Facile synthesis and growth mechanism of mesoporous anatase titanium dioxide nanoparticles via sol-gel method

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Abstract. An investigation on the synthesis of highly monodispersed mesoporous anatase titanium dioxide (TiO$_2$) nanoparticles has been reported in this work. The mesoporous nanoparticles were obtained by a facile sol-gel method where titanium isopropoxide (TTIP) was used as the titanium precursor in basic solution. Here, the effect of reaction time was studied to study the growing mechanism of TiO$_2$ nanocrystal. The as-synthesized nanoparticles were characterized with X-Ray Diffraction (XRD), Fourier Transform Infrared (FTIR), Brunauer-Emmett-Teller (BET) Surface Area Analyzer, and High Resolution Tunneling Electron Microscopy (HR-TEM). Based on the result, it is found that a highly monodispersed mesoporous anatase TiO$_2$ nanoparticles with large surface area could successfully be synthesized. It is also believed that the morphology of as-synthesized particles could easily be controlled by the reaction time. Results show that uniform mesoporous TiO$_2$ nanoparticles with perfect spherical morphology could be obtained when the reaction was performed in 3 hours of reaction time.

1. Introduction
Over the last several decades, nanostructured titanium dioxide (TiO$_2$) has attracted many interests due to its excellent physical and chemical properties [1]. Studies have reported that TiO$_2$ nanoparticles with high surface area could potentially be useful in many different applications such as photocatalysis, electronics, sensing devices, and renewable energy generation [2–4]. It is believed that the ability to control particle size distribution, morphology, crystallographic structures, and phases, as well as porosity of TiO$_2$ nanoparticles has been the important key factor in obtaining the desired intrinsic properties of such material [5]. For instance, Jang and co-workers have reported that particle size distribution and phase composition of TiO$_2$ nanoparticles had a significant influence in its photocatalytic activity against various types of dyes [6]. It is believed that the smaller the particle size distribution of TiO$_2$ nanoparticles, the better the photocatalytic activity [5–6]. Therefore, many efforts have been carried out to develop a facile method for the synthesis of TiO$_2$ nanostructures, which allows one to control the aforementioned properties.

Typically, there are three main crystalline phases of TiO$_2$, i.e. rutile, anatase, and brookite. Among these three crystalline phases, anatase has attracted many attentions due to its high thermodynamic stability and ability to show an excellent photocatalytic activity in comparison to other phases [5]. In industry, TiO$_2$ is commonly manufactured by treating ilmenite mineral (FeO•TiO$_2$) at acidic condition to produce titanyl sulfate (TiOSO$_4$), which further hydrolyzed to anatase or/and rutile crystals in hydrothermal condition [7]. Nevertheless, fabrication of large-scale TiO$_2$ using such method still posts several disadvantages such as the inability to control particle distribution and morphology of the crystal, the potential of obtaining mixed crystal phases, relatively high cost, and not environmentally friendly. Hence, an alternative synthetic method for the fabrication of large-scale TiO$_2$ nanoparticles...
that enables full control of various parameters such as particle size and crystalline phase is highly desired.

According to literature, the sol-gel method is considered as one of the most frequently used technique to prepare TiO₂ nanoparticles with full control in particle size distribution and crystalline phase [6]. The precipitate from the sol-gel method is typically in the form of amorphous TiO₂. However, it can further be transformed into various crystal phases using calcination process. In this work, a facile sol-gel method at basic condition was developed in order to prepare mesoporous anatase TiO₂ nanoparticles where titanium(IV) isopropoxide (TTIP) was used as the titanium precursor. Here, the effect of reaction time was also studied towards the particle size and crystalline phase of the product in order to provide a better insight into the particle's growth mechanism.

2. Materials and methods

2.1. Materials
TTIP (CAS Number 546-68-9) was used as the starting material and purchased from Sigma-Aldrich (purity: 97 %). NH₄OH solution (28–30 % NH₄ in H₂O) (CAS Number 1336-21-6) and ethanol absolute (CAS Number 64-17-5) were also purchased from Sigma-Aldrich and used in the synthesis of TiO₂ nanoparticles.

2.2. Synthesis of mesoporous anatase TiO₂ nanoparticles
Mesoporous anatase TiO₂ nanoparticles were synthesized according to a method reported by Li and co-workers [8]. However, TTIP was used as titanium precursor instead of tetrabutyl titanate. In this work, the nanoparticles were synthesized by dropwise addition of 0.75 mL TTIP into a mixture of 100 mL absolute ethanol and 0.3 mL NH₄OH. The mixture was then vigorously stirred at 45 °C for (3, 6, 12, and 24) hours. The resulting suspension was then centrifuged at 6000 rpm and the obtained white precipitates were collected and dried in an oven at 60 °C for overnight. Finally, the resulting white powder was then calcinated at 450 °C for 2 hours and used for further investigation.

2.3. Characterization
To investigate the physical and chemical properties of the as-synthesized mesoporous anatase TiO₂ nanoparticles, several characterization techniques were carried out. To study the crystallographic structure of the as-synthesized nanoparticles, X-ray Diffraction (XRD) analysis was done using PANalytical X’Pert Pro MPD (PANanalytical B.V., Almelo, Netherlands) equipped with fast detector X’Celerator. The measurement was performed using Cu Kα radiation as the X-ray source. Meanwhile, Fourier-transform Infrared spectroscopy (FTIR) analysis was done using Shimadzu IR Prestige 21. Brunauer-Emmett-Teller (BET) surface area and adsorption-desorption isotherm were measured using QUADRASORB evo (Quantachrome Instruments) equipped with FloVac Degasser. Before BET analysis, the samples were degassed at 300 °C for 3 hours. Finally, micrographic images of the nanoparticles were collected using TECNAI G2 Spirit Twin High Resolution-Transmission Electron Microscope (HR-TEM).

3. Results and discussion

3.1. Synthesis of mesoporous anatase TiO₂ nanoparticles
In this study, the effect of reaction time during sol-gel synthetic method to the formation of anatase crystal phase was firstly investigated. Figure 1 shows both XRD pattern and FTIR spectra of the as-synthesized TiO₂ nanoparticles at different reaction time. Based on the result, it is demonstrated that all of the obtained white powder after calcination process. Based on the result, it can be observed that the reaction time has contributed no effect on the type of crystalline phase of the reaction product. All the Bragg peaks in XRD diffractogram suggest that the main crystal phase of the reaction product was anatase and no other peak was obtained for both rutile or brookite phases (JCPDS, No. 21-1272) (figure 1a). Furthermore, peak broadening of (101) anatase phases also suggests an indication that very small grain particles were formed during the reaction. It is believed that, even though rutile is widely known as the most thermodynamically stable crystal phase of TiO₂ in bulk, anatase is the preferred phase when the surface is of TiO₂ becomes very large due to the reduction of grain size into nanoscale [9]. Furthermore, the formation of TiO₃ is also supported by the result from FTIR analysis. Based on the result in figure 1b, it is shown that all reaction products synthesized at different reaction time
rendered a very similar IR spectrum containing a strong IR peak at 650 cm\(^{-1}\) specifics for the lattice vibration of Ti-O-Ti stretching. In addition, the peaks at 3300 cm\(^{-1}\) and 1627 cm\(^{-1}\) could also be ascribed for O-H bending and stretching modes, respectively, in surface OH terminal groups or water molecules [8].

Furthermore, the surface physical properties of the as-synthesized TiO\(_2\) nanoparticles were also studied by investigating their adsorption-desorption isotherm using BET surface area analysis. Figure 2 shows the adsorption-desorption isotherm of the as-synthesized TiO\(_2\) obtained different reaction time. Based on the result, it can be observed that all reaction products follow type V of N\(_2\) adsorption-desorption isotherm, which indicates the mesoporous feature of the TiO\(_2\) nanoparticles [5,10]. In addition, the hysteresis loop of the isotherm seems to shift towards higher relative pressure when the sol-gel reaction was carried out more than 3 hours. This suggests that the surface morphology of the obtained mesoporous TiO\(_2\) nanoparticles becomes irregular with the increment of sol-gel reaction time. Moreover, it is also reasonable to believe that hysteresis loop could be attributed to the total contribution of both inter-particles and intra-particles pores due to the mesoporous and nanoparticles co-exist features [5].

In addition, BET surface area and Barret-Joyner-Halenda (BJH) desorption parameters, i.e. pore volume and pore radius were found to be increasing with reaction time (table 1). However, when the reaction was carried out for 24 hours, both BET surface area and BJH parameters were decreased. It is believed that this phenomenon occurs mainly due to the presence of both mesoporous and nanoparticles features [5]. As a result, this coexists two features would result in the formation of bimodal pore distribution consisting of smaller inter-particles and larger intra-particle pores. At low sol-gel reaction time (less than 12 hours), it is believed that the particles are in a regular morphologic feature causing the smaller inter-particles pores becomes predominant. Whereas, longer reaction time would render a more irregular particle assembly causing larger intra-particles pore as the major feature rather than smaller inter-particle pore.

3.2. Growth mechanism

To further study the effect of sol-gel reaction time towards the growth mechanism of the mesoporous anatase TiO\(_2\) nanoparticles, investigation of micrographic images obtained from HR-TEM was also carried out. Figure 3 presents the TEM images of the as-synthesized mesoporous TiO\(_2\) nanoparticles obtained at various reaction time. Based on the result, it is observed that the morphology of the as-prepared mesoporous TiO\(_2\) nanoparticles was significantly affected by the duration of the sol-gel reaction time. Observation under an electron microscope revealed that perfectly spherical particle...
Table 1. BET surface area and BJH desorption parameters of the as-synthesized TiO$_2$ nanoparticles.

| Reaction time (h) | BET surface area (m$^2$/g) | BJH desorption parameters |
|-------------------|-----------------------------|---------------------------|
|                   |                             | Pore volume (cc/g) | Pore radius (Å) |
| 3                 | 42.197                      | 0.067                     | 19.313          |
| 6                 | 99.281                      | 0.229                     | 36.115          |
| 12                | 108.627                     | 0.240                     | 31.195          |
| 24                | 72.427                      | 0.104                     | 19.376          |

Figure 2. N$_2$ adsorption-desorption isotherm of the as-synthesis TiO$_2$ nanoparticles from sol-gel method at (a) 3, (b) 6, (c) 12, and (d) 24 hours of reaction time.

morphology could be obtained when the reaction was carried out less than 6 hours (figure 3a and figure 3b). From the result, the average diameter of the as-synthesized mesoporous TiO$_2$ nano-sphere particles obtained from 3 h and 6 h sol-gel reaction time were found to be ~457.55 nm and ~649.59 nm, respectively. It is believed that these TiO$_2$ nano-sphere particles were formed by self-assembly of many small TiO$_2$ nanoparticles seeds (ø = ~5-10 nm) during sol-gel reaction. As a result, the longer the reactions time the bigger the size of the obtained nanoparticles. Furthermore, this self-assembly is also thought to be responsible for the formation of intra-particle pores, which contributed to the overall mesoporous feature of the as-synthesized TiO$_2$ nanoparticles.

Nevertheless, TEM images also revealed that a more uniform particle size distribution was obtained when the reaction was carried out for 6 hours instead of 3 hours. This phenomenon could be understood by assuming that, at 6 hours sol-gel reaction time, the LaMer’s crystal growth mechanism
Figure 3. TEM images of the as-synthesized mesoporous TiO₂ nanoparticles obtained at various sol-gel reaction time, i.e. (a) 3, (b) 6, (c) 12, and (d) 24 hours (scale bar: 200 nm); and (e) HR-TEM images of TiO₂ obtained from 24 hours sol-gel reaction.

Scheme 1. The proposed schematic growth mechanism of anatase TiO₂ nanoparticles during the course of sol-gel reaction.

has already passed the rapid self-nucleation process and reached the steady-state crystal growth process [11]. As a result, the remaining seed particles would preferably coalesce onto smaller particles clusters due to their higher surface energy creating a very narrow overall particle size distribution. However, when the sol-gel reaction proceeded at longer reaction time and all the remaining seed particles have been used during steady-state crystal growth, the adjacent particle clusters would further coalesce to form more irregular larger cluster particles via Ostwald ripening process [12]. This is proven by the fact that no specific particle morphology could be obtained when the reaction was carried out for 12 and 24 hours (figure 3c and figure 3d). Therefore, the overall proposed schematic growth mechanism of mesoporous anatase TiO₂ nanoparticles during the course of the sol-gel reaction could be illustrated according to scheme 1.

4. Conclusions
In summary, a facile method for the synthesis of mesoporous anatase TiO₂ nanoparticles has been investigated in this study. Based on the result, it is observed that the duration of sol-gel reaction had no significant effect on the formation of crystal phase of the TiO₂ nanoparticles. It is demonstrated that all reaction products could unambiguously be indexed as anatase phase regardless of how long the sol-gel reaction proceeded. The result from BET adsorption-desorption isotherm also suggests that all the reaction product follows the type V isotherm which indicates the mesoporous feature of TiO₂.
Furthermore, it is also observed that perfect spherical particles with high surface area could be obtained when the reaction was carried out for no longer than 6 hours. Meanwhile, irregular large particle clusters were obtained when the reaction was done for 12 and 24 hours. It is believed that Ostwald ripening process was responsible for the formation of these irregular large particle clusters due to the coalescence of adjacent two or more TiO$_2$ nano-spheres.

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