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Synthesis of Titania Nanoparticles by Supersonic Plasma Expansion: Effect of Lowering Chamber Pressure

M. Kakati^{1,*}, N. Aomoa¹, B. Bora², and H. Bhuyan²

¹*Thermal Plasma Processed Materials Laboratory, Centre of Plasma Physics, Institute for Plasma Research, Sonapur 782402, Assam, India*

²*Departamento de Física, Pontificia Universidad Católica de Chile, Casilla 306, Santiago 22, Chile*

In this work we have synthesized titania nanoparticles by supersonic thermal plasma expansion process. Some interesting recent experiments, where we explored the effect of lowering chamber pressure, changing plasma current and precursor feed rate are presented in this communication. Control and reduction of the average particle size and the phase composition of the titania nanoparticles are also demonstrated in this experiment. Combination of all favourable conditions had produced titania with an average size of 9 nm (estimated by XRD) which is the smallest reported value by a thermal plasma assisted method.

Keywords: Thermal Plasma, Titania Nanoparticles, Effect of Pressure.

Nanostructured titanium dioxide (titania) is a key nanomaterial because of its wide application potential as photo-catalyst, photonic crystals, gas sensors, nanoceramics, pigments etc. Out of the two major phases as a combination of which titania is often synthesized, the anatase is generally considered to be more efficient photo-catalyst compared to the rutile. However, it was also observed that rutile with small crystal sizes and large surface area could actually possess high catalytic activity.¹ It was also observed that mixed phase titania containing a small amount of rutile, or rutile doped with nitrogen can be more efficient for these reactions compared to a phase pure anatase sample.² It is therefore obvious that control on phase structure is sought after as an important attribute of all titania synthesis processes. Size of the particles is yet another very important issue, as this material is known to exhibit significant enhancement in photo-catalytic activities when particle size is reduced beyond 10 nm level.^{3,4}

As a processing medium for high temperature ceramic nanomaterials, the thermal plasmas have established a visible edge in terms of their typically high production rate. Plasma assisted techniques are usually very fast, most often a single step process and continuous in operation in contrast to batch processes. Because of the very high temperature of the plasma jet, plasma assisted methods

most often generate titania nanomaterials with a very good crystallinity, thereby avoiding further heat treatment processes for crystallization with associated problems of grain growth and phase change.^{5–9}

We have recently developed a thermal plasma based experimental chemical reactor for synthesis of different high temperature ceramic materials in nanostructured form, where the plasma jet laden with the vapour phase precursors are accelerated to supersonic velocities, while expanding through converging nozzle into a low pressure sample collection chamber.^{8,9} By this technique we have recently demonstrated that some typical problems associated with the conventional plasma assisted methods, namely serious inter-particle agglomeration/aggregation and wide size distribution can be successfully reduced while processing titania nanoparticles. Control on phase structure of the synthesized material with respect to the oxygen/hydrogen feed ratio and average particle size by metal precursor injection rate was also demonstrated.

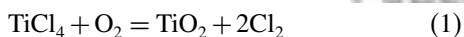
In this communication we present some more interesting results from further experiments on supersonic plasma assisted synthesis of titania nanoparticles, where we study the effect of lowering chamber pressure, plasma current and also precursor feed rate. Our recent numerical studies on nucleation and growth of particles in this specific reactor configuration indicate the pressure in the sample collection chamber to be an important control parameter.¹⁰ In most of the other plasma assisted systems it is not possible

*Author to whom correspondence should be addressed.

to observe the effect of changing chamber pressure exclusively alone, because most often the discharge is strongly coupled to the ambient pressure. For example, while trying to investigate the effect of reducing pressure on synthesis of alumina nanoparticles, Fu had observed that the transferred arc extinguishes below a certain pressure level.¹¹ The main advantage of the present experimental system is that the chamber pressure can be adjusted without affecting the discharge characteristic since the plasma production zone is physically separated from the particle nucleation/sample collection chamber with a supersonic nozzle. Thus, we anticipated that the effect of chamber pressure can be studied alone in the present experimental system. It would be interesting to see the effects in case of titania. Operating gas phase processes at higher vacuum also ensures less impurity impregnated into the product particles, which also is a motivation.

A non transferred segmented plasma torch assisted chemical reactor is used to produce the titania nanoparticles. Detailed descriptions of the experimental system are found elsewhere.^{7,8} The reactants (titanium chloride and oxygen) are injected in gas phase into the injection section just in front of the anode. The gas phase precursor laden plasma is then accelerated to supersonic velocity while traversing through a converging nozzle across which a sufficient pressure difference is maintained. Particles are nucleated as the plasma expands into a sample collection chamber maintained at low pressure just below the nozzle. Samples are collected from a movable substrate kept at a distance of 120 mm downstream of the nozzle and sent for characterization. A combination of an 8000 litre per minute (lpm) roots vacuum pump backed by a 1500 lpm rotary vacuum pump is used for conducting the experiment.

The overall reaction leading to the synthesis of titania can be represented as follows,



Equilibrium diagram shows that TiO_2 starts condensing around 3000 K.¹²

The identity and phase composition of the synthesized titania were analyzed by X-ray diffraction (Seifert 3003 TT, using $\text{Cu } K\alpha$ radiation, Dept. Physics, IIT, Guwahati). The weight fraction of anatase in the product was calculated from the following equation,⁵

$$f_A = \left(1 + 1.26 \frac{I_R}{I_A} \right)^{-1} \quad (2)$$

Where f_A is the weight fraction of anatase, I_R is the intensity of the (110) reflection of rutile and I_A is the intensity of the (101) reflection of anatase. The average size of the particles/grains was determined from the XRD spectra using Scherrer's Formula. The high pressure synthesized particles were photographed with a Tecnai 20 G2

(UGC-DAE CSR, Indore) Transmission Electron Microscope (TEM) and the low pressure synthesized samples by TEM JEOL JEM 2100 (CIF, IIT, Guwahati).

Under the following experimental conditions: plasma current 100 amperes, 12 lpm argon, furnace temperature set to 90 C, 5 lpm sweeping argon through the furnace, 3 lpm oxygen and for 8 mbar of ambient pressure in the chamber, milky white nanoparticles were rapidly synthesized. XRD confirmed the samples to be nanoparticles of titania with a relative anatase phase composition of 70% and the remaining in rutile (Fig. 1). From the peak broadening the average size of the anatase particles were measured to be 9 nanometres. Results from this sample may be compared with samples synthesized at higher chamber pressure of 40 mbars, where anatase phase was seen to remain almost similar (72%), while the average size had increased to 18 nm.

TEM photographs of these samples are presented in Figures 2(a) and (b) for low pressure and high pressure synthesis conditions respectively. They also clearly show that particle size decreases for lower pressure and under that condition there are more particles with size less than 10 nanometers as compared to high pressure situation. They are also somewhat irregularly shaped compared to the geometrically shaped particles produced at high pressure. This along with the SAED pattern (Fig. 3(a)) confirm particles are not as good crystalline under low pressure environment, but still not amorphous like as demonstrated by the XRD (Fig. 1) and HRTEM photographs (inset, 3(a)).

A different picture had emerged as the plasma power was increased, while keeping all the other parameters similar and pressure low (8 mbar). Particles were seen to get bluish first as current was increased from 100 to 170 ampere, which was then converted into deep grey as current was further increased to 240 ampere. Our previous experience indicates that the phase contribution of rutile was actually increasing under these experimental conditions. Quantitative estimation from the XRD pattern (Fig. 4) shows that the relative composition of the rutile phase increased significantly to 80% from 30% when the

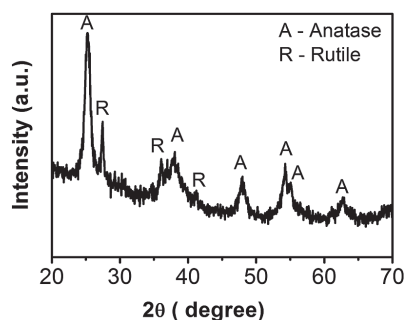


Fig. 1. XRD Pattern of the as synthesized titania nanoparticles at 8 mbar chamber pressure, furnace temperature 90 C, 100 A plasma current, 12 lpm argon, 5 lpm sweeping argon, and 3 lpm oxygen.

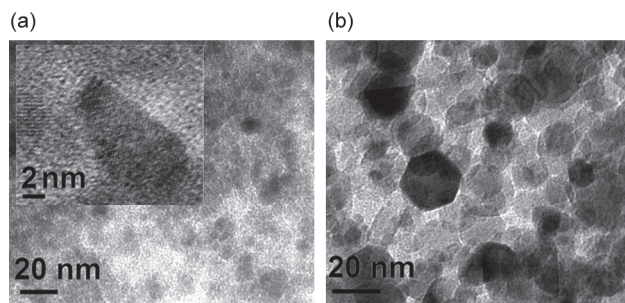


Fig. 2. TEM image of the as synthesized titania nanoparticles (a) at 8 mbar and (b) 40 mbar chamber pressure.

current increases to 240 ampere. The estimated composition of the rutile phase and the average particle size corresponding to the 100, 170 and 240 amp current are found to be 30%, 43%, 80% and 9 nm, 14 nm, 18 nm respectively.

In another set of experiments, the effect of reactant feed rate was explored under low pressure situations. The XRD patterns from these measurements are presented in Figure 5. The combined effect of lowest reactant feed rate (90 C furnace temperature) and minimum possible chamber pressure is already reported to have synthesized particles with average sizes of 9 nm, which is the smallest average value for titania nanoparticles synthesized by a plasma assisted technique. As the chloride feed rate was further increased, for 130, 170 and 220 C furnace temperature, the corresponding particle sizes were measured to be 11, 13 and 20 nm. All measured particle parameters produced under different experimental conditions are summarized in Table I.

Previous studies on synthesis of nanostructured titania by other thermal plasma sources had established that formation of anatase is always promoted in an oxygen rich reaction environment.⁶ In a recent transferred arc assisted experiment, lowering the pressure was however seen to readily decrease the amount of anatase in the samples, which was explained as happening because lowering total ambient pressure had invariably depleted the amount of oxygen in the reaction zone.¹² In contrast to this, in our supersonic plasma beam assisted system, the reaction zone is physically separated from the sample collection chamber

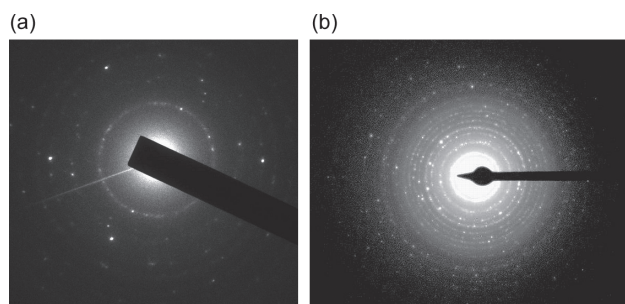


Fig. 3. SAED of the as synthesized titania nanoparticles (a) at 8 mbar and (b) 40 mbar chamber pressure.

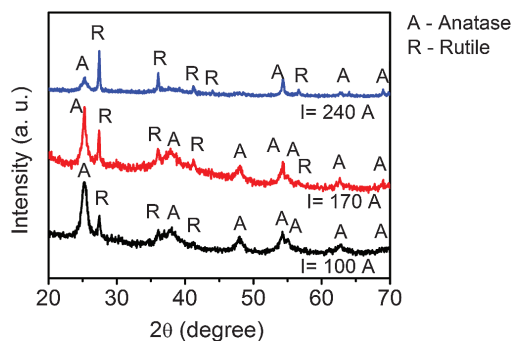


Fig. 4. XRD Pattern of the as synthesized titania nanoparticles at 8 mbar chamber pressure, furnace temperature 90 C, 12 lpm argon, 5 lpm sweeping argon, 3 lpm oxygen and for different plasma current.

where pressure can be independently controlled. It may be recalled that we had identified the presence of TiO molecules which is considered to be a precursor for titania formation in the so called injection zone, where temperature is so high that the material does not condense.⁹ Temperature decreases rapidly downstream of that region, across the nozzle and beyond,⁸ where the nanoparticles nucleate by homogeneous nucleation.

In this system once the plasma jet becomes supersonic, further reduction in pressure in the sample collection chamber does not influence conditions in the reaction zone. This ensured that although the pressure was decreased in the collection chamber, there was no corresponding depletion of oxygen in the reaction zone. Hence the phase composition remained almost similar (anatase), while a lower collisionality in the chamber because of reduced pressure translated into smaller sizes. On the other hand, the degree of ionization in the reaction zone increases with current, which leads to the increase in plasma pressure and corresponding higher plasma flow velocity through the nozzle. Hence oxygen concentration decreases in the injection zone as plasma power is increased and corresponding observed depletion of anatase composition.

Control and reduction of the average particle size of titania nanoparticles by reducing the pressure in the sample collection chamber is demonstrated in a supersonic plasma

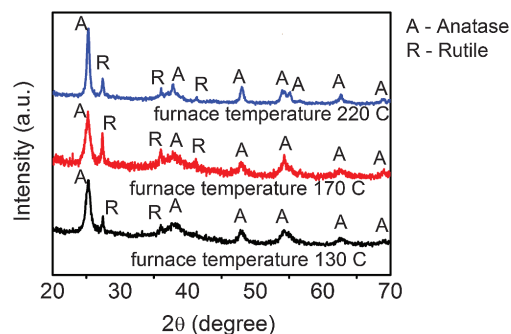


Fig. 5. XRD Pattern of the as synthesized titania nanoparticles at 8 mbar chamber pressure, 100 A plasma current, 12 lpm argon, 5 lpm sweeping argon, 3 lpm oxygen and for different furnace temperature.

Table I. Average size and phase structure of the synthesized titania nanoparticles for different sample collection chamber pressure, tubular furnace temperature and plasma current. The fixed parameters are: plasma argon 12 lpm, sweeping argon 5 lpm and oxygen 3 lpm.

Sample collection chamber pressure (mbar)	Tubular furnace temperature (C)	Plasma current (A)	Average particle size (nanometer)	Relative anatase phase content
40	90	100	18	72%
8	90	100	9	70%
8	90	170	14	57%
8	90	240	18	20%
8	130	100	11	73%
8	170	100	13	75%
8	220	100	20	76%

beam assisted experimental reactor system. Average particle size was measured to be 9 nm which is the smallest by a thermal plasma assisted method. In contrast to transferred arc based systems, there was no corresponding depletion in anatase phase composition, which is important for use of the material in photo catalytic reactions. Control on the phase composition with respect to plasma power and average particle size by precursor injection rate was also demonstrated.

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