

Synthesis of TiO₂ by polymerizable precursor method using Titanium citrate complex as precursor

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Abstract

The fine powder of TiO₂ has been synthesized by totally alkoxide free sol gel method. The ammonium citratoperoxotitanate (IV) has been synthesized and used as molecular precursor which is highly stable in air. This starting precursor allows us to avoid the use of titanium alkoxide or titanium tetrachloride, which are extensively reported in literature. The synthesis has been carried out in ambient atmospheric conditions. The modified polymerizable precursor method has been adopted for the sol gel chemistry of TiO₂. The final powder precursor has been analysed by thermal analysis (TG and DTA) to explore the thermal kinetics. The X-ray diffraction analysis through Rietveld method confirms that the final product is highly pure rutile TiO₂ powder. The laser granulometry and SEM analysis show the agglomeration of fine particles with size in the order of 200 nm.

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Introduction

The titanium oxide (TiO_2) is one of the most promising material due to its potential applications in various fields such as, photocatalysis, solar energy, emulsion and gas sensors [1-4]. Apart from these applications, the recent developments of polymer electrolytes with dispersed TiO_2 powder also spurred the research interest in this material [5]. Hence there is strong urge to develop fine powder of TiO_2 material for these applications and various authors reported the formation of fine powders by various methods (wet chemical method, sol gel method etc.,) [6-8]. Especially the sol gel method, which is well known for the synthesis of metal oxides is studied extensively for the preparation of TiO_2 powder. The conventional sol gel methods are based on the hydrolysis and condensation of the molecular precursors. So far the researchers developed the titanium oxide by sol gel methods using the titanium alkoxides (such as titanium isopropoxide etc.,) or titanium tetrachloride (TiCl_4) as molecular precursors which are highly reactive and sensitive to moisture. Further it is very difficult to control hydrolysis reaction rates of these molecular precursors due their high reactivity, which results in the loss of microstructural control over the final oxide. Hence the whole experiments should be carried out in an inert atmosphere, which makes the synthesis process more difficult in nature. P.Arnal et al, [9] suggested the use of non-hydrolytic method to control the reactivity of these molecular precursors and to synthesize titanium oxides. Even this non hydrolytic method needs complicated reactions such as etherolysis and alcoholysis of TiCl_4 to reduce the reactivity of the molecular precursor TiCl_4 . Hence there is a strong need to find a simple and atmospheric friendly way to obtain a titanium oxide using the sol gel synthesis. Recently Kakihana et al [10], reported the formation of highly water soluble titanium citrate complex, by using titanium metal powder and citric acid. This titanium citrate complex has been used as molecular precursor for the synthesis of TiO_2 by polymerizable method and the detailed procedure of synthesis has been described in this paper.

EXPERIMENTAL

For the synthesis of fine powder of TiO_2 , Ti powder (98.5 %) from Fluka ,hydrogen peroxide (30 %) from Carlo Erba and ammonia (35 %) from Fischer Scientific, citric acid (99.5 %) and ethylene glycol (99 %) from Aldrich are used as starting materials. The detailed procedure of the synthesis is given in the next part of the paper. Thermal analysis (TGA and DTA) were performed with a Setaram TGDTA92 equipment at a heating rate of $5\text{ }^\circ\text{C min}^{-1}$ in

air using Pt crucibles. Powder X-ray diffraction patterns ($\text{CuK}\alpha$ radiation) have been recorded at room temperature with a Philips X'Pert PRO diffractometer, equipped with a X'celerator detector, in the 2θ range from 5 to 123° with an interpolated step of 0.008° . The Rietveld method [11] using the Fullprof program [12] is used for the structural refinement with a peak shape described by a pseudo-Voigt function. In addition to the lattice and atomic parameters, the zero shift, the scale factors and the background parameters are refined.

Microstructure observations were performed using a Hitachi 2300 Scanning Electron Microscope (SEM). Granulometry has been carried out with a Beckman Coulter equipment in water at room temperature. In-situ ultrasonic vibration has been used before measurement of the particles size.

RESULTS AND DISCUSSION

Synthesis and calcination of the polymer precursor

The crucial step in this modified Pechini-type method was to prepare a highly water soluble precursor to avoid the use of alkoxides, which are not stable in open air. This has been carried out by dissolution of Ti metal in hydrogen peroxide and ammonia solution, as previously reported [13]. Initially 0.25 g of Ti metal powder is dissolved in cold aqueous solution containing 20 ml of H_2O_2 (30 %) and 5 ml ammonia solution (35%) at room temperature. This yields a yellowish transparent solution which is a peroxo complex of titanium, such as peroxy titanate $[\text{Ti}(\text{OH})_3\text{O}_2]^-$ ion [13]. In order to form titanium metal citrate complex, 0.1 mol% of Citric acid (19.2 g) is added in excess to the above titanium peroxo solution. This reaction yield citratoperoxotitanate $[\text{Ti}(\text{C}_6\text{H}_4\text{O}_7)\text{O}_2]^{2-}$ which is highly soluble in water [14]. This titanium metal citrate complex has been added with 0.4 mol% of Ethylene glycol (25 g), which results in redish color viscous solution. The citric acid / ethylene glycol molar ratio was taken as 1:4. This ratio ensures a large excess of hydroxyl groups to promote the formation of low molecular weight oligomers [15]. The temperature is then increased to 150°C to promote esterification between the hydroxyl groups of ethylene glycol and the carboxylic acid groups of citric acid and polymerization. A black polymer precursor, which is stable in air, is then formed. Therefore pyrolysis of the polymer is performed at 350°C that yields a black powder precursor, called hereafter "powder precursor". The black color indicates that the powder contains carbon. The final powder precursor is subjected to calcination in open air for 2 hours at 900°C . The calcination at 900°C

°C yields highly pure and rutile phase TiO₂ powder. Fig.1 shows the typical flow chart of the synthesis procedure used to prepare TiO₂.

TGA-DTA analysis

Fig.2 shows the TGA and DTA curves obtained from the powder precursor in air using a heating rate of 5 °C min⁻¹ in the temperature range from 30 to 1200 °C. The TGA curve indicates a small weight loss of 3 % up to 100 °C, an abrupt weight loss of 81 % in the temperature range from 300 to 500 °C and no further weight loss up to 1200 °C. The first weight loss is mostly due to water desorption. The second abrupt weight loss is due to the degradation of the polymer, converting the organic component into CO₂ and H₂O.

The DTA curve shows three exothermic peaks in the temperature range from 300 to 600 °C. They can be associated to the weight loss shown in the TGA curve and are indicative of organic combustion steps. The main exothermic peak around 500 °C is due to the degradation of organic material from the powder precursor that is accompanied to CO₂ and H₂O gases evolution and then to a considerable weight loss. After this, there is no change in weight, which confirms the complete burnout of residual carbon from the precursors.

XRD analysis

Fig. 3 shows the powder X-ray diffraction pattern of the rutile TiO₂, synthesized by sol gel method. The X-ray diffraction pattern has been analysed by pattern matching through the Fullproof software. The theoretical and experimental peaks matches well and no impurity phases have been identified by this pattern matching analysis. The structure of the rutile TiO₂ has been identified as tetragonal (space group P 42/M N M) and the cell parameters are found to be $a = b = 4.5938 \text{ \AA}$ and $c = 2.9598 \text{ \AA}$, which agrees with previous reported values [16].

Morphology of the TiO₂ powder

Fig. 5 shows SEM micrographs of TiO₂ after calcination at 900 °C. It reveals the microstructure of the ceramic. It can be observed that after heating at 900 °C for 2 hours, the ceramic is made of small grains of diameter around 200 nm (Fig. 4a). However these grains agglomerate as shown in Fig. 4b. These agglomerates, as big as 100 µm can be observed. This is clearly revealed by laser granulometry, as shown in Fig. 6, which shows the average agglomerated particle size as ~60 µm. This histogram has been obtained from the same TiO₂

powder as used for SEM experiments. The powder has been ultrasonically treated in-situ in water for 1 min with a power of 20 W. This indicates that the grains are strongly bounded with each others.

CONCLUSION

The rutile phase, TiO_2 , has been synthesized by a Pechini-type polymerizable precursor method using highly water soluble Titanium metal citrate molecular precursor. This highly water soluble precursor helps us to avoid the use of alkoxides, which are not stable in open air. The final powder, obtained by heating the powder precursor at 900 °C for 2 hours in air, is a pure and well crystallized rutile phase of TiO_2 as revealed by powder X-ray diffraction. Both SEM and granulometry showed that the final powder is made of small particles of around 200 nm in size.

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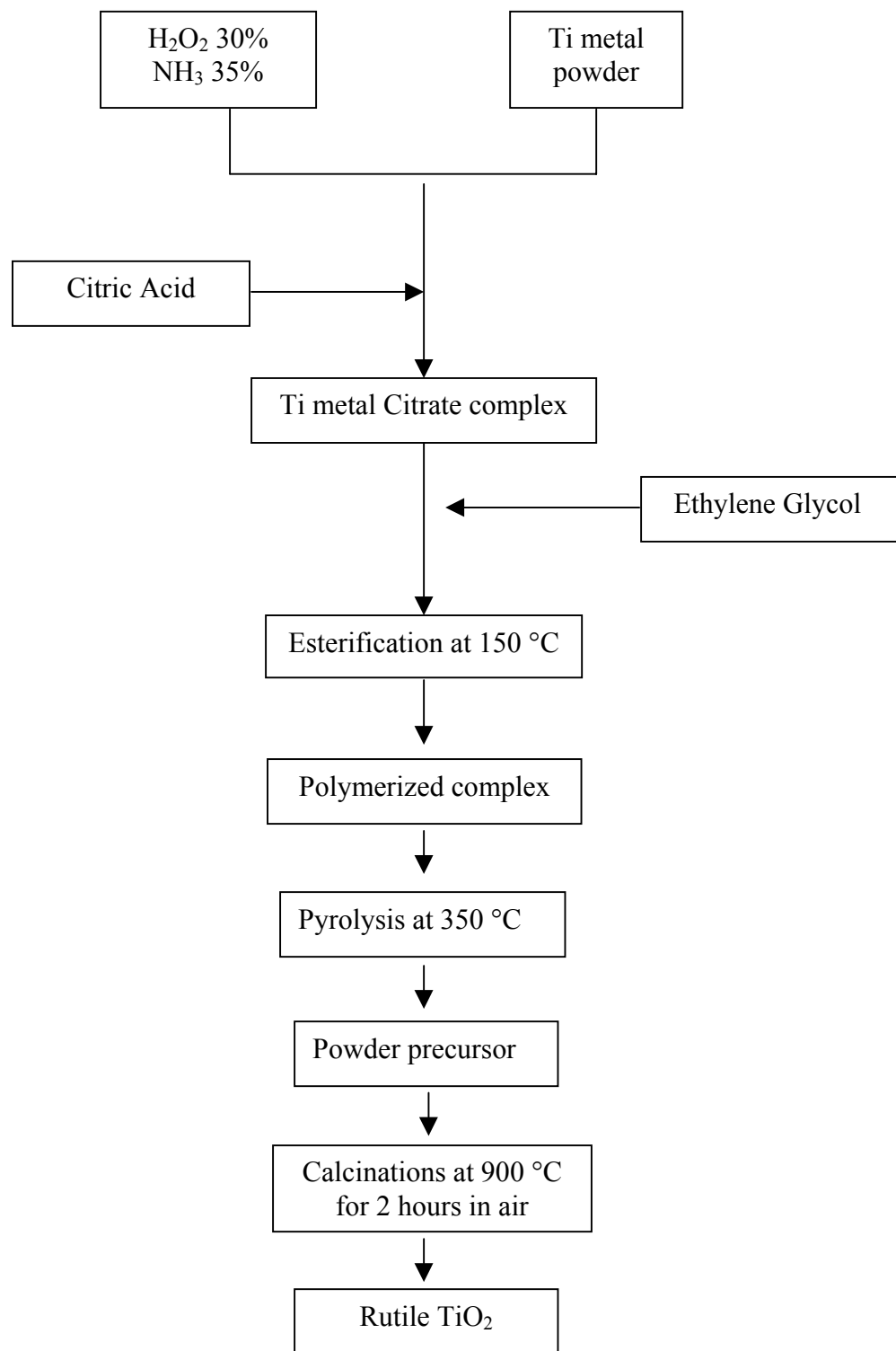


Fig.1 – Flow chart for preparing TiO₂ by a modified Pechini-type polymerizable precursor technique.

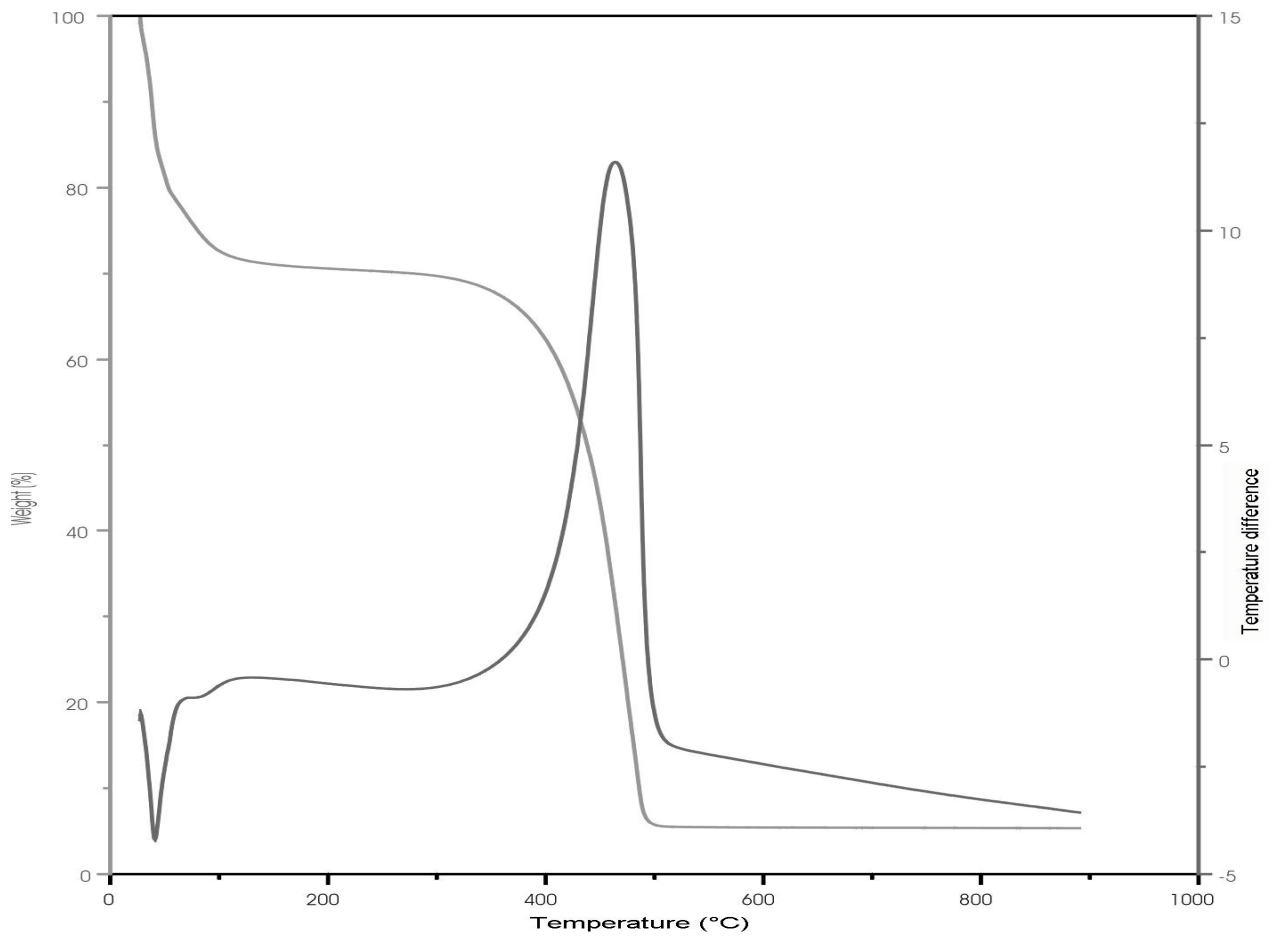
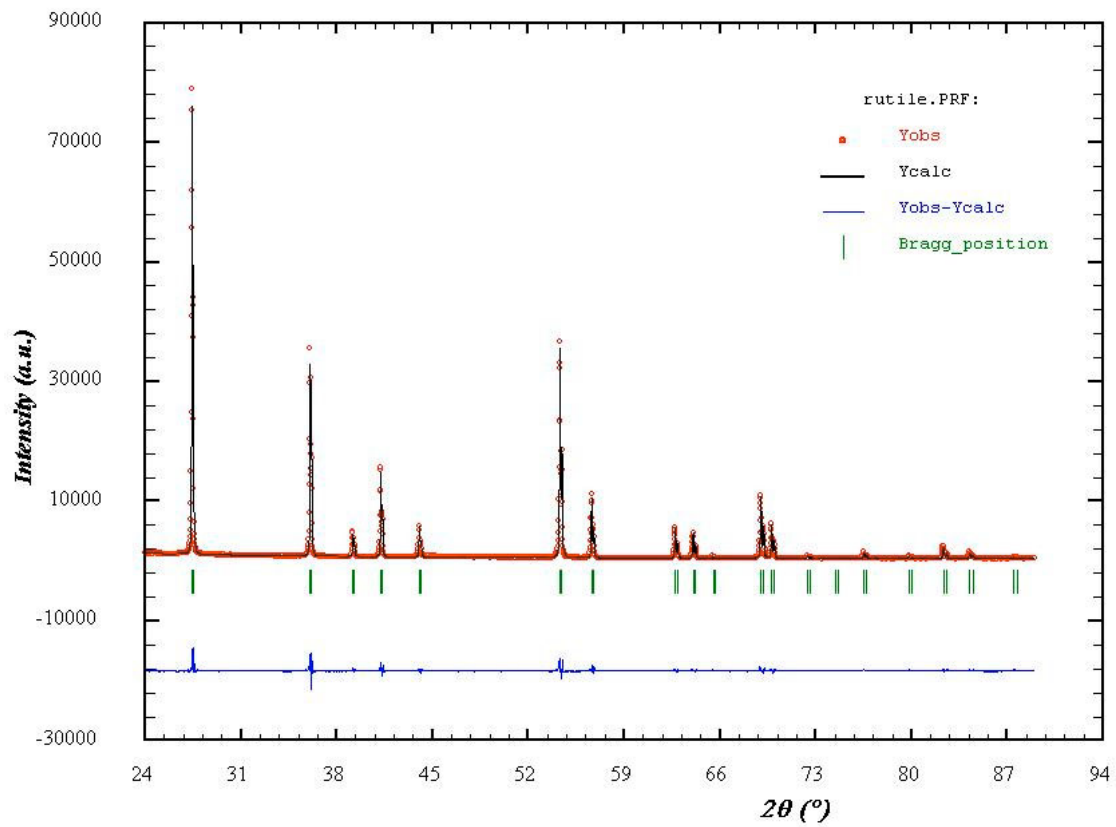


Fig.2 TG and DTA spectrum of the TiO_2 precursor measured in open air atmosphere

Fig.2 Calculated and observed powder X-ray diffraction pattern of TiO₂ sample prepared by a modified Pechini-type polymerizable precursor technique



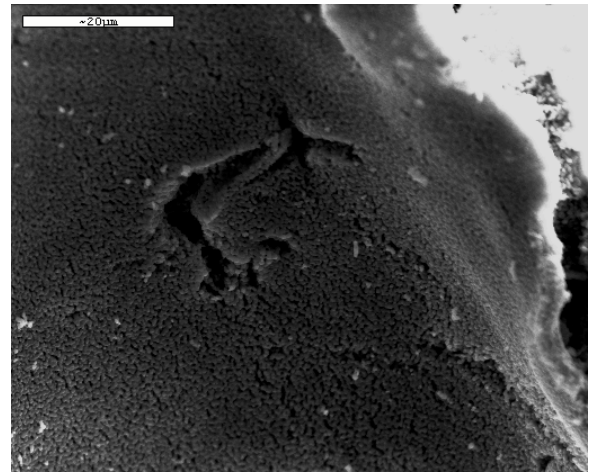
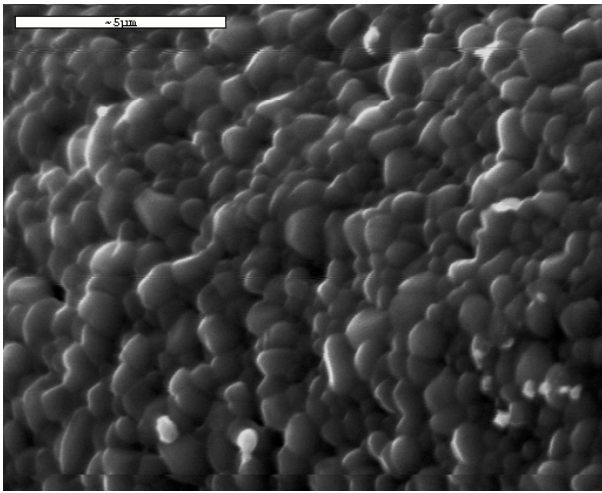


Fig. 4 SEM image of the rutile TiO_2 synthesized by polymerizable precursor method.

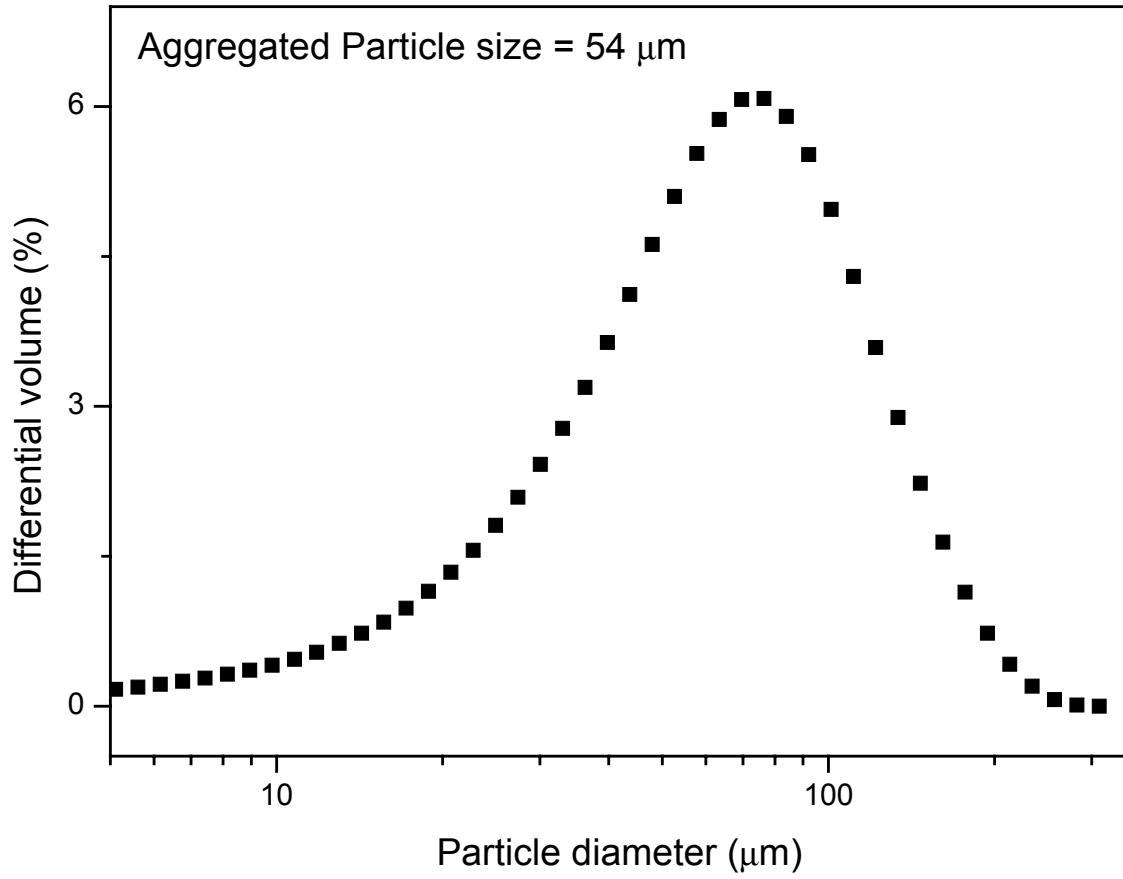


Fig. 5. Laser granulometry spectrum of TiO_2