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Short Communication

Comparative investigations of synthesis TiO_2 Nano-Particles from four different types of alcohols by Sol-Gel method and evaluation of their antibacterial activity

Mariam Farag Ambarak[a,*], Fawzia Muftah Aljazwia[b], Randa Fawzi Alsupikhe[a]

[a] Department of Chemistry, Faculty of Science, University of Benghazi, Benghazi, Libya

[b] Department of Botany, Faculty of Science, University of Benghazi, Benghazi, Libya

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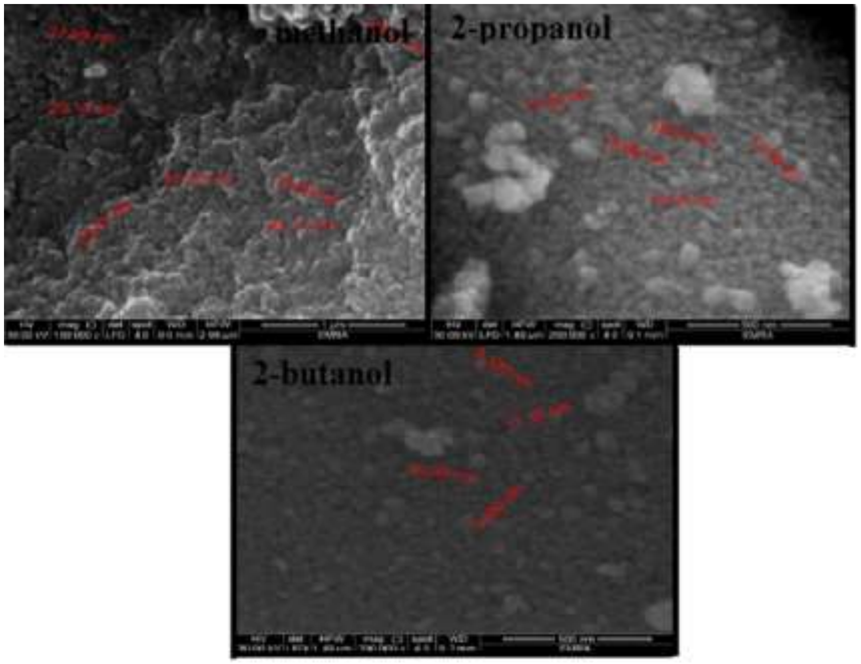
ABSTRACT

TiO_2 nanoparticles were synthesized using a simple reaction of $TiCl_4$ with different types of primary and secondary alcohols. Four different alcohols (ethanol, isopropyl, isobutyl, and isobentyl alcohol) were investigated. The experiments were carried out to compare the products of the reactions with different precursors. The gelatine products were calcined at 400 °C and at 1000 °C in a box furnace and the effect of calcination temperature on the feature of nano-particles was studied. The synthesized TiO_2 nanoparticles were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results revealed that the average particle size was 8.9-18.4 nm. The antibacterial result of titanium dioxide nanoparticles at four types of bacteria was two gram-positive (Staphylococcus aureus and Streptococcus sp.) and two gram-negative (Escherichia coli and Klebsiella sp.). Also, nanoparticles titanium dioxide did not have any effect on these types of bacteria. The sol-gel method could be used for applications that involve nano-crystalline TiO_2 with anatase phase with low cost and simple preparation.

Corresponding author, email: mariam.ambarak@uob.edu.ly (M.F. Ambarak).
Tel.: 0923327488.

Graphical Abstract



Introduction

Nanotechnology is the control of matter at dimensions between nearly to 1-100 nm [1]. Nanoparticles have been studied in recent years as their potentials in catalysis, mechanical, optical, and electronic devices [2]. Titanium dioxide (TiO_2) nanoparticles show high surface area per unit absorption of ultraviolet light in toners and coating materials [3]. Furthmore, titanium dioxide is used as semiconductor in wide range of applications such as photosensor, photocatalysis, dyes sensitized solar cells, optical filters, photovoltaic devices, UV light sensor, and biomedical applications [4]. Metal and metal oxide nanoparticles have been synthesized using various chemical and physical methods. Some of the commonly used synthetic methods are non-sputtering, solvothermal, reduction, electrochemical technique, and sol-gel technique [5]. Sol-gel method is an hydrolysis and poly-condensation processes which forms a solid coating. This technique requires low temperature and is a manageable final product process [6, 7]. Alcohols and benzene are commonly used in this mthod [8]. In this work, the most popular methods for oxides preparation in Sol-Gel method were used to synthesize TiO_2 nanoparticles. The advantages of sol-gel method include molecular homogeneity, probability of use a big variation of precursors, microstructural and properties control, low purity conditions, simplicity of use at moderately low temperatures and low costs.

Experimental Technique

Materials and methods

Titanium tetrachloride $TiCl_4$ (99.99%, BDH, England), absolute ethanol (99.99%), isopropyl alcohol (99.99%), isobutyl alcohol (99.99%), and isobentyl alcohol (99.99%) were used in this study.

Synthesis of TiO_2 nanoparticles

In synthesize of TiO_2 nanoparticles by sol–gel method, $TiCl_4$ was used as the precursor. 10 mL of $TiCl_4$ was added to 250 mL well dried conical flask. After that, 100 mL of choosing alcohol was added from a burette, the reaction was set up in a fume hood. Addition of alcohol was dropped by the drop at constant stirring to obtain more homogenous nanoparticles. The alcohols were ethanol (C_2H_5OH), isopropyl (C_3H_7OH) and isobutyl (C_4H_9OH) alcohol. A pale yellow solution was obtained with gelatinized precipitates with ethanol, isopropyl alcohol and isobutyl alcohol reactions. Whereas isobentyl alcohol produces a black oily liquid with a bad smelling. pH of the solution was 1.5 and the weight of gelatines was about 20 gr Figure 1 shows the TiO_2 nanoparticles gels prepared from methanol, 2-propanol and 2-Butanol . then the Sol-Gels were vaporized at 80 °C until dry gels were obtained. The three dry gels from (Ethanol, isopropyl and isobutyl alcohol) were calcined for one and a half in the box furnace at 400 °C and 1000 °C to get titanium dioxide nano powders.

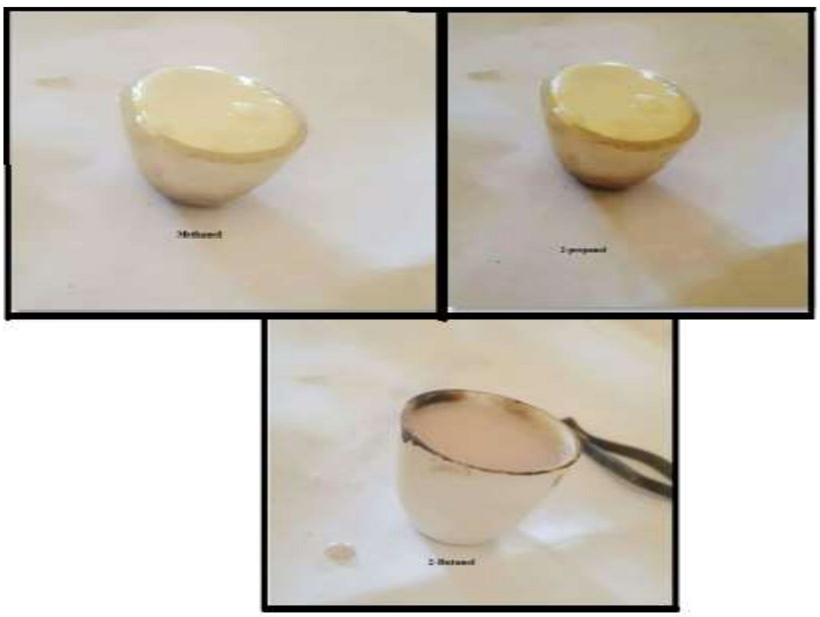


Figure 1. TiO_2 nanoparticles Gels prepared from methanol, 2-Propanol, 2-Butanol

Characterization of TiO_2 nanoparticles

X-ray diffraction (XRD-5500 2kw type), shows the crystallinity shape of the synthesized nanoparticles at room temperature. Scanning Electron Microscopy (SEM, Tescan VEGA2 SB) have been used to identify the morphological (size and shape) of the TiO_2 nanoparticles that prepared in different types of alcohols.

Result and Discussion

Titanium tetrachloride reacts with compounds containing active hydrogen atoms with loss of HCl. The replacement of chloride is usually unfinished in the non-appearance of an HCl acceptor like amine or alkoxide ion. The alkoxides are solids or liquids that can be distilled or sublimed such as Titanium isopropoxide (TIP) in chemical structure ($C_{12}H_{28}O_4Ti$) and tetra-n-butyl orthotitanate

(TNB) in chemical structure ($C_{16}H_{36}O_4Ti$). They are extremely hydrolysed by even traces of water, to give polymeric species with -OH- or -O- bridges. Even though monomeric types can exist, for example, when made from secondary and tertiary alcohols, and in dilute solution, alkoxides are usually polymers. Solid Ti $(OC_2H_5)_4$ is a tetramer (with tetrahedral geometrical structure) that hydrolysis subsequently to TiO_2 [9].

X-ray diffraction (XRD) analysis

Figure 1 presents the X-ray diffraction pattern, SQD concentration (signal Quality Detector) and S-Q for TiO_2 Nano powders prepared in methanol, isopropanol and isobutyl alcohol that calcined at 400 °C S-Q shown that, the purity of the samples was 100%, and TiO_2 was anatase with tetragonal geometry shape has molar mass 77.96 g/mol the SQD shown the sample consist of 40.1% oxygen and 59.9% titanium elements.

Crystalline sizes of TiO_2 have been obtained by Scherrer's formula given by equation [10] (1):

$$D= \frac{K\lambda}{\beta\cos\theta}$$

At which K is a constant that depend on the crystallite shape (0.9, with the supposition of sphere-shaped particles), λ is the X-ray wavelength, β is the full width at half maximum of the selected peak and θ is the Bragg's angle of diffraction for the peak [11].

The XRD pattern results the sizes of Nanoparticles were identified at 2θ values 25.4°, 37.2°, 48.2°, 54.3°, 55.2° matches to the crystal planes of (101), (004), (200), (105) agreement with the standard X-ray diffraction pattern (JCPDS files No 21-1272). The sizes of TiO_2 nanoparticles have been calculated from Scherrer's equation, it was 11.55, 8.97, 13.90, 10.85 and 18.54 nm for all TiO_2 prepared from different alcohols. There is no different in the size or the shape for TiO_2 whatever the kind of alcohols that prepared from. The difference observed in the speed of reaction whereas the small mass alcohols shows faster reaction comparing to heavy mass alcohols, also there are differences in the colours of the produced Gels, it was white Gel with methanol, yellowed white Gel with isopropanol and pale grey to white with isobutyl alcohol. With Bentyl alcohol ($C_5H_{11}O$) we suppose the crowded on Titanium atom prevented to producing a TiO_2 gel**.**

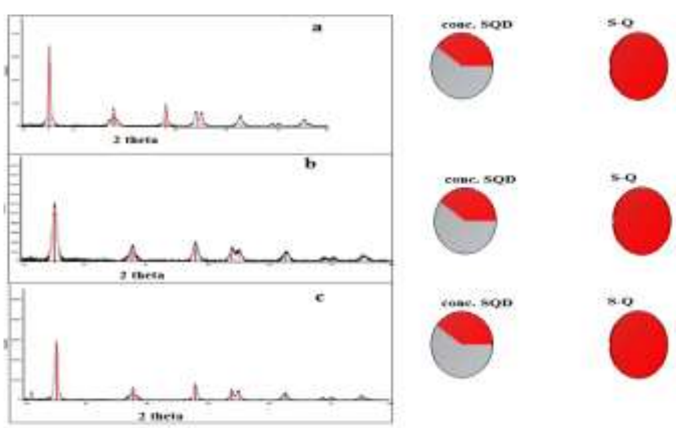


Figure 2. The XRD pattern, a) SQD conc., S-Q for TiO_2 nanoparticles prepared, b) methanol, and c) isopropanol, isobutyl alcohol calcined at 400 °C

Table 1. Crystal sizes of TiO_2 nanoparticles prepared from different type of alcohols and calcined at 400 °C

Alcohol type	Phase of obtained TiO_2	2Θ (DEG)	D value	Grain size (nm)
Methanol (COD 1526931)	100% Anatase	25.412°	3.501	11.54
		37.209°	2.414	8.95
		38.143°	2.357	11.80
		54.334°	1.885	17.54
Isopropanol (COD 9009086)	100% Anatase	25.304°	3.516	14.97
		36.949°	2.430	17.32
		37.793°	2.332	8.97
		48.037°	1.892	13.98
Isobutyl alcohol (COD 5000223)	100% Anatase	25.271	3.521	10.98
		37.699	2.384	9.87
		38.509	2.335	14.99
		47.980	1.894	17.32

Scanning electron microscope (SEM)

The SEM images in Figure 3 show that, the TiO_2 gels have a crudely randomLy shapes with sizes around the range 15 nm. After the thermal treatment for obtain TiO_2 powders and release the H_2O particles the shapes tend to be more homogeneous spherical spongy phase. Figure 4 shows the effect of temperature on shapes and sizes of TiO_2 powder at 400 °C.

From the Figure 4 when the temperature increase the size of TiO_2 decreased and the shapes become more homogenous. But at 1000 °C the condition changes the particles tend to accumulate and stick together so that the agglomeration becomes apparent, as shown in Figure 5. These results are in agreement with the data were reported by Haider A J [11].

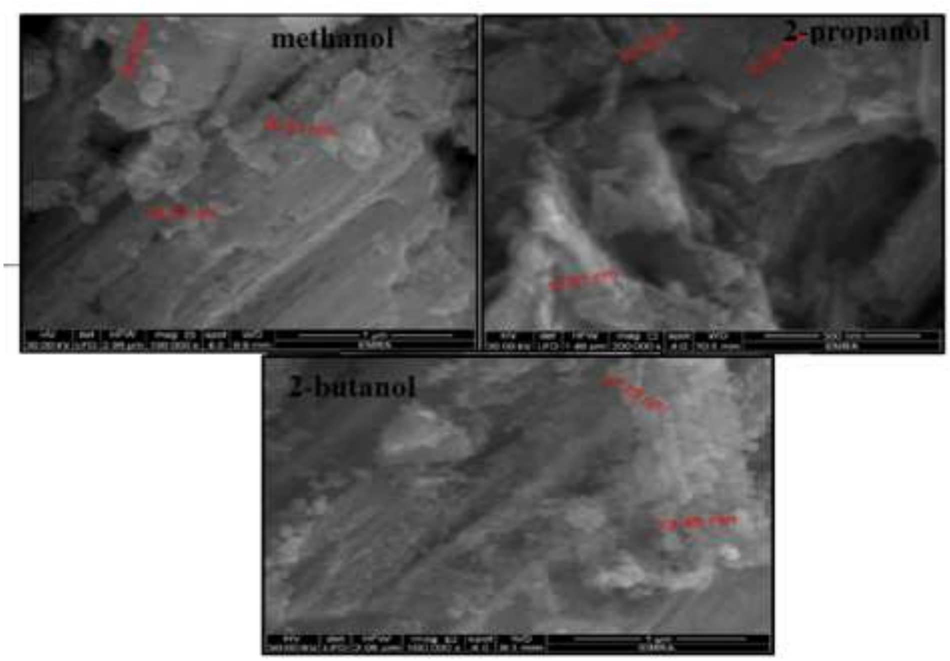


Figure 3. SEM images for TiO_2 nanoparticles Gel prepared by a) methanol b) Isopropanol, and C) Isobutyl alcohol

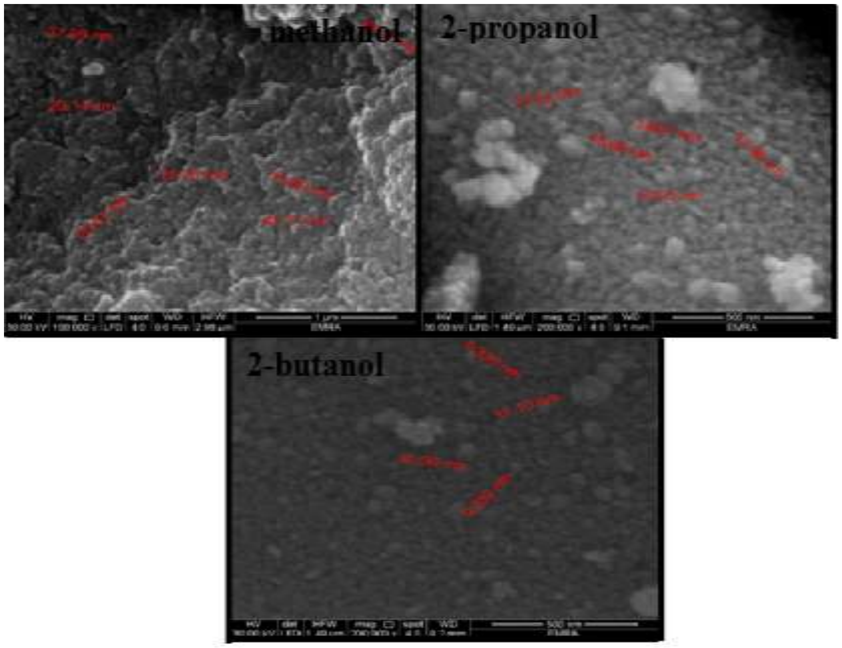


Figure 4. SEM images for TiO_2 nano powders calcined at 400 °C prepared by a) methanol, b) isopropanol, and c) isobutyl alcohol

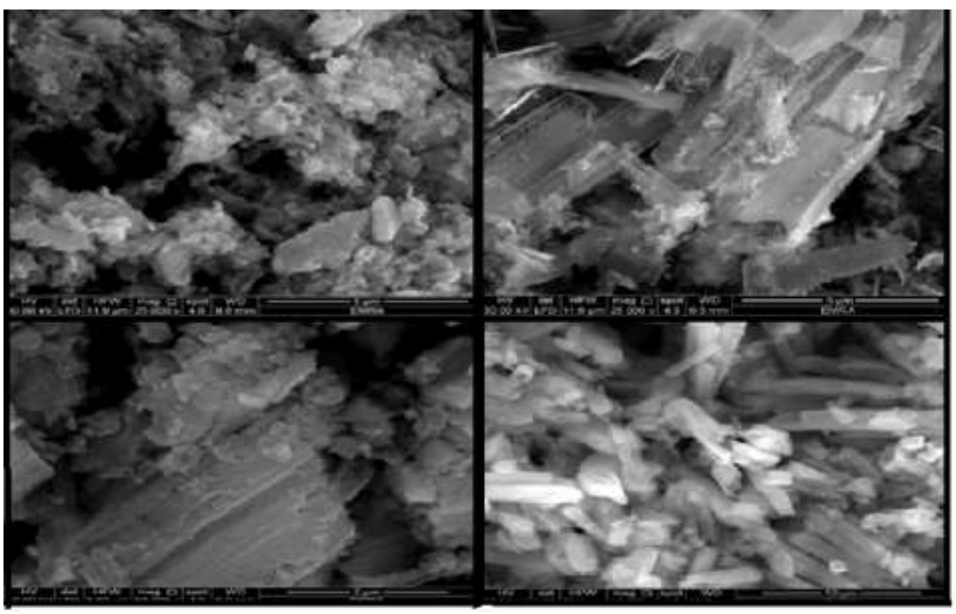


Figure 5. SEM images of TiO_2 nano powders calcined at 1000 °C prepared from a) methanol, b) isopropanol, and c) isobutyl alcohol

Test microorganism

Four clinical isolates of bacteria were used for the study: two gram-positive (*Staphylococcus aureus* and *Streptococcus* sp.) and two gram-negative (*Escherichia coli* and *Klebsiella* sp.) bacteria were used to evaluate the antibacterial activity of titanium dioxide nanoparticles (TiO_2 NPs).

Preparations of different concentration titanium dioxide nanoparticles

Suspensions of TiO_2 NPs with concentrations (50, 200, and 800 µg/mL) were prepared by suspending them in distilled water.

Evaluation of antibacterial activity

Antibacterial activities of the different concentrations of TiO_2 NPs were evaluated using well diffusion method on Mueller-Hinton agar (Jahangirian *et al.,* 2013). Media was poured on two replicates petriplates of each species bacteria. After the media is solidified the four wells (7 mm diameter) were made in each plate and 100 µl of the different concentrations of TiO_2 nanoparticles (50, 200, and 800 µg/mL) and 100 µl of sterilized distilled water (negative control) were added in these wells. Also, the bacteria were added to media at 37 °C. After 24 hours of incubation, each plate was examined and measured for the diameters of the zones of complete inhibition including the diameter of the wells.

Results and discussion

Antibacterial activity

In this study, results were obtained for the different concentration of synthesized nanoparticles tested (TiO_2 NPs, 50, 200 and 800 µg/mL) against four bacteria are presented in Figure 6. According to Figure 6 showed no effect of any bacteria treated with the different concentration of TiO_2 nanoparticles.

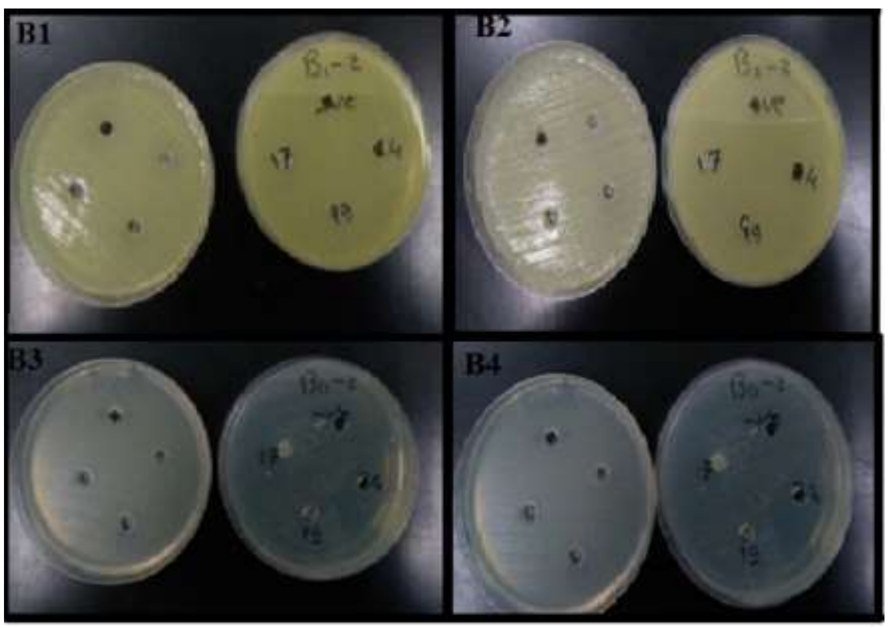


Figure 6. Effect of the different concentrations of of TiO_2 NPs (17= 800 µg/mL, 19= 200 µg/mL and 24=50 µg/mL) and sterilized distilled water (-ve= negative control) on B1) *Escherichia coli*, B2) *Klebsiella* sp, B3) *Staphylococcus aureus*, and B4) *Streptococcus* sp

The reason for emergence of bacterial resistance to TiO_2 is due to the structural composition of bacteria and preparation of TiO_2 which makes it difficult for TiO_2 to penetrate. We suggest that these particles are probably not transferred from the exposure suspension to bacteria. Our results are not similar with another report using TiO_2 nanoparticles that showed the antibacterial effect on gram-positive and gram-negative bacteria [12–15].

Conclusion

The morphological and optical properties of the titanium dioxide nanoparticles were found not affected by the type of alcohol that prepared from. There are no difference in quality and the properties of producing TiO_2 nanoparticles. The calcination temperature was studied at 400 °C and 1000 °C. The SEM results revealed that as the calcination temperature increase, the accumulation and the crystal size increased.The antibacterial result improved the TiO_2 do not have any effect as antibiotic.

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Disclosure statement

No potential conflict of interest was reported by the authors.

Orcid

Mariam Farag Ambarak 0000-0002-2888-6590

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