SYNTHESIS AND CHARACTERIZATION OF TITANIUM DIOXIDE NANOMATERIALS VIA HORIZONTAL VAPOR PHASE GROWTH (HVPG) TECHNIQUE

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Abstract

This study aims to synthesize and characterize titanium dioxide nanomaterials via horizontal vapor phase growth (HVPG) technique toward making a sensor for detecting engine oil degradation. The growth temperature was varied at 1000 °C, 1100 °C, and 1200 °C with the fixed baking time of 6 hrs and ramp rate of 10°C/min. The said nanomaterials grown on glass substrate were characterized by scanning electron microscope (SEM) and energy dispersive x-ray (EDX) to analyze the surface structure morphology and determine the elemental composition, respectively. Results showed that various sizes of titanium dioxide particles were found on the substrate surface at the proposed growth mechanisms.

Keywords: Horizontal vapor phase growth technique, Nanomaterials, Titanium dioxide

Introduction

Titanium dioxide (TiO_2) nanomaterials, one of the well-known metal oxides, have gained research interest and used in wide range of applications especially in gas sensor, batteries, air purification, and solar cell applications because of its wide band gap, high refractive index, high physical and chemical stability, electronic and optical properties, low cost, and non-toxicity [1,2]. Recently, it has been utilized for fabricating the sensor applied in engine oil degradation monitoring because of its high sensitivity, chemical stability, and electrical properties of the nanomaterials used. In the study of [3], TiO_2 nanolayers pasted on glass substrate were proposed for acidic sensing of the used and fresh engine oil. In addition, the work conducted by [4], imprinting the TiO_2 nanoparticles on quartz crystal microbalance (QCM) was employed successfully for capric acid detection with the aim of determining the engine oil's quality. Moreover, in the work of [5], TiO_2 layers were selected as a favorable material for interacting with acidic products generated by engine oil oxidation. The study done by [6], TiO_2 layers coated on shear transverse wave (STW) resonators were used as receptors for detecting oxidized products produced from the engine lubricant degradation.

There are several methods of fabricating the TiO_2 nanomaterials that were used in previous studies such as sol-gel [1,3-7], chemical vapor deposition [8,9], and physical vapor deposition. However, the said methods are still inefficient strategies to synthesize the TiO_2 nanomaterials for an engine oil sensor. The disadvantages of the existing methods are the following: the slow process of fabrication and costly implementation. Other disadvantages are the difficulty in controlling the surface morphology and the complex methodology of the material synthesis. Some of the methods also produce problems on chemical disposal and human health hazards. Therefore, the horizontal vapor phase growth (HVPG) technique was recently introduced to synthesize the different kinds of nanomaterials because of the benefits such as an economical and reliable method and less source material with high purity and the larger quantity of the nanomaterials generated. Distinct metal oxide nanomaterials were successfully fabricated through the said technique for sensor applications. For instance, iron oxide nanoparticles and zinc oxide nanomaterials and different nanostructures of tin oxide were fabricated successfully via HVPG for glucose detection [10] and gas sensing application [11,12,13], respectively. Moreover, this said technique was also used to produce the distinct nanocomposites for coating application including silver-titanium dioxide [14,15,16,17] and silver-graphene[18]. Hence, HVPG technique is proposed in this study to synthesize the titanium oxide (TiO_2) nanomaterials for engine oil applications instead of the previous techniques.

Theory

As presented in Figure 1, the HVPG technique, a top-down synthesized method, is categorized as spontaneous growth using evaporation-condensation process at a very low pressure around 10^{-6} Torr [19]. It has three basic principles including the vaporization of the material, transportation of the vapor, and condensation [19,20,21]. First, the source material in the formation of powder is vaporized in the shape of atomic species or molecular species heated by high-temperature source i.e. furnace. Second, this vaporized material is then transported to the substrate surface and lastly it is condensed and deposited on the substrate surface because of the temperature differences along the tube from the hottest zone to the coolest zone to produce the distinct kind of nanomaterials.

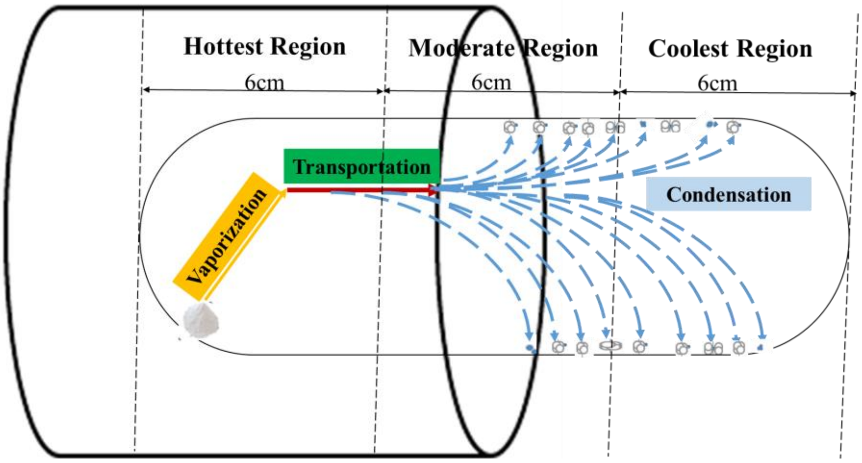

Figure 1. HVPG technique

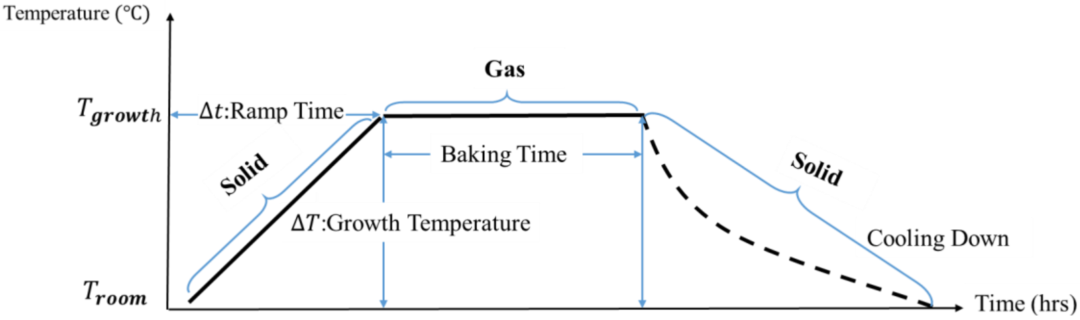

Figure 2. HVPG growth temperature profile

As seen in Figure 2, the relationship between the phase transition of the source powder and temperature changes is presented in the growth temperature profile. It has two phase changes including sublimation and deposition. In the first transition, the source powder in the form of solid is changed into vapor once the temperature is increased up to the ultimate point. The deposition is then taken place by transforming the vapor to solid for generating the nanomaterials grown on the glass substrate when decreasing the temperature.

Methodology

The quart tube with dimensions of an inner diameter of 10 mm, an outer diameter of 12 mm, and a length of 300 mm substrate was prepared and then sealed fully its one end as seen in Figure 3(a). It was then cleaned using an ultrasonic cleaner in the duration of 30 minutes and allowed to dry in the air as presented in Figure 3(b). A 35 mg of TiO_2 (anatase) powder was weighed and loaded into the cleaned tube as shown in Figure 3(c). After which, it was then connected to the thermionics high vacuum system for the purpose of lowering the pressure to approximately 10^{-6} Torr as revealed in Figure 3(d). After reaching the desired pressure, the tube was sealed fully and detached using a mixture of oxygen and LPG blowtorch. For the sake of nanomaterials fabrication, the closed-end tube was placed halfway inside the thermolyne horizontal tube furnace to create the temperature gradients along the tube between the hottest zone and coolest zone as seen in Figure 3(e). That condition induced various types of nanomaterials to grow optimally at the divided zones. In this study, the furnace was set at the fixed baking time of 6hrs and ramp rate of 10℃/min and the varied temperature of 1000 ℃, 1100 ℃, and 1200 ℃. After finishing baking, the tube was allowed to cool down until reaching the room temperature. And then, the baked tube was brought out from the furnace and divided into three zones namely A (hottest zone), B (moderate zone) and C (coolest zone) and then cracked slowly to obtain the glass substrate containing a different kind of nanomaterials using for characterization purposes. Scanning electron microscope (SEM) and energy dispersive x-ray (EDX) were utilized for analyzing surface morphology and topology and determining the chemical composition, respectively.

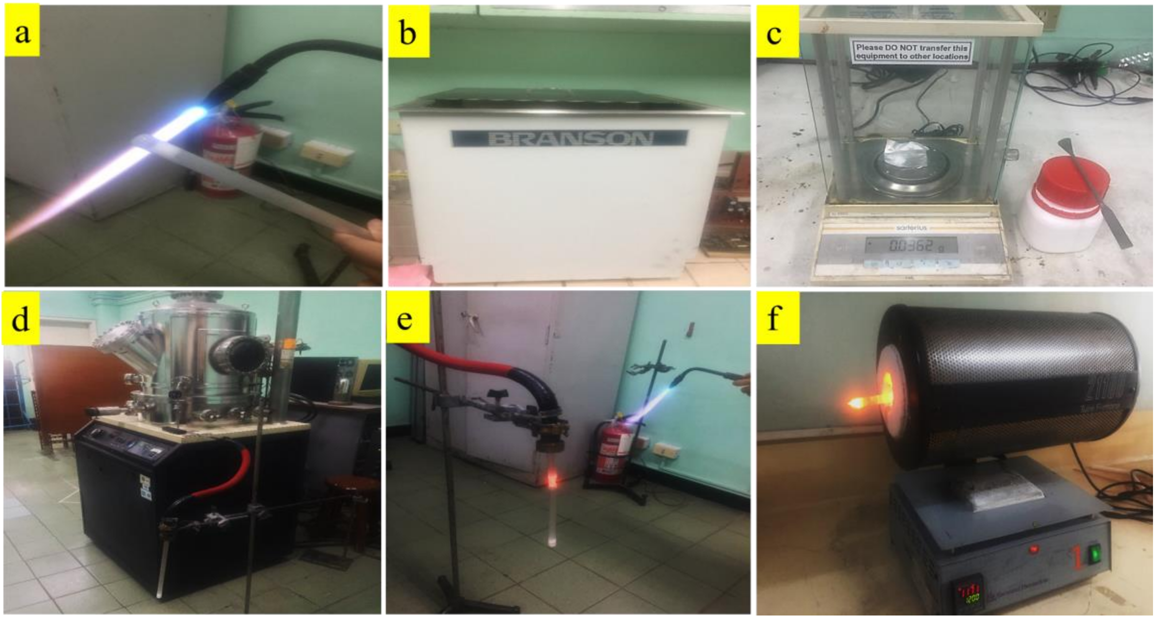

Figure 3. (a) Sealing one end of the tube (b) cleaning the tube using ultrasonic cleaner (c) weighing the TiO_2 powder (d) lowering the pressure inside the tube to about 10^{-6} Torr and sealing its other end after reaching the desired pressure, and (e) placing the tube haft way inside the furnace

Results and Discussion

Scanning electron microscope (SEM) and energy dispersive x-ray (EDX) were used as a tool to characterize the surface structure morphology and the elemental composition of the grown nanomaterials, respectively. Nanomaterial characterization was needed to study the structure of the grown nanomaterials for the purpose of selecting the appropriate nanomaterials such as nanoparticles for fabricating the engine oil sensor. The selected surface structure was very important for sensor fabrication since it affects sensor performance.

Scanning Electron Microscope (SEM) Results

Based on SEM results, various sizes of the TiO_2 particles were grown on the glass substrate in zone B and zone C at the varied growth temperature and baking time as seen in Figure 4-9. These results presented a similar type of TiO_2 particles with the previous study on the synthesis of titanium dioxide nanomaterials via sol-gel methods [22]. In the case of the same type and formation of particles generated, it can be noted that particle size, aggregation, and agglomeration were changed in terms of varying the growth mechanisms and selecting zones. As shown at 1000℃ and 6hrs for both zone B and C, the particle sizes were decreased when raising the growth temperature up to 1100 ℃ and 1200 ℃. Moreover, there were more agglomeration and aggregation of the particles once the controlled temperature was increased. Unlike, it was less agglomerated and aggregated when the low temperature was selected. Furthermore, the shape of grown particles was changed to spherical forms in the matter of decreasing the growth temperature. As presented in Table 1 and Table 2, the measured diameters of the grown TiO_2 particles are listed for zone B and zone C, respectively. For the purpose of fabricating the engine oil sensor, the grown TiO_2 particles were selected because of its high sensitivity of acidity detection based on literature[3,4,5,6].

Zone B

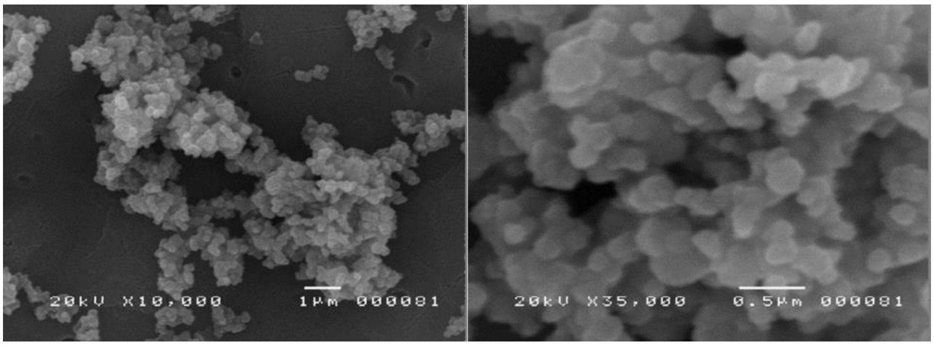

Figure 4. TiO_2 particles generated at 1200 ℃ and 6 hrs

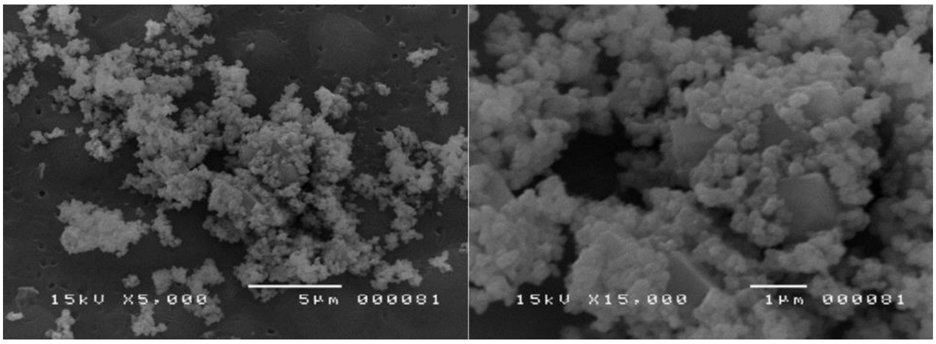

Figure 5. TiO_2 particles generated at 1100 ℃ and 6 hrs

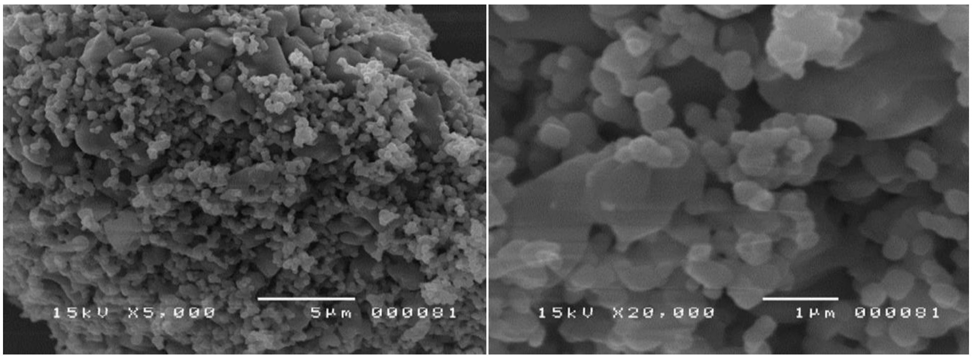

Figure 6. TiO_2 particles generated at 1000℃ and 6hrs

Zone C

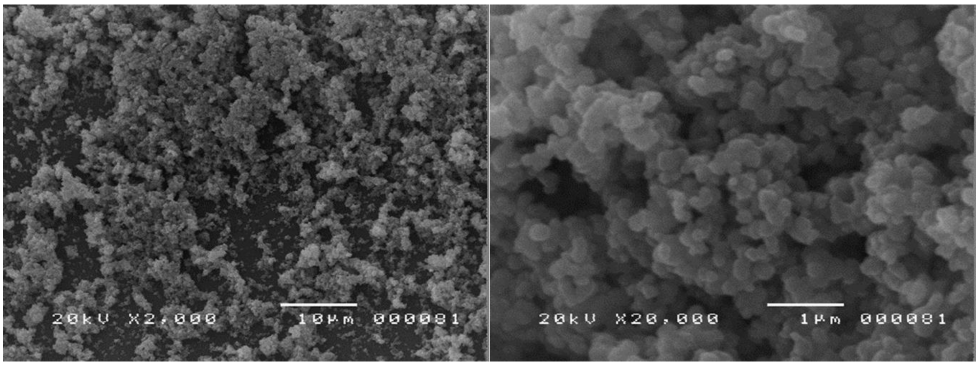

Figure 7. TiO_2 particles generated at 1200℃ and 6hrs

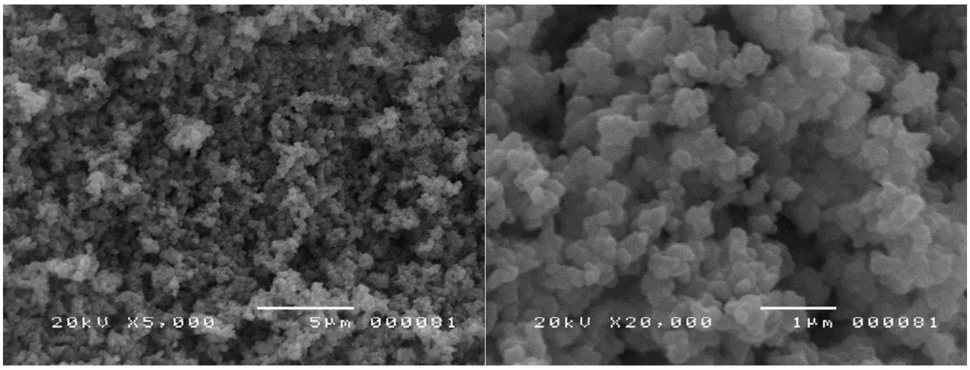

Figure 8. TiO_2 particles generated at 1100℃ and 6hrs

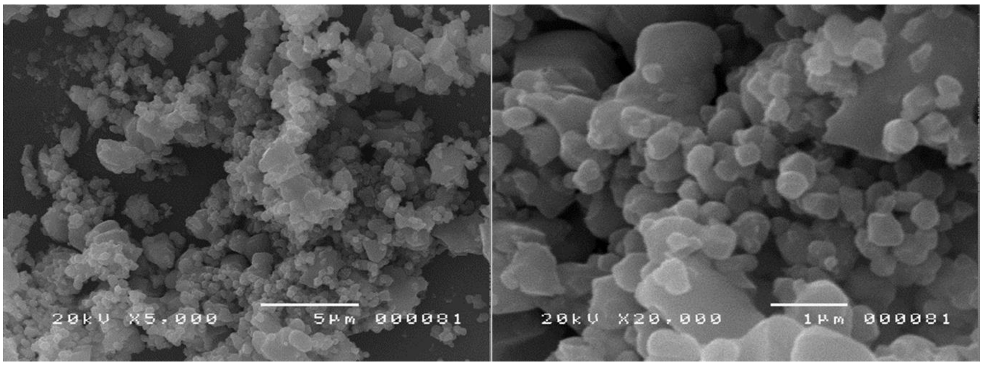

Figure 9. TiO_2 particles generated at 1000℃ and 6hrs

Table 1. Diameter Measurement of the TiO_2 Particle in Zone B

Growth Temperature (°C)	Baking Time (hrs)	Diameter Range (nm)
1200	6	80-160
1100	6	91-168
1000	6	135-260

Table 2. Diameter Measurement of the TiO_2 Particle in Zone C

Growth Temperature (°C)	Baking Time (hrs)	Diameter Range (nm)
1200	6	113-173
1100	6	115-206
1000	6	189-319

Energy Dispersive X-ray (EDX) Results

All of the grown particles at the varied growth temperature and fixed baking time were proceeded with EDX analysis to determine the elemental composition. As shown in Figure 10, Figure 11, and Figure 12, results revealed the atomic percentage of titanium and oxygen of the grown particles. It can be concluded that all of them had the right atomic ratio of titanium to oxygen which is around 1:2.

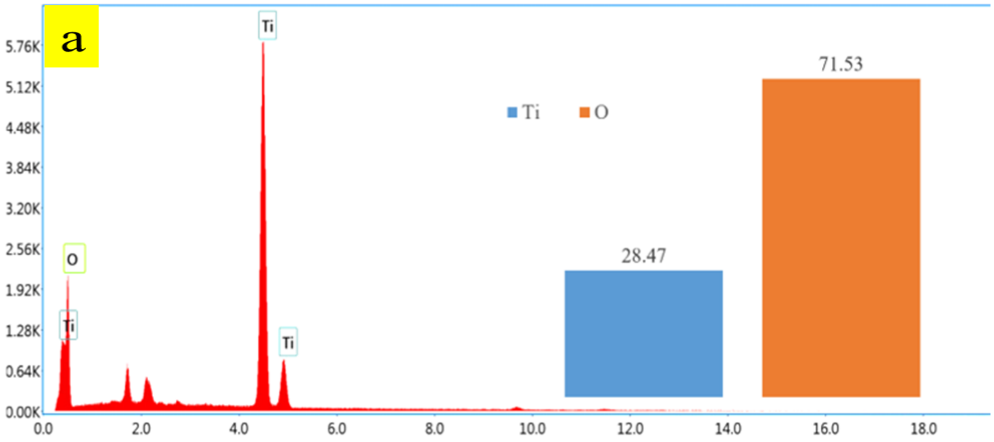

Figure 10. EDX spectrum of TiO_2 particles at 1000°C

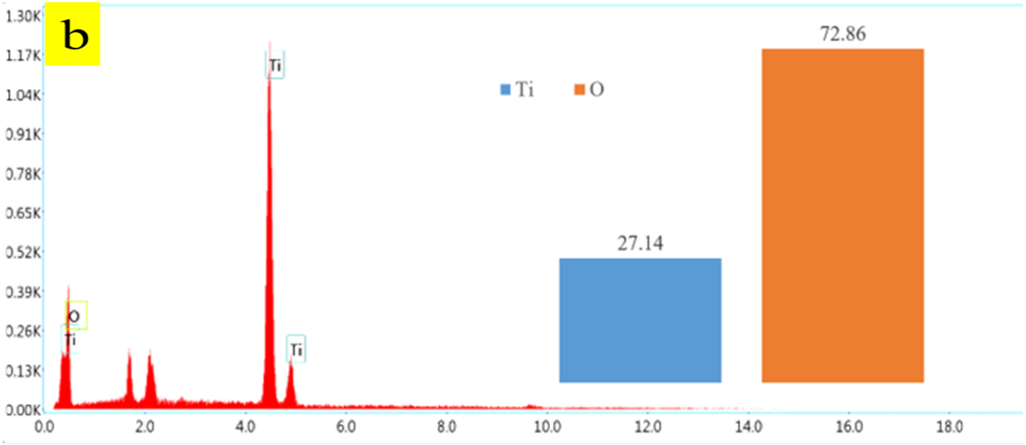

Figure 11. EDX spectrum of TiO_2 particles at 1100°C

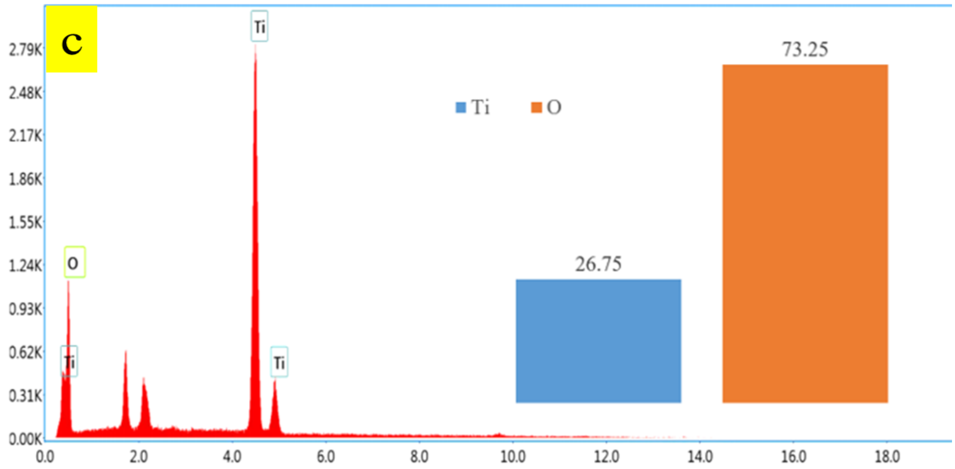

Figure 12. EDX spectrum of TiO_2 particles at 1200℃

Conclusions

Results proved that different forms and sizes of the titanium dioxide particles were synthesized successfully using HVPG at the various growth temperature of 1000 ℃, 1100℃, and 1200 ℃ with the fixed baking time of 6hrs and ramp rate of 10 ℃/min for fabricating the sensor device. Based on SEM results, it can be noted that the particle size, aggregation, and agglomeration were changed in terms of varying the growth temperature. For the further synthesis of TiO_2 nanomaterials via HVPG, researchers should focus on increasing the growth temperature up its melting point to enhance the understanding of the changes in the amount of the grown particles due to its higher melting point.

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