



Rapid Thermal Synthesis of Nano Titanium Dioxide Powders Using a Plasma Torch

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ABSTRACT

Spherical TiO₂ nano- to microparticles are rapidly synthesized by spraying clear stock solution as a nano aerosol into an atmospheric-pressure microwave plasma torch at 550–600°C. The stock solution was prepared by an initial H₂O/TiCl₄ (titanium tetrachloride) volume ratio of 8. At about 0.15 s, anatase TiO₂ powders were produced and collected by 14-stage impactors. The size distribution shows that 98.47% of the particles in number were in the < 10-nm impactor, with the normalized particle number percentage ($dn'/d\log Dp$) of 327.1, although the mass distribution of the powders was mainly in the size range of 2.5–6.2 μ m. Scanning electron microscopy and transmission electron microscopy images show that most of the spherical TiO₂ particles had a primary particle size of about 10 nm. Moreover, larger secondary particles (several μ m), likely aggregated small particles were also presented. The chemical composition and elemental analyses show that the structure of the powders is mainly composed of TiO₂ with traces of TiO₂-xNx. Hence, the total reaction pathway is proposed as $\text{Ti}(\text{OH})_x\text{Cl}_{4-x} + \text{H}_2\text{O} + \text{N}_2 + \text{O}_2 \rightarrow \text{TiO}_2 \text{ nuclei} + \text{HCl} + \text{other byproducts}$. Moreover, the ultraviolet-visible absorption spectrum and photocatalytic performance of the synthesized powders during exposure to ultraviolet or visible light are comparable to those of commercial TiO₂ powders.

Keywords: Synthesis; Photocatalyst; Nanoparticles; Size distribution; Discharge.

INTRODUCTION

Nanoparticles of TiO₂ photocatalyst for ultraviolet (UV) or visible light catalysis have great potential in the environmental and energy industries (Harizanov *et al.*, 2001; Yu *et al.*, 2002; Seery *et al.*, 2007). TiO₂ is significant current interest for photocatalytic applications, such as the remediation of pollutants, water splitting, the destruction of highly toxic molecules, the selective and synthetically redox transformations, the production of hydrogen, and for the conversion of solar energy to electric power (Shie *et al.*, 2009; Han *et al.*, 2012; Chang *et al.*, 2013).

Titania-based photocatalysts are usually prepared via liquid-phase or gas-phase synthesis. Commonly used liquid reaction approaches include the sol-gel method (Guan *et al.*, 2001), the microemulsion method (Hsieh *et al.*, 2008), the precipitation method (Parida *et al.*, 2009), and the

hydrothermal method (Cheng *et al.*, 1995; Lu *et al.*, 2008). In addition, by physical approach, larger TiO₂ stock powders carried by the high-speed airflow can be broken into nanoparticles under the action of crushing, friction and extrusion forces (Yang *et al.*, 2012).

Titanium dioxide powders (5–400 nm) can be synthesized using a liquid-phase reaction. The advantage of liquid methods is easy control for producing nano-size particles and particle size uniformity. Drawbacks include long reaction time (1–24 h), complex processes or multiple stages, residual carbon matter, and high cost of precursors, such as TTIP (C₁₂H₂₈O₄Ti, C/Ti atom ratio = 12) and TEOT (C₈H₂₀O₄Ti, C/Ti atom ratio = 8) (Guan *et al.*, 2001; Wang *et al.*, 2006; Hsieh *et al.*, 2008).

To reduce the reaction time (or residence time), gas-phase reactions can be conducted using a high-temperature flame aerosol method, such as premixed flame (Arabi-Katbi *et al.*, 2001; Johannessen *et al.*, 2001; Kammler *et al.*, 2002; Tsantilis *et al.*, 2002; Kammler *et al.*, 2003), diffusion flame (Pratsinis *et al.*, 1996; Akurati *et al.*, 2007), and detonation processes (Ouyang *et al.*, 2008a, b), by using TTIP or TiCl₄ as the feeds.

In addition, plasma approaches, such as radio-frequency

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(RF) plasma (Nicholas *et al.*, 2009), microwave (MW) plasma (Hong *et al.*, 2005; Hong and Uhm, 2007), dielectric barrier discharge (DBD) (Chen *et al.*, 2007), and DC plasma (Li *et al.*, 2008; Vijay *et al.*, 2009), with gas-phase precursors have been proposed. Solid precursors (TiO_2 and Cu powders) for synthesizing Cu-doped TiO_2 also can be achieved by using a DC torch (Tsai *et al.*, 2013). The advantage of plasma methods is the fast plasma-chemical reaction with high electron or gas temperature, resulting in the reduction of activation energy and synthesis time. However, the operating conditions for the rapid gas-phase synthesis of titanium are not easy to control. In addition, the usage of precursors such as vaporized TiCl_4 or TTIP gas results in the emission of a large amount of Cl-containing compounds or the production of C-containing impurities in the particles (Chen *et al.*, 2007; Hong and Uhm, 2007; Li *et al.*, 2008). Moreover, the particle size distribution of TiO_2 powders, especially on the nano-to-micro scale, has not been studied extensively.

The present study uses an inexpensive reactant, TiCl_4 , for the production of TiO_2 powders. Moreover, for reducing Cl atoms to remain or dope in the structure of as-prepared TiO_2 powders, the hydrolysis of TiCl_4 ($\text{TiCl}_4 + \text{H}_2\text{O}$) is utilized to remove the part of Cl atoms by producing HCl or Cl_2 and to form a clear, low-viscosity stock solution. The Cl atoms can be recovered and recycled for the production of TiCl_4 . In addition, the stock solution, used as a source of precursors, was sprayed as a nano aerosol by an atomizer into a MW plasma reactor for rapidly (< 1 second) synthesizing mainly anatase-structure TiO_2 powders. Moreover, the mass and particle size distribution of the TiO_2 powders were determined to characterize the powders. Finally, the photocatalytic performance of as-synthesized powders was compared with that of commercial TiO_2 powders (Degussa, P25).

EXPERIMENT

A continuous MW plasma system (Fig. 1) was assembled with a commercially available magnetron (National Electronics YJ-1600, 2.45 GHz), whose maximum stationary

power is 5 kW in continuous-wave mode. The microwaves passed through a circulator and a waveguide with a three-stub tuner, then reached a cavity with an arc to ignite the plasma. A quartz tube intersected the waveguide (ASTEX WR340) and a resonator was placed perpendicular to it. The gases in the axial gas were N_2 (1.5 standard liters per minute (slm)) and O_2 (1.5 slm). The flow rate of the swirl N_2 gas was 12 slm. The flow rate of the gas was regulated by a mass flow controller. Before the reaction, the chamber was flushed with mixing gases to remove residual impurities.

Titanium tetrachloride solution with an $\text{H}_2\text{O}/\text{TiCl}_4$ inlet volume ratio of 8 was sprayed as an aerosol into the reactor. A power of 900 W and temperatures of 550–600°C were used for producing TiO_2 powders. The powders were collected using a micro-orifice uniform deposit impactor (MOUDI, Model 110, MSP), with a working flow rate of 30.0 ± 0.2 L/min, combined with a downstream nano-micro orifice uniform deposit impactor (nanoMOUDI, Model 115, MSP), with a working flow rate of 10.0 L/min. The latter was used for collecting particles with sizes < 57 nm ($\text{Dp}50\%$ cutoff diameters of 32, 18, and 10 nm). Each sample set comprised 15 aerosol samples from micro to nano, with calibrated $\text{Dp}50\%$ cutoff diameters of 18 μm , 10 μm , 6.2 μm and 2.5 μm , 1.8 μm , 1.0 μm , 0.54 μm , 0.32 μm , 0.19 μm , 0.10 μm , 57 nm, 32 nm, 18 nm, 10 nm, and < 10 nm. Aluminum foils (47 mm ϕ , MSP) were used as the impact substrate and a quartz fiber filter (2500QAT-UP, 47 mm ϕ , pore size 0.8 μm , Pall) was placed at the base of the nanoMOUDI as an after-filter for collecting particles < 10 nm (Hsieh *et al.*, 2009). Although some powders in the nuclei mode may have diameters of around 3 nm, the smallest aerosol aerodynamic diameter is generally defined as 5 nm (McMurry and Woo, 2002). The particles collected on the quartz after-filter were thus designated as being in the 5–10 nm range.

The crystal structure of the as-prepared powders was determined using an X-ray diffraction (XRD) spectrometer (X'Pert PRO, MPD) with CuK_α radiation that scanned from 15° to 85° (2 θ). The powders were also examined using a scanning electron microscope (SEM, Hitachi S3000N) and a high-resolution transmission electron microscope (TEM,

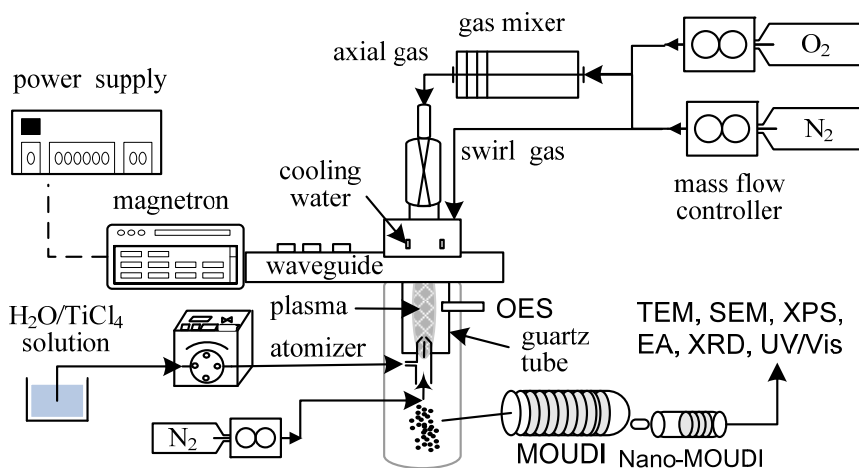


Fig. 1. Experimental apparatus.

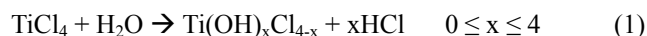
Philips CM-200) to determine their size, morphology, and microstructure. The surface analyses and the determination of the chemical composition were performed using X-ray photoelectron spectroscopy (XPS, Fison ESCA210). An optical emission spectrometer (OES, Ocean Optics, HR 4000CG) was used to measure the active species involved in the formation of the powders in the discharge zone. The absorption spectrum and photocatalytic activity of the as-synthesized powders were measured using a UV-Visible spectrometer (PerkinElmer, V-670).

RESULTS AND DISCUSSION

Preparation of Clear Solution

In order to avoid blocking the atomizer, the precursors must be in the form of a clear and transparent liquid. Various $\text{H}_2\text{O}/\text{TiCl}_4$ volume ratios (4–26) were tested to prepare the clear solution and reduce the amount of Cl-containing compounds in the feedstock, Cl_2 and HCl in the gaseous effluents, and Cl atoms in the powders.

The results show that at an initial $\text{H}_2\text{O}/\text{TiCl}_4$ volume ratio of 8, the final stock solution with a $[\text{Ti}^{4+}]$ concentration of 1.14 M and a Ti/Cl atomic ratio of 0.9 is clear and transparent. Yellow and white precipitations were found for $\text{H}_2\text{O}/\text{TiCl}_4$ volume ratios of < 7 and > 10 , respectively. Because TiCl_4 easily reacts with H_2O to form yellow $(\text{Ti}(\text{OH})_x\text{Cl}_{4-x})$ or white $(\text{Ti}(\text{OH})_4)$ precipitation via the following reaction (Ritala *et al.*, 1993):



The size distribution of aerosol particles fed into the plasma reactor was measured using a scanning mobility particle sizer (SMPS). The results show that the aerodynamic diameters were in the range of 20–300 nm, with a mean value of 46.1 nm. This clear solution can thus be sprayed as a nano aerosol by the atomizer into the glow discharge to react with O_2 in the plasma reactor.

Size Distributions of Mass and Particle Number of TiO_2 Powders

The size distribution of TiO_2 powders (in mass) was evaluated by calculating the mass sampled, the mass percentage, and the normalized mass percentage:

$$\text{Mass of TiO}_2 (M) = \text{mass difference of filters before and after sampling} \quad (2)$$

$$\text{Mass percentage of TiO}_2 (M') = M/\text{total mass of powders} \times 100\% \quad (3)$$

$$\text{Normalized mass percentage} = dM'/d\log Dp (\%) = dM'/d(\log Dp, u - \log Dp, l) \quad (4)$$

M = mass (mg)

M' = mass percentage (%)

$dM'/d\log Dp$ = normalized mass percentage (%)

Dp = midpoint particle diameter (μm) = $(Dp, u + Dp, l)/2$

Dp, u = upper channel diameter (μm)

Dp, l = lower channel diameter (μm)

The size distribution of particle number of TiO_2 powders was evaluated by calculating the mass distributions under the assumption that all powders have the same density.

$$\text{Particle number of TiO}_2 (n) = M/(4/3 \pi (Dp/2)^3) \times (1/\text{density of TiO}_2) \quad (5)$$

$$\text{Particle number percentage of TiO}_2 (n') = n/\text{total TiO}_2 \text{ particles} \quad (6)$$

$$\text{Normalized particle number percentage} = dn'/d\log Dp (\%) = dn'/d(\log Dp, u - \log Dp, l) \quad (7)$$

n = number of particles

n' = particles number percentage (%)

Density of $\text{TiO}_2 = 4.23 \text{ g/cm}^3$

$dn'/d\log Dp$ = normalized particle number percentage (%)

The mass-fractionated particle samples (0.005–50 μm) were collected by a 14-stage impactor (MOUDI + nanoMOUDI). The size distributions were then calculated.

Table 1 shows that the most of the mass was contributed by particles in the size of 2.5–6.2 μm , reaching 33.0% of the total mass with a normalized particle number percentage of 83.66. The second and third largest mass contributions were by particles in the size ranges of 6.2–10 μm and 1.8–2.5 μm , with total mass ratios of 27.63% and 14.59%, respectively. The total mass ratio of the former three samples reached 75.2%. Fig. 2(A) shows that the mass distribution has a single peak. The mass increases with increasing particle size until a peak at 2.5–6.2 μm , indicating an association with the growth of nuclei from the injected $\text{Ti}(\text{OH})_x\text{Cl}_{4-x}$ aerosol. Moreover, higher normalized mass percentages ($dM'/d\log Dp$) of 133.09 and 102.24 were also found at 6.2–10 μm and 1.8–2.5 μm , respectively, to be around of 2.5–6.2 μm .

Although the mass peak is in the micrometer range, Table 1 shows that 98.47% of the particles (in particles number) were collected in the 5–10 nm stage impactor, with a normalized particle number percentage ($dn'/d\log Dp$) of 327.1. This indicates that the plasma processing produces mainly nano powders via the nubulization, desolvation, volatilization, dissociation, reaction/recombination, and nuclei growth processes. Fig. 2(B) shows that the particles number percentage significantly decreases with increasing particle size. The second and third highest particle number peaks are at 10–18 nm and 18–32 nm, with normalized particle number percentages of only 4.4 and 1.0, respectively (Table 1 and Fig. 2(D)).

Morphology and Proposed Growth Process of Powders

The morphology and shape of the as-synthesized powders are nearly spherical with a primary particle size of 10 nm, as obtained from SEM (Fig. 3(A)) and TEM images (Fig. 3(B)). Agglomerated powders with a particle size of several μm (Fig. 3(C)) were produced when the nano aerosols were vaporized and reacted with O_2 to form nano TiO_2 particles in the discharge environment. The TiO_2 nuclei agglomerated and formed large clusters of thermal nanoparticles when

the nanoparticles passed through the afterglow discharge zone and sampling line. The TEM image in Fig. 3(D)

shows that the large particles are composed of many nano-size grains.

Table 1. Size distribution of mass and particle number of as-prepared TiO₂ powders.

Size distribution (μm)	Medium size, D_p (μm)	TiO ₂ mass percentage, M' (%)	$dM'/d\log D_p$ (%)	TiO ₂ particle number percentage, n' (%)	$dn'/d\log D_p$ (%)
0.005–0.01	0.008	0.56	1.85	98.47	327.1
0.01–0.018	0.014	0.04	0.16	1.120	4.389
0.018–0.032	0.025	0.05	0.22	0.257	1.030
0.032–0.056	0.044	0.11	0.45	0.096	0.395
0.056–0.1	0.078	0.29	1.16	0.046	0.182
0.1–0.19	0.145	0.04	0.14	0.0009	0.0033
0.19–0.32	0.255	0.81	3.57	0.0036	0.0160
0.32–0.54	0.430	1.45	6.37	0.0014	0.0060
0.54–1	0.770	2.42	9.05	0.0004	0.0015
1–1.8	1.400	6.33	24.79	0.00017	0.00067
1.8–2.5	2.150	14.59	102.24	0.00011	0.00077
2.5–6.2	4.350	33.00	83.66	0.00030	0.00008
6.2–10	8.100	27.63	133.09	0.000004	0.00002
10–18	14.00	10.41	40.79	0.0000003	0.0000009
18–50	34.00	2.27	5.12	0.0000000	0.0000001

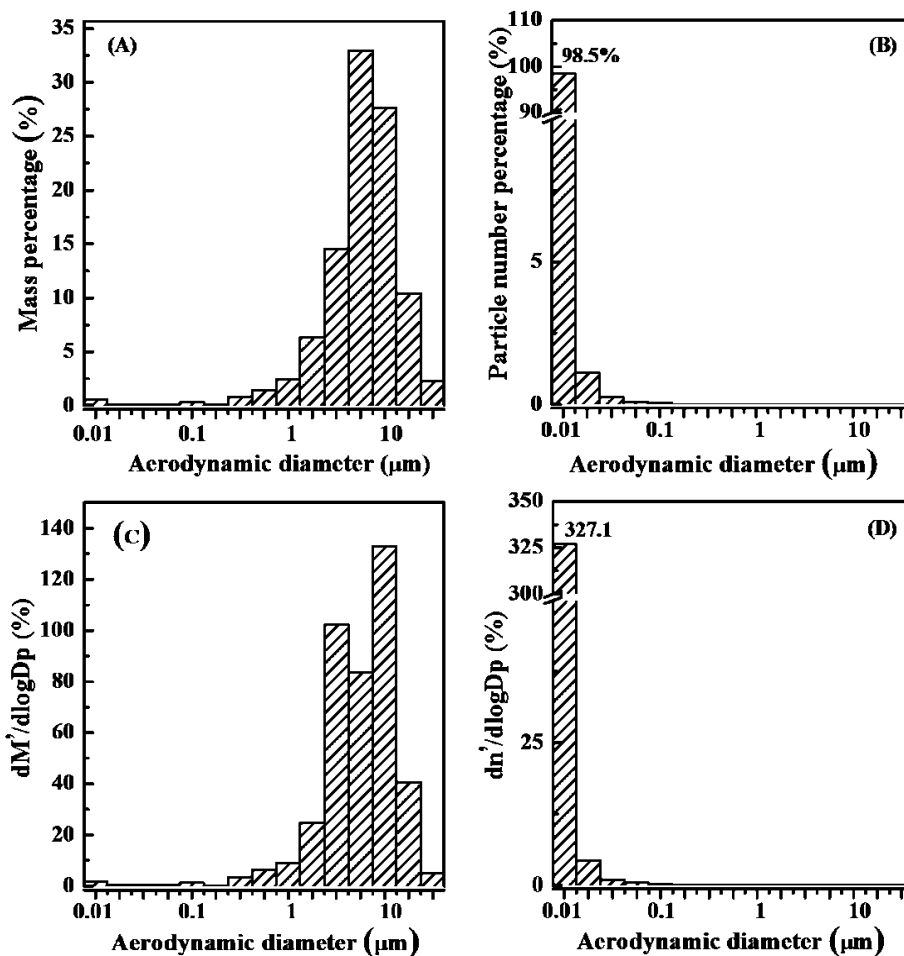


Fig. 2. Size distributions of (A) mass and (B) particle number with corresponding (C) normalized mass and (D) particle number percentages.

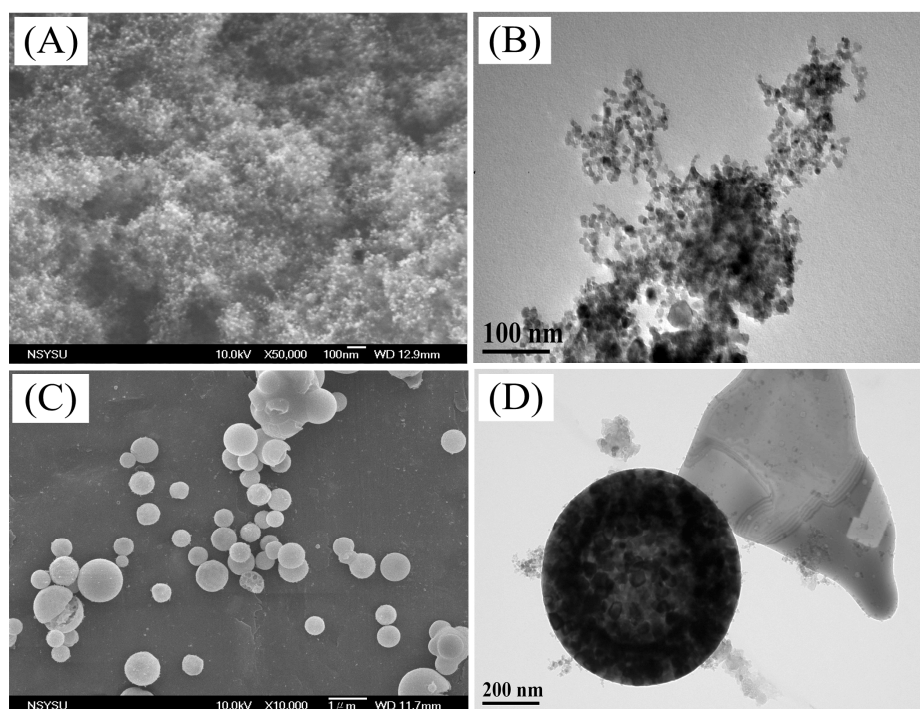
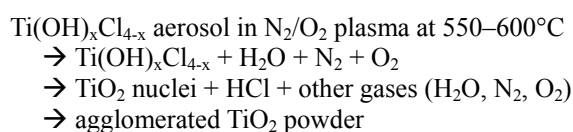


Fig. 3. Morphology of powders. (A) SEM and (B) TEM images of particles in 10–18 nm stage impactor; (C) SEM image of particles in 1–1.8 μm stage impactor; (D) TEM image of secondary particle as aggregation of primary particles.

XRD patterns (Fig. 4) show that the powders before and after sintering were mainly the anatase phase. Moreover, the average grain size calculated by XRD data is about 13–14 nm, to be consistent with the primary particle size, indicating that the larger secondary particles are aggregated mainly by the smaller primary particles. Ti atoms react with O to form crystalline TiO_2 (anatase phase) at 550–600°C; however, amorphous TiO_2 existed in the as-prepared powders before calcination due to the short reaction time (about 0.15 s), resulting the weak peak was found in XRD patterns.

The proposed simplified reaction pathway is as follows:



However, traces of $\text{TiO}_x\text{N}_{2-x}$ powders were produced due to the active N-containing species possibly reacting with TiO_2 or doping TiO_2 .

Surface Compositions and UV-Visible Spectrum of Powders

The surface compositions and functional groups of as-synthesized powders were measured by XPS. Elemental analysis shows that the N atom concentration was about 0.12 at.%, indicating N doping with a chemical bonding energy at 399.1 eV, corresponding to N_{1s} . This can be attributed to N-O bonds (Fig. 5(A)) (Guan *et al.*, 2001; Valentin *et al.*, 2005).

The O_{1s} peak region was deconvoluted into surface

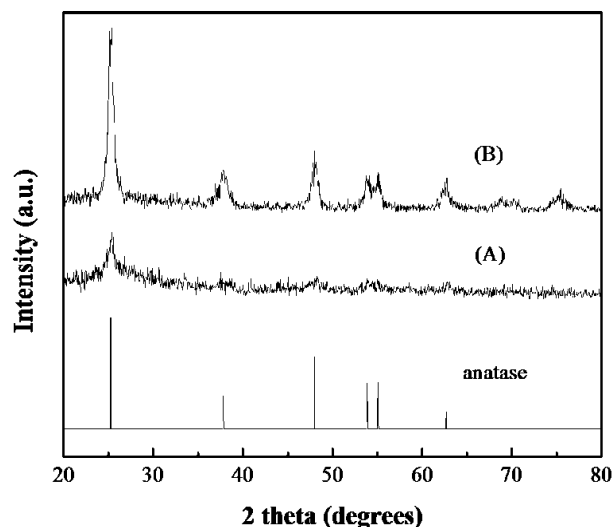


Fig. 4. XRD patterns of synthesized TiO_2 powders (A) before and (B) after calcination.

functional group contributions, as shown in Fig. 5(B). It was found that the O_{1s} peak can be fitted to two line shapes with binding energies at 529.2 and 531.2 eV, assigned to Ti-O and O-N bonds, respectively (Chen *et al.*, 2007). The total area of the O_{1s} peak was 91.75% Ti-O and 8.25% O-N. The peak regions of Ti at 463.7 eV and 458.0 eV correspond to $\text{Ti}_{2p_{1/2}}$ and $\text{Ti}_{2p_{3/2}}$, respectively, in the XPS spectrum (Fig. 5(C)), and can be attributed to the Ti-O functional group (Chen *et al.*, 2007). The total area of the Ti peak region was 27.36% $\text{Ti}_{2p_{1/2}}$ (at 463.7 eV) and 72.64% $\text{Ti}_{2p_{3/2}}$ (at 458.0 eV), respectively. These results

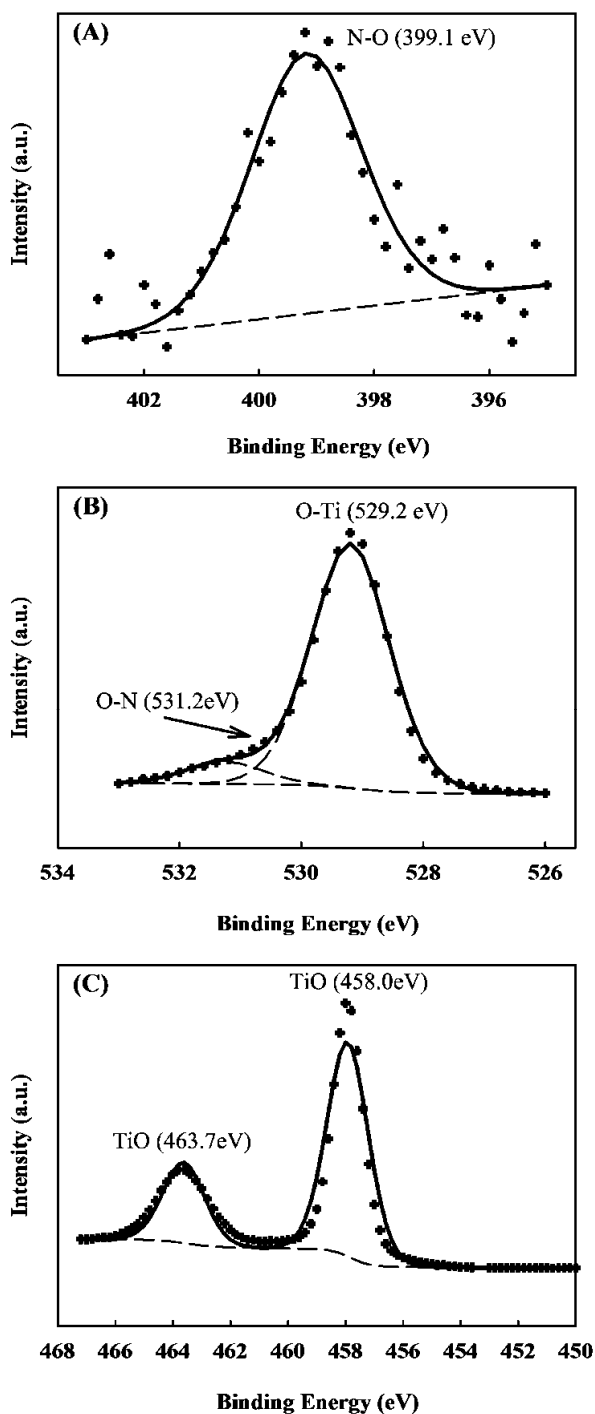


Fig. 5. XPS spectra of (A) N_{1s} , (B) O_{1s} , and (C) Ti_{2p} for as-synthesized powders (dots: measured XPS data; dashed lines: fittings of binding energy spectra to XPS data; solid lines: sum of the fitted data).

suggest that the main functional groups for plasma-induced thermally synthesized titanium oxide powders are Ti-O bonds, with traces of O-N bonds. The powders are mostly composed of TiO_2 with some N-doped $TiO_{2-x}N_x$.

The UV-Visible Kubelka-Munk absorption spectrum was measured to confirm the band gap and red shift of TiO_2 powders (Francisco *et al.*, 2000). Fig. 6 shows that

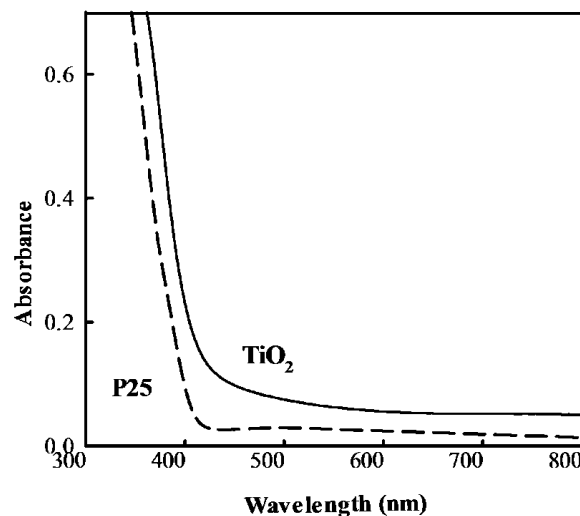


Fig. 6. UV-Visible Kubelka-Munk absorption spectrum of as-prepared TiO_2 powders and commercial P25 powders.

the band gap of the as-prepared powders was 410 nm, slightly higher than that (396 nm) of commercial P25 powders, and confirms that N-doped TiO_2 powders were produced by the rapid plasma thermal synthesis process.

The photocatalytic performance of the synthesized TiO_2 powders is comparable to that of commercial P25 powders for UV light degradation (Fig. 7(A)) and visible light degradation (Fig. 7(B)). This indicates that a MW plasma torch can be used for rapidly producing nano- and microparticle TiO_2 powders.

CONCLUSIONS

An atmospheric-pressure, high-temperature MW plasma torch was used to rapidly synthesize anatase TiO_2 particles with a size of about 10 nm by spraying a clear titanium chloride solution ($Ti(OH)_xCl_{4-x}$) as a nano aerosol. This solution significantly reduced the emission of Cl-containing compounds, mainly HCl, during the synthesis process. Size-fractionated particle samples were collected and the results show that the percentage of particle number decreased with increasing particle size. Most particles were in size ranges of 5–10 nm, 10–18 nm, and 18–32 nm, with particle number percentages of 98.47%, 1.12%, and 0.257%, respectively. SEM and TEM analyses show that the powders had larger particles, which were agglomerated by primary particles when the TiO_2 nuclei passed through the afterglow discharge zone and sampling line. In addition, elemental analyses show that trace N atoms doped the structure of the powders, resulting in the production of $TiO_{2-x}N_x$ powders with a shift of the band gap from 396 nm to 410 nm.

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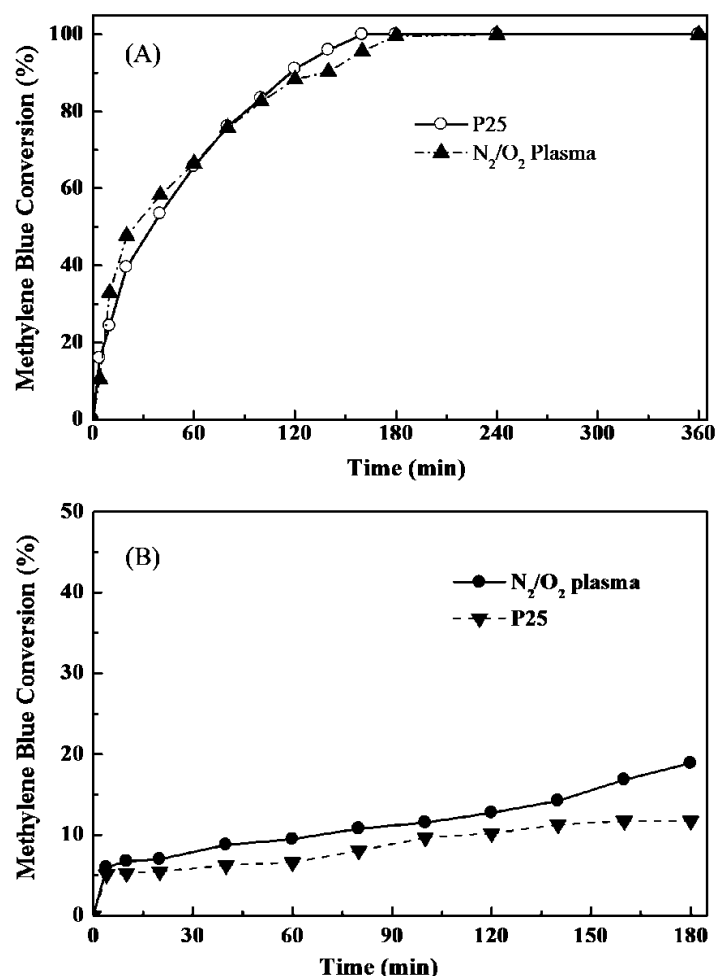


Fig. 7. Photocatalytic conversion of methylene blue for as-prepared (N₂/O₂ Plasma) and commercial TiO₂ powders (P25) under (A) UV light and (B) visible light irradiation ([MB] = 15 ppm, 10 mL).

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