SYNTHESIS OF TITANIUM OXIDE NANO POWDER BY A NOVEL GEL COMBUSTION METHOD

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Because of special properties and different applications of titanium dioxide nano particles, many methods have been applied for fabrication of these nano powders which most of them are slow and so expensive, then finding a cheap and fast method for fabrication of this material become so much important. In this study, gel combustion method was used to prepare titanium dioxide nano powder. Titanyl nitrate and different fuels of glycine, urea, and citric acid were used with various ratios of fuel to salt and experiments conducted with different primary pH, followed by calcinations in different temperatures. The results showed that by using glycine, fuel to raw material ratio of 1, neutral pH, and calcinations temperature of 400^{o}C the optimum conditions for prepare nano TiO_2 were achieved and nano powder with 62 m^2/g specific surface areas was fabricated.

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1. Introduction

Titanium dioxide (TiO_2) is an n-type semiconductor, a very interesting material which has many attractive properties. These properties include high refractive index, high dielectric constant and chemical stability. Crystalline nano TiO_2 is the most important candidate for using in many applications, including photo catalytic materials [1-3], solar cells [4], semiconductor electrodes [5] and biosensors [6-8]. Many methods have been used for synthesis of nano titanium dioxide powders, such as sol–gel process [9-12], chemical precipitation, combustion, etc. [13-18] which most of them are so slow, have low nanopowder yield and were applied in laboratory scale only. On the other hand, gel combustion method is performed very fast, has very high nano powder yield and have the ability to scale up without any trouble.

In the gel combustion method, the raw materials, which are usually a nitrate compound and a fuel, are dissolved in water. After controlling the pH, by a weak base such as ammonia, the mixed solution is heated to change the sol to a high viscosity gel. Increasing temperature causes an exothermic combustion process and organic materials as a reducing agent (fuel) reacts with nitrates as an oxidation agent. Reaction change the gel to a very fine and intensively porous substance which later will convert to final product by calcination. Calcination promotes metallic cation solubility and hence prohibits preferred crystallization during evaporation of the primary water [14-16]. Due to preserve stoichiometry, Gel combustion gives a homogenous, high purity, and high quality nano powders [16].

Several works were reported in the field of TiO_2 powder preparation by gel combustion method. Chi Hwan Han et al. [14] synthesized nano crystalline TiO_2 by hybrid sol-gel combustion method. They used titanium isopropoxide and acetylene black as starting materials but did not investigate effective parameters of fabrication process and products precisely. K. Nagaveni et al.

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[4] synthesized TiO_2 nano powder by gel combustion method. They used titanium isopropoxide and glycine as starting materials and fabricated powders were optimized for solar cell application [4]. Sivalingam et al., [3] synthesized TiO_2 nano powder by gel combustion method in the range of 8-10 nm and investigated on the catalytic properties of nano titania products. Also, Cheng Youpin et al. [19] investigated on catalytic properties of nano titania products which are fabricated by gel combustion method.

In the past researches effect of fabrication parameters on structure of TiO_2 nano powders synthesized by gel combustion method did not studied well, so aim of this research is investigate on the effect of fabrication parameters such as type of fuel, fuel to material ratio, pH, and calcinations temperature on structure and morphology of fabricated nano titanium oxide powders.

2. Experimental procedures

The raw materials used in this study were of titanium isopropoxide ($C_{12}H_{28}O_4Ti$, 284.25 g/mol, Merck), glycine ($NH_2.CH_2.COOH$, 75.07 g/mol, BDH), urea (NH_2CONH_2, 60.06 g/mol, Merck), and citric acid ($C_6H_8O_7.H_2O$, 192.124 g/mol, Merck) all of materials were used in this study had analytical purity. TiO_2 powder was synthesized by an amount of 5 g per batch according to the flow chart shown in figure 1. The titanyl nitrate ($TiO(NO_3)_2.H_2O$) was synthesized by the reaction of titanyl hydroxide [$TiO(OH)_2$] obtained by the hydrolysis of titanium isopropoxide [Ti(*i*-OPr)$_4$] with nitric acid.

$$Ti(i - OC_3H_7)_4 + 3H_2O \rightarrow TiO(OH)_2 + C_3H_7OH$$
$$TiO(OH)_2 + HNO_3 \rightarrow TiO(NO_3)_2 + 2H_2O$$

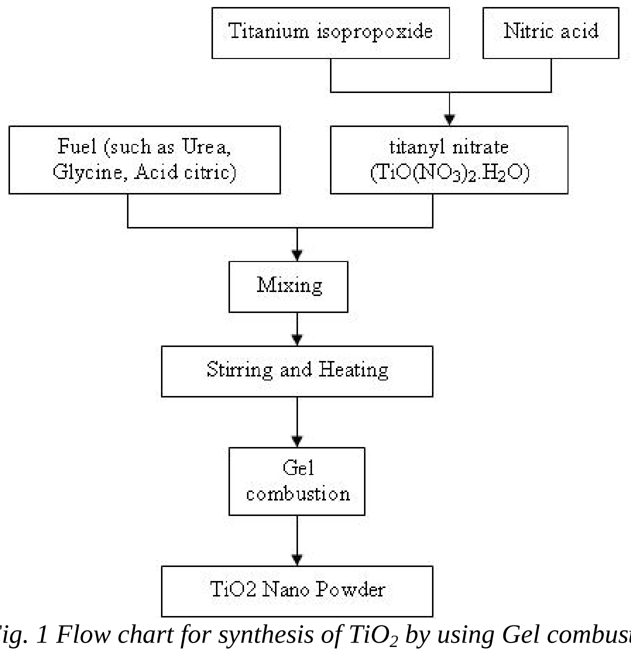


Fig. 1 Flow chart for synthesis of TiO_2 by using Gel combustion method

After fabrication of titanyl nitrate, mixture of it and fuel were dissolved in ionized water, then homogenized and heated on a hot plate up to 300^oC. During heating, soultion became more viscous, then it became solid paste and after that, combustion accrued. After combustion was completed, products were calcinated at 500^oC for 1 hour. The fuel to titanyl nitrate ratio was selected as 0.5, 1, and 2. Composition of materials in each experiment and their codes are shown in table 1, pH in these experiments was adjusted at 2-4.

Table 1. Composition of Materials and their codes were used in this research

Sample code	Type of fuel	Fuel to Nitrate ratio (F/M)
A1		0.5
A2	Urea	1
A3		2
B1		0.5
B2	Glycine	1
B3		2
C1		0.5
C2	Citric acid	1
C3		2

For Study the effect of pH, glycine was selected as a fuel; it was weighed, dissolved in ionized water, mixed with titanyl nitrate and homogenized on a magnetic stirrer. Then pH was adjusted to desired value (acidic, neutral and basic) by using Nh4OH. Then samples were heated and combustion and calcination were conducted as same as other experiments. Sample codes and pH of experiments was listed in table 2.

Table 2. Composition of raw materials with different amount of pH which are used in our study.

Sample code	Fuel	Fuel to Nitrate ratio (F/M)	pH
D			2-4
E	Glycine	1	6-8
F			10-12

Reaction of raw materials was investigated by DTA (1640 Polymer Lab., 5 ^{o}C/min, England) in order to find information about their reaction parameters. Surface area of fabricated nano powders were measured by BET instrument (Micro merticf, USA) and their microstructure was studied by Scaning electron microscope (SEM, Phillips XL30).

3. Results and discussion

Reaction of raw materials with three fuels was studied by DTA and the results are shown in Fig. 2.

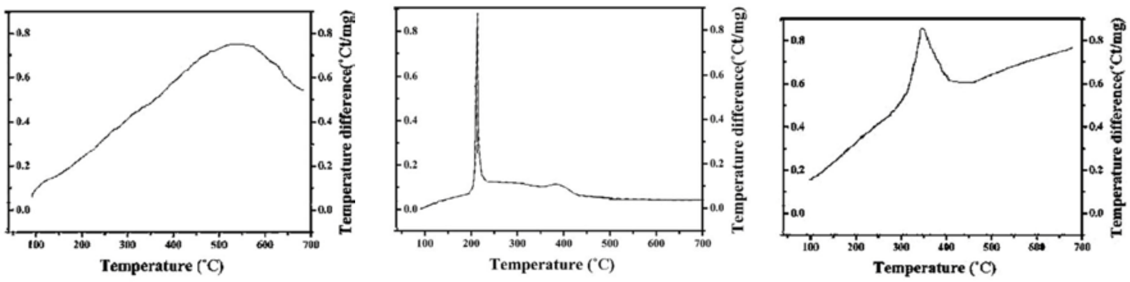


Fig. 2. DTA result from reaction of titanyl nitrite with different fuels (a)Urea (b) Glycine (c) Citric acid

As shown in Fig. 2, exothermic combustion of glycine was clearly happened at 210^{o}C, for citric acid fuel this behavior was quite obvious at 350^{o}C, but for urea combustion behavior is unclear and was taking place only when samples heat treated in the furnace.

Surface area of TiO_2 nano powders which were synthesized by different amount of fuel to material ratio and products was studied by BET and results have been plotted in Fig. 3. Based on this figure, by increasing fuel to material ratio, specific surface area was increased and after reaching the maximum, was decreased linearly. Maximum amount of surface area were achieved by using glycine and in glycine, the best result were attained by using fuel to material ratio of 1.

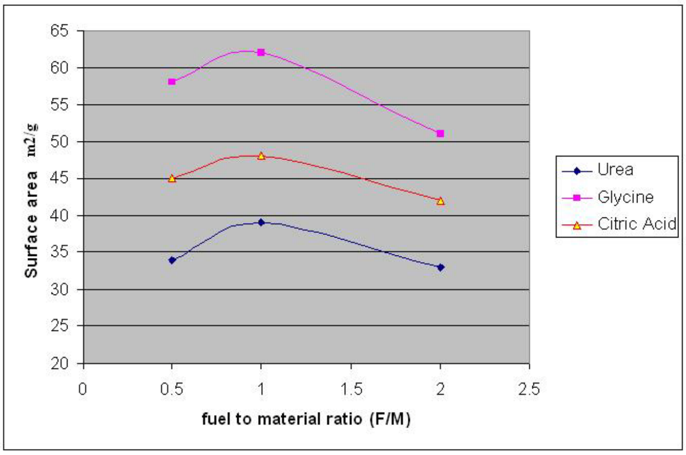
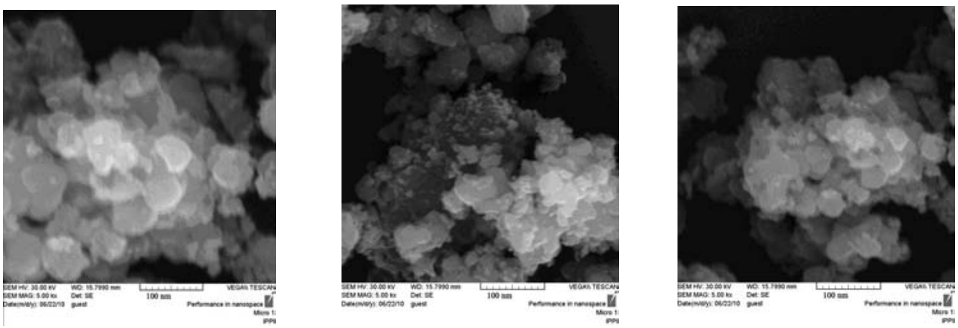


Fig. 3. Specific surface area of TiO_2 samples were fabricated by different fuel to material ratio

Microstructure of samples with different types of fuel has been shown in Fig. 4.From SEM microstructures and BET results, it is possible to find out that glycine as fuel, and fuel to raw materials ratios of 1, gave better result.

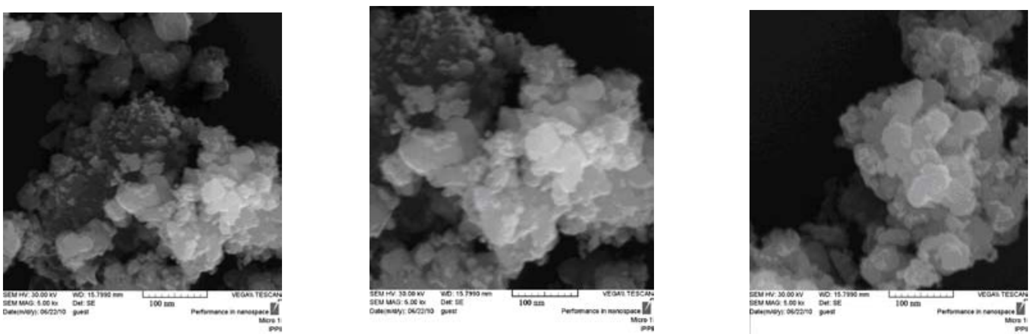


(a) (b) (c)

Fig. 4. SEM of TiO_2 nano powder with different fuel (a) urea, (b) glycine, (c) citric acid.

Therefore, it is possible to induce that using glycine can bring down the formation temperature of product due to easier complex formation and homogeneous gel, thus the crystallites size are smaller in comparison to other fuels. When glycine was used, the release heat during combustion is more and as a result the combustion reaction enthalpy is more which yields both a growth on crystallite size and on a complete combustion reaction with more crystallize phase.

Surface area and morphology of samples fabricated by glycine fuel and different types of pH (acidic, basic, and neutral) have been shown in table 3 and figure 5 respectively.



(a) (b) (c)

Fig. 5. SEM of TiO_2 powder with different pH (a) pH=2-4 (b) pH=6-8 (c) pH=10-12

Table 3. Results of surface area D-F samples.

Sample code	Fuel	Fuel to Nitrate ratio (F/M)	pH	Surface area (m^2/g)
D	Glycine	1	2-4	56
E			6-8	62
F			10-12	67

Fig. 5 reveals that the pH of solution has a significant impact on the TiO_2 nano powder size. On the other hand based on table 3, finer nano powders were achieved by acidic solutions. These results show that TiO_2 nano particles with different size can be obtained by change pH of reacting solution between 2 and 12. Changing the pH of reaction will change the size of nano particles. With decreasing the pH, the concentration of H^+ becomes higher. The oxygen atom in the Ti–O that has alone electron pair and it's easy to form a bond with the H^+. Thus the intensity of Ti–O bonds is weakened and this will promote system to combustion easer. Then if solution becomes more acidic, combustion performs faster and nucleation of TiO_2 nano particles increases so much. As a result of faster nucleation, the size of nano particles will decrease which lead to finer distribution of TiO_2 nano powders which is named D sample (table 3). So it's possible to control nano TiO_2 particle size by regulating the pH of solution.

4 Conclusions

The following results were obtained:

1- It is possible to prepare fine TiO_2nano powder by using gel combustion method.

2- Using glycine as a fuel in gel combustion method, make the better TiO_2nano powders than urea and citric acid.

3- The most desired fuel (glycine) to raw materials ratio is 1.Increase or decreases of this ratio decreases the efficiency and deteriorates morphology of synthesized nano powders.

4- Using acidic solutions in gel combustion method creates finer and more homogenous TiO_2 nano powder than neutral or basic solutions.

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