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Synthesis of Nano Titanium Dioxide Powder using MWP (microwave plasma) and its Characterization

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Abstract:
Titanium dioxide (titania) powders finds lot of engineering applications in many areas such as waste water detoxification, electronic circuits as mermisters, quantum dots, hydrolysis , LCD screens etc. The performance is influenced by particle size and its purity. It is preferred to have smaller particle size with high purity.

This work describes the application of microwave plasma synthesis technology to prepare a photo catalytically active TiO_2 nano powder using oxygen as plasma forming gas as well as carrier gas. The powder thus produced is characterized by means of SEM (Scanning electron microscopy), XRD , BET surface area test. The average particle size for the powder obtained is determined to be around 60-70 nm, which is quite compatible with the commercially available titania powder (P-25). The prepared powder has 67 % Anatase and 33 % Rutile phase in it with high purity and better controlled particle size .The nano titania powder obtained through MWP is tested for photo catalytically activenessTiO_2 powder is synthesized using methylene blue for decolourisation effect shown as satisfactory results..

Keywords: Photo catalysis, Microwave plasma (MWP, titania, Methylene blue, XRD (X-Ray diffraction), BET (Brunauer, Emmett and Teller).

1. Introduction

Nanopowders have a combination of small particle size, narrow size distribution and high surface area to volume ratio. The physical and chemical properties of these nano particles often deviate from their bulk materials when the particle size decreases to a specific regime. The powder shows a dramatic increase in photo catalytic action and increases strength, hardness and cutting efficiency as particles become nano sized.

Titanium dioxide occurs in nature as well as in known mineral forms such as rutile(tetragonal), anatase(tetragonal) and brookite(orthorhombic). Most common form of titania is rutile, which is also the most stable form. Anatase and brookite both convert to rutile upon heating. Rutile, anatase and brookite all contain six coordinated titanium. Titanium dioxide powder is commonly referred to as Titania.

Plasma processing of materials makes use of high energy content of 'partially ionize gas' commonly referred to as the fourth state of matter. Plasma is also encountered in our daily life such as in a lightning bolt, the conducting gas inside a fluorescent -tube and inside neon sign. Plasma consist of charged excited and neutral partial ionization of atom or molecules of a gas and therefore, is an electrical conductor, however any gas cannot be called a plasma as there is small degree of ionization in any gas .Plasma provides convenient sources of energetic ions and activated atoms which are now widely employed in densification and synthesis of ceramics, decomposition and etching of materials.

Titanium dioxide is useful in many varied applications, such as paints, pigments, films, hydrolysis, photo catalyst, water detoxification, antifouling, UV rays absorptions etc.[5]

Titanium dioxide is the most widely used white pigment because of its brightness and very high refractive index (n = 2.7), in which it is surpassed only by a few other materials. Approximately 4 million tons of pigmentary TiO_2 are consumed annually worldwide. When deposited as a thin film, its refractive index and colour make it an excellent reflective optical coating for dielectric mirrors and some gemstones like "mystic fire topaz". TiO_2 is also an effective opacifier in powder form, where it is employed as a pigment to provide whiteness and opacity to products such as paints, coatings, plastics, papers, inks, foods, medicines (i.e. pills and tablets) as well as most toothpastes. In paint, it is often referred to offhandedly as "the perfect white", "the whitest white", or other similar terms. Opacity is improved by optimal sizing of the titanium dioxide particles. In ceramic glazes titanium dioxide acts as an opacifier and seeds crystal formation.

Titanium dioxide is often used to whiten skimmed milk; this has been shown statistically to increase skimmed milk's palatability. Titanium dioxide, particularly in the anatase form, is a photo catalyst under ultraviolet (UV) light. Recently it

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has been found that titanium dioxide, when spiked with nitrogen ions or doped with metal oxide like tungsten trioxide, is also a photo catalyst under either visible or UV light. The strong oxidative potential of the positive holes oxidizes water to create hydroxyl radicals. It can also oxidize oxygen or organic materials directly. Titanium dioxide is thus added to paints, cements, windows, tiles, or other products for its sterilizing, deodorizing and anti-fouling properties and is used as a hydrolysis catalyst. It is also used in dye-sensitized solar cells, which are a type of chemical solar cell.

The photo catalytic properties of titanium dioxide were discovered by Akira Fujishima in 1967 and published in 1972. The process on the surface of the titanium dioxide was called the *Honda-Fujishima effect* [8, 9].

Titanium dioxide has potential for use in energy production: as a photocatalyst, it can carry out hydrolysis; i.e., break water into hydrogen and oxygen. Were the hydrogen collected, it could be used as a fuel. The efficiency of this process can be greatly improved by doping the oxide with carbon. Further efficiency and durability has been obtained by introducing disorder to the lattice structure othe surface layer of titanium dioxide nanocrystals, permitting infrared absorption [10].

Titanium dioxide can also produce electricity when in nanoparticle form. Research suggests that by using these nanoparticles to form the pixels of a screen, they generate electricity when transparent and under the influence of light. If subjected to electricity on the other hand, the nanoparticles blacken, forming the basic characteristics of a LCD screen [6].

Nokia has already built functional Titanium dioxide is also used as a material in the memristor, a new electronic circuit element. It can be employed for solar energy conversion based on dye, polymer, or quantum dot sensitized nano crystalline TiO_2 solar cells using conjugated polymers as solid electrolytes.[7]

Micro Wave Plasma:

The plasma used here, falls under thermal plasma. The microwave used here is a high frequency electromagnetic wave and the generator used here is a electrode less generator.

This plasma falls under category of thermal plasma .the microwave plasma employs a high frequency electromagnetic wave and a electrode less generator. the MWP is advantages over the powder making methods such as

- Very clean plasma generated since no electrodes are used.
- Powders, liquids, vapours, and gases can be fed into the reaction chamber.
- High production rate when compared to other processes (120g/hr approx.)
- Possibilities for forming excited species of ions.

The micro wave unit is designed for production of ultra dispersed (below 100nm) powders of oxides by means of condensation from high temperature chemically reacting gaseous flow. Chemical reaction yielding the condensed product occurs in the flow of oxygen heated to 1500-3000 k due energy of micro wave irradiation.

2. Experimental setup:

The experimental set-up used in this work is represented schematically in Fig.1.

Fig. 1: Microwave plasma unit .

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Microwave irradiation generated by the generator heats a stationary flow of plasma forming gas, which is delivered in plasmatron. Heated and ionized flow delivers into reactor. Chemical reagents as vapour mixed with gas carrier are delivered into the upper part of the reactor through input attachments. Dosing device ensures a uniform delivery of the reagents. In the reactor, the reagents mix with high temperature flow, and chemically react in gas phase. The chemical reaction yields highly oversaturated vapor, which yields ultra dispersed product upon condensation properties of resulting powder, can be controlled in a certain range by changing conditions like concentration, temperature and cooling rate. Gas dispersed mixture formed in the reactor delivers to heat exchanger for cooling, and then to filter ,where dispersed phase is separated from gas flow. The product gets accumulated in the collector. The process duration is approximately 30 min.

2.1 Specification of MWP unit:

- Maximum output of the micro wave generator - 5kw.
- Frequency of microwave generator 2450MHz

2.2 Components of MWP

Magnetron: It is the unit that produces the micro waves that are to be introduced into the plasma. It basically contains one cathode and multiple anodes each carrying a current 1.4 Amp. The output of this unit is upto 5 kw. This system unlike others has separate cooling systems such as fans. The magnetron is followed up by a isolator which performs the function of directing waves only in one particular direction to avoid reflected waves which would otherwise generate more heat which is not desirable. Wave guides are also provided which more or less perform the same function of aligning the waves in one direction.

Plasmatron: Super high frequency plasmatron is designed for heating of stationary gas flow of oxygen to 1500-3000 k due to absorption by ionized gas of microwave irradiation delivered from magnetron via wave guides. Gas is introduced into plasmatron first passes through twisting chamber. Primary gas ionization, which is necessary for initiating stationary gas micro wave discharge, is performed by a short term insertion of stainless steel wire into the discharge zone. Plasmatron provides stable "burning "of discharge in the range of gas flow of 1.8-4.0 m^3/hr,and input power of 2- 5kw. Plasmatron housing is supplied with cooling water to absorb the heat generated [5].

2.2.1 Technological Equipment

Reactor: it is a water cooled tube consisting of two separate sections .high temperature plasma jet and chemicals participating in the reaction are fed to the upper part of the reactor. They interact in the reactor and form condensed products as ultra-dispersed powder.

Injector: It is for introduction of reagents and is placed between plasmatron and the upper part of the reactor, and it is used for feeding the starting material participating in plasma chemical process. The case of the injector is supplied with water cooling.

Heat Exchanger: It is assigned for reduction of temperature of exiting dust-gas flow before it is fed into the filter. It consists of two co axially located water cooled cylinders, with axis perpendicular to the axis of running high temperature flow.

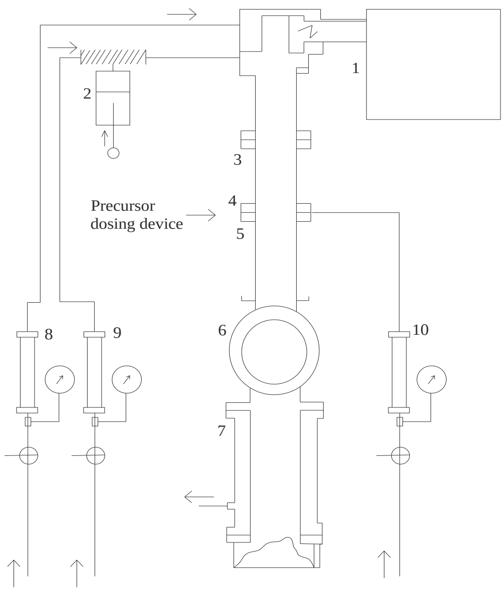

Fig 2: Schematic diagram of Microwave plasma

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(1) Microwave generator (2) Dosing device for reagents (3) Reactor zone1
(4) Inter connector (5) Reactor zone 2 (6) Heat-exchanging device
(7) Filter (8).(9).(10) Rota meters

Filter: It is assigned for isolation of ultra dispersed powder from cooled dust-gas flow and its accumulation during the technological process. Filtration of dust-gas flow is performed when the flow passes through a bag filter made of thermo stable phenylon tissue.

Dosing Device: This is connected to the injector for reagents and is assigned for controlled feeding of the stock into plasma chemical reactor. Performance of dosing device for a large scale production of powder is based on the entrainment of the liquid chloride vapours by carrier gas from thermostating space of the dosing device

3. Synthesis of TiO_2:

The input substance which is used to prepare the required product is called precursor. Here the precursor used is $TiCl_4$ which is in liquid state. It is very sensitive to moisture and has high vapour pressure. It is feed into the plasma at rate of 107 X 10^{-6} m^3/hr. Carrier gas is used to carry the vapours of the precursor into the reaction chamber. The carrier gas used here is oxygen and is feed at rate of 0.3 m^3/hr. oxygen is used as plasma forming gas here at a rate of 2.2 m^3/hr.

The precursor $TiCl_4$ reacts with the oxygen which is sent inside as the plasma forming gas as well as the carrier gas according to the following reaction.

$$TiCl_{4\,(l)} + O_{2(g)} \rightarrow TiO_{2(s)} + 2Cl_{2(g)} \qquad (1)$$

The powders were quenched at the wall of the heat exchanger and then separated from the gas by the filter bag via a tube. powder deposited directly in the bag provided is designated in this work as bag fraction and the residual powder stuck along the walls of the output tube is designated as tube fraction.

4. Characterization and Results:

4.1 Photocatalytic activity:

The nano titania powder obtained from tube ,bag fraction is kept in two separate beakers and mixed it with Methylene blue to form a concentrated homogenous solution, for checking the photocatalytic nature. Similarly, commercially available titania powder is mixed in a beaker containing methylene blue. The sample weighs typically for each is ,

Tube fraction	:	0.0252gm
Bag fraction	:	0.0247gm
P-25	:	0.0258gm

Some amount of pure methylene blue is taken for reference. The three beakers containing TiO_2 powder are kept in the ultrasonifier for fine dispersion of nano powder in the methylene blue solution. All the 4 beakers are introduced to direct sunlight with light intensity measuring upto 70 mW/12mm^2. [4]. Methylene blue is used to test for photo catalytic activity of powder manufactured. Its unique ability to remain un reacted upon action with UV rays and being a common pollutant makes it apt for this activity.

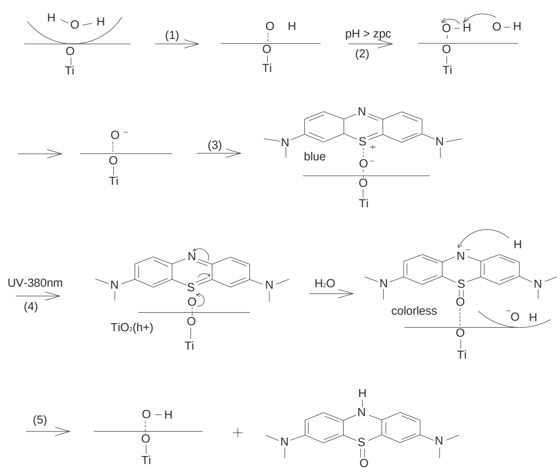

Fig 3: Reactions involved in photocatalysis

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(a) Before Exposure to Sunlight **(b)** After Exposure to Sunlight:

(1) Only methylene solution (2) Commercially available powder

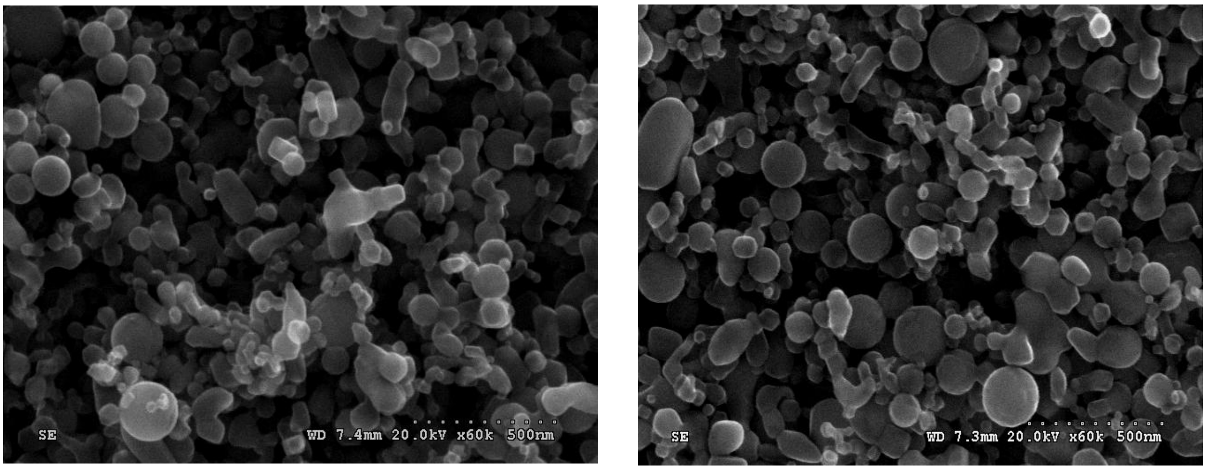
(3) Bag fraction powder (4) Tube fraction powder

Fig 4: Bottles as they stand in order from left

- The activity was carried out for 20 min in daylight.
- The deviation in colour in the samples containing TiO_2 powder from the reference solution colour justifies the photo catalytic action of TiO_2 .
- The colour change is first observed in bag fraction.

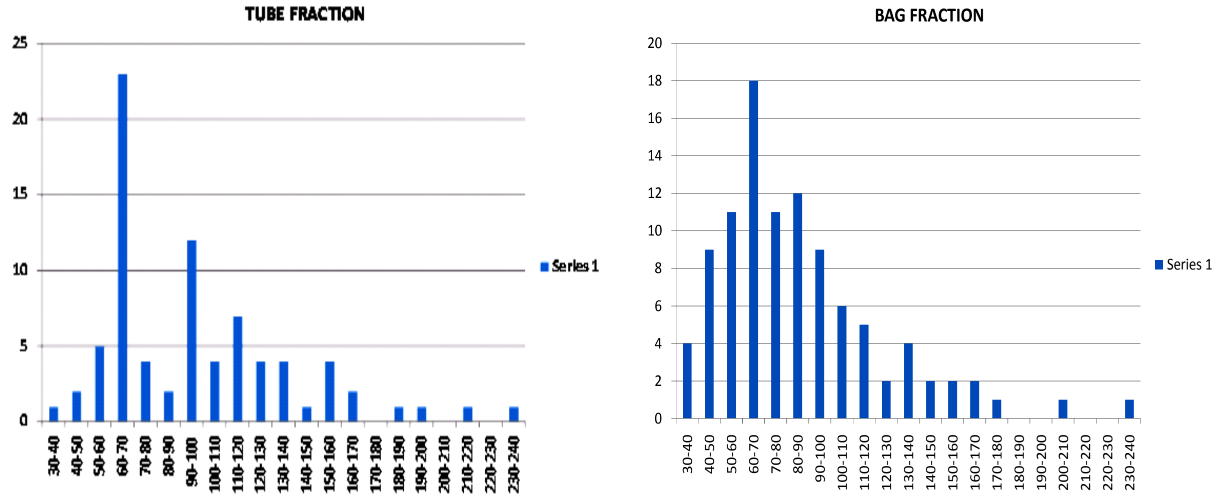
4.2 SEM analysis

The drop of finely dispersed TiO_2 powder in distilled water is kept on a carbon tape as per standard test procedure. It is then kept under the scanning electron microscope, which has very high resolution power. Photograph of samples obtained from tube and bag fraction of nano TiO_2 atoms in nanometer dimension are shown in Fig (5)



(a) Tube fraction **(b)** Bag fraction

Fig 5: SEM images of tio2 obtained through MWP.



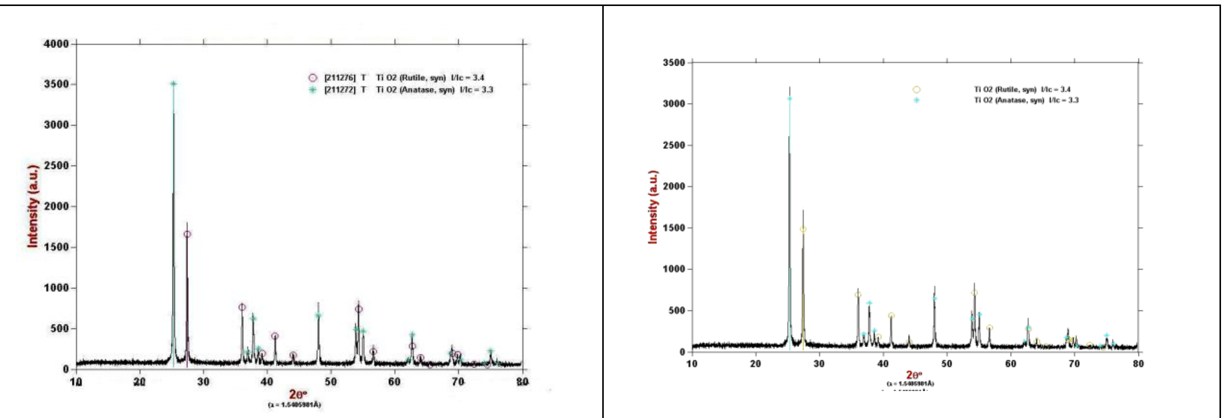
(a) Tube fraction **(b)** Bag fraction

Fig 6: The average particle size of the atoms are plotted on Graphs using SEM photographs

From the SEM analysis , it is found that

- The average particle size in tube fraction is 78 nm.
- The average particle size in bag fraction is 97 nm.

4.3 XRD analysis of powder preared through micro wave plasma:
The samples obtained from tube and bag fraction are subjected to XRD analysis. The photograph of samples obtained from tube and bag fraction of nano TiO_2 atoms in nanometer dimension are shown in Fig (5).



(a) (b)

Fig 7: XRD graphs of **(a)** Tube fraction **(b)** Bag fraction

Based on the above, the XRD results obtained are as fallows.

Average particle size:

Tube fraction: The average anatase crystallite size is 46.69nm. The average rutile crystallite size is 46.67 nm.

Bag fraction: The average anatase crystallite size is 59.17nm. The average rutile crystallite size is 51.11nm

%composition :
Tube fraction: Anatase is 67.77% and the Rutile is 32.23%
Bag fraction: Anatase is 67.73% and the Rutile is 32.27%

4.4 BET surface area test for the powder obtained by MWP:
BET of Make: MICROMERITICS, model ASAP 2020 V3.00 H, is employed for measuring surface area . The powder particles are then surrounded by nitrogen molecules and thus gives the empirical value of the surface area of the required nano powder. The surface area of powder in tube fraction is

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20.0731 m^2 /gm and the surface area of the powder in the bag fraction is 18.067 m^2 /gm where as surface area of the sample of P-25 was found to be 15.27 m^2 /gm.

5. Conclusion:

Nano powder of tio2 is successfully made using MAW plasma technique., with high percentage of antase. The powder is of nano nature as characterized by SEM, XRD. A photocatalytically active nano TiO_2 powder is successfully synthesized using micro wave oxygen plasma and its compatibility with commercially available power is checked using the photocatalytic activity and the size range is justified using the SEM analysis and slight deviation is observed in tube fraction from bag fraction. composition and phases are also analyzed using XRD analysis. The nano particles produced are of superior quality, however efforts are required to reduce manufacturing cost for large scale production..

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