8                |
| HCl+HNO$_3$  | Isopropanol| TTIP      | 300°C                 | 25.18°              | 3.3                |

3.2. **SEM analysis**

SEM micrographs of TiO$_2$ nanoparticle samples are shown in figure 4. Irregular shapes of nanoparticles were seen in SEM micrographs, specifically for those synthesized with HCl and HCl+HNO$_3$ stabilizers. The nanoparticles, synthesized with HNO$_3$ stabilizer, were relatively smaller in size and but more agglomerated. However, particle size was uniform as compared to other two samples.

![Figure 4](image_url)

Figure 4. SEM micrographs of TiO$_2$ nanoparticles synthesized with: (a) HCl, (b) HNO$_3$, and (c) HCl+HNO$_3$ stabilizers.
The nanoparticles, synthesized with HCl and HCl+HNO$_3$ stabilizers, were poorly agglomerated. These particles revealed sharp rock like edges [20, 27]. Some soot or tiny buds were also seen on these nanoparticles. We could not study these buds due to limited magnification of SEM equipment, however, these buds might be oxidized form of the nanomaterial.

3.3. **UV-Visible analysis**

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:

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

where $E_g$ represents the band gap energy electron volts (eV) and $\lambda$ is the wavelength of absorption edge obtained from the spectrum [28, 29]. Figure 5 shows the absorption spectra of nanoparticle samples obtained with 3 stabilizers.

![Graphs showing UV-Visible spectra of TiO$_2$ nanoparticles with different stabilizers](image)

**Figure 5.** UV-Vis spectra of TiO$_2$ nanoparticles synthesized with: (a) HCl, (b) HNO$_3$, and (c) HCl+HNO$_3$ stabilizers.
The band gap energy of nanoparticles was calculated about 4.10 eV, 6.16 eV and 6.14 eV for HCl, HNO$_3$ and HCl+HNO$_3$ stabilizer, respectively. As the particle size decreases, the corresponding band gap increases and absorption edge seems to be shifted towards higher energy end (blue shift) [30].

The nanoparticles, stabilized with HCl, show absorbance up to wavelength of 302 nm. The nanoparticles, stabilized with HNO$_3$, show absorbance up to wavelength of 201.2 nm. Similarly, the nanoparticles stabilized with HCl+HNO$_3$ mixture exhibit absorbance up to wavelength of 201.73 nm.

4. Conclusion
In this work, TiO$_2$ nanoparticles were synthesized through sol-gel method by using three different stabilizers. Sol-gel is the most suitable technique for synthesis of such kind of nanomaterials due to its low cost and low process temperature. The minimum time to develop a sol was 90 minutes, which was converted into gel after 2 hours of processing with HCl+HNO$_3$ stabilizer. Irregular shapes of nanoparticles were seen in SEM micrographs, specifically for those synthesized with HCl and HCl+HNO$_3$ stabilizers. The nanoparticles, synthesized with HNO$_3$ stabilizer, were relatively smaller in size and but more agglomerated. However, particle size was uniform as compared to other two samples. The band gap energy of nanoparticles was calculated about 4.10 eV, 6.16 eV and 6.14 eV for HCl, HNO$_3$ and HCl+HNO$_3$ stabilizer, respectively. As the particle size decreases, the corresponding band gap increases and absorption edge shifts towards higher energy end (blue shift).

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