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Facile Synthesis and Characterization of Zirconia Nanoparticles in Dental Applications

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ABSTRACT

Scientists and dentists use tiny particles called ZrO_2/Nps (Zirconia Nanoparticles) in medicine. In addition, zirconia particles are commonly used in the realm of medicine and dentistry. They are ideal for tooth structure because of their beneficial properties. The objective of this research is to prepare zirconium oxide nanoparticles in a simple and easy way. Nano-zirconium oxide is prepared using the co-precipitation method. The produced powder was diagnosed using tools like X-ray diffraction, microscopy, and spectroscopy, which also analyzed its properties such as X-ray spectroscopy and density measurement. The XRD results confirmed that the powder product has high purity. The crystal size range is 27.97nm. The results match the (JCPDS (ZrO_2) sheet No.79-1769). The EDX test revealed the presence of the following elements (Zr–O). The test of SEM (Scanning Electron Microscope) shows that the particles nearly spherical and the size was 74.03nm. The Zr–O stretching modes and the Zr–O_2–Zr bending modes were confirmed by the FTIR (Fourier transform infrared). The density of ZrO_2/Np was measured several times and determined it to be (5.07±0.12 g/cm^3).

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طريقة سهلة لتصنيع وتوصيف جسيمات الزركونيا النانوية في تطبيقات طب الأسنان

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الكلمات المفتاحية:

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الترسيب المشترك
BET
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الـــخُـــلاصـــة

يستخدم العلماء وأطباء الأسنان جسيمات صغيرة تسمى ZrO_2/Nps (جسيمات الزركونيا النانوية) في الطب. بالإضافة إلى ذلك، تُستخدم جزيئات الزركونيا بشكل شائع في مجال الطب وطب الأسنان. إنها مثالية لبنية الأسنان بسبب خصائصها المفيدة. الهدف من هذا البحث هو تحضير جزيئات أكسيد الزركونيوم النانوية بطريقة بسيطة وسهلة. يتم تحضير أكسيد الزركونيوم النانوي باستخدام طريقة الترسيب المشترك. تم تشخيص المسحوق المنتج باستخدام أدوات مثل حيود الأشعة السينية، والمجهر، والتحليل الطيفي، والتي قامت أيضًا بتحليل خصائصه مثل التحليل الطيفي للأشعة السينية وقياس الكثافة. أكدت نتائج XRD أن المنتج المسحوق ذو درجة نقاء عالية. نطاق الحجم البلوري هو 27.97 نانومتر. تطابقت النتائج مع ورقة (JCPDS (ZrO_2) رقم 79-1769). أظهر اختبار EDX

وجود العناصر التالية Zr–O)). اظهر اختبارSEM (المجهر الإلكتروني الماسح) أن الجسيمات كروية تقريبًا وكان حجمها 74.03 نانومتر. تم تأكيد أوضاع التمدد Zr – O وأوضاع الانحناء Zr – O2 بواسطة FTIR (تحويل فورييه للأشعة تحت الحمراء). تم قياس كثافة ZrO_2/Np عدة مرات وتم تحديدها لتكون (5.07±0.12 جم/سم3).

1. Introduction

Teeth are important for oral health and body aesthetics. Many people have dental diseases like cavities and pulpitis [1]. Some gum diseases can cause problems with teeth and their function [2,3]. This may need reconstructing the anatomical structure [2-4]. Researchers study dental materials to improve the look and function of teeth. Dental materials are improving and can now provide customized dental care [5]. When receiving treatment, it is ideal to use ceramic materials. They look natural, strong, and look good [6-8]. Earlier, they used titanium implants. ZrO_2/Np is a popular material in dentistry. It is a biological material with a beautiful white color and high hardness. It has excellent strength and stable chemical properties [9,10]. ZrO_2/Nps are also corrosion resistant and have significant antibacterial activity. Used by dental implants [11]. Scientists and industries have found that Nano-zirconium oxide is a top dental material. Researchers use nano-zirconium oxide as a material for biological implants [12–14]. The ZrO_2/Np provides more application scenarios, nano-powder filling (for example) [15], Nano coating [16], [17], sintering of the raw materials [18], etc. It is used to promote mechanical and biological properties of dental ceramics and the tissue engineering scaffold. Besides, ZrO_2/Nps has many important uses in dental care [12]. Dentists use ZrO_2/Nps to make dental prostheses, such as crowns, dentures, and implants [19]. The ZrO_2/Np is insulating and stable, even at high temperatures. It has three different crystal structures: m-ZrO_2, c-ZrO_2 and t-ZrO_2. Each structure is stable at different temperatures [20]. Scientists study nanoparticles because their size determines various applications. The ZrO_2/Nps is an important material in dentistry. It is durable, and resistant to corrosion, bacteria and chemicals [21,22]. Zirconia nanoparticles usually have three crystal structures: cubic, tetragonal, and monoclinic [23]. One control the shape of particles by controlling a few factors namely, pH, time, temperature, solvent used and the solute amount affect the result of the reaction. The objective of the study is to synthesize nano-zarcunim particles using the co-precipitation method, which is a widely used and easy method for preparing nanoparticles. This method has been successfully employed to obtain various nano-materials such as CaF_2, TiO_2, Fe_3O_4, hydroxyapatite, and ZnO through co-precipitation [24-27]. Physio-chemical test was performed on the nanoparticle ZrO_2 powder obtained through Co-precipitation. The test included XRD, FTIR, EDX, SEM, and BET.

2. Experimental Method

Researchers usually use a cheap technique called co-precipitation to prepare zirconia nanoparticles. In This study sodium hydroxide NaOH (M.W.40.00 PL/29/3350/1273-09/10/16 THOMAS BAKER) and zirconyl chloride octahydrate (98% purity, Sigma-Aldrich, Lot#: STBK8573).

2.1. Synthesize of quaternary Nano powder (ZrO_2)

To Prepare ZrO_2/Nps, 0.2 mol of $ZrOCl_2.8H_2O$ was dissolved in 150 ml distilled water taken in 250 ml canonical flask. Then, 0.2 mol of NaOH was dissolved in 100 ml of distilled water and added it to the flask under vigorous stirring on a magnetic stirrer (DRAGON LAB, MS-H-Pro). The liquid mixture was stirred for 2 hours. When the temperature increases by 80C°, the mixture becomes white and opaque. The mixture was placed in a centrifuge and spun at 6000 rpm for 10 minutes, and washed three times with distilled water to remove chloride and sodium ions. Finally, dried the product at 80 C° for 18 hours to remove the remaining water. Finally, the product powder calcined at 400 C° for 2h to obtain the final product, Figure 1.

$$ZrOCl_2.8H_2O + NaOH \rightarrow Zr(OH)_4 + NaCl_2 + H_2$$

$$Zr(OH)_4 \rightarrow ZrO_2 + 2H_2O$$

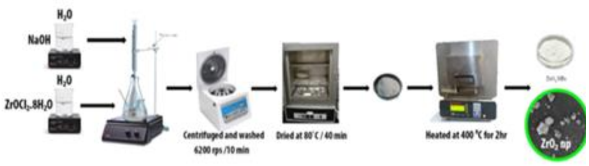

Fig.1, The preparation Steps to ZrO_2 nanoparticle.

2.2. Physio-chemical characterization

The properties of nano-zirconium oxide were analyzed using Physio-chemical testing (XRD, FTIR, EDX, BET, SEM and density measurement). XRD analysis were performed on Nano-zirconium oxide using (Leiden, Netherlands a Philips PW 1700 series). The range was 2θ = 10-80°, with a step size of 2θ = 0.0400°. Each step had a counting time of 0.250 seconds. According to a Scherer equation, determined the crystal size (D) [28].

$$D = \frac{\beta\lambda}{W\,cos\theta} \quad \dots\dots\dots\dots(1)$$

λ represents the incident X-ray wave length, which is 0.154060nm, β is Scherer's constant, ranging from 0.9 to 1. The value of β depends on the particle's shape, with a value of 0.89 for spherical crystals of cubic symmetry, θ represents the diffraction angle. (W) denotes the full width at the half greatest (FWHM in radians). The diameter of the sphere (L) can be estimated assuming a spherical crystal [29].

$$\langle L \rangle = \frac{4}{3}(D) \quad \dots\dots\dots\dots(2)$$

Where (D) is the size of crystal.

XRD is also used to find the size of the ZrO_2/Nps along the axial (c) and (a) orbitals. The distance between the lattice planes can be measured using the following relationship.

$$d = \frac{ac}{\sqrt{c^2(h^2+k^2)+(a^2l^2)}} \quad \dots\dots\dots\dots\dots(3)$$

A spectrometer was used to record the FTIR (Shimadzu Co. Kyoto, Japan) spectra of zirconia nanoparticles at room temperature. The sample was prepared for FTIR measurement. Zirconia nanoparticles calcined with KBr were ground into fine powders. The powder was then pressed to characterize the size and morphology. The (SEM) was used (VEGA TESCAN-Czech). The microscope image shows the out distance of the sample. X-ray analysis (EDX) and SEM were used together to verify chemical compositions. calculate the specific surface area of ZrO_2/NPs through BET analysis. The BET method is also used in conjunction with Chembet-3000. Applying the BET method expresses the mean diameter (d_{BET}) as [29]:

$$d_{BET} = \frac{6}{A_s\rho} \quad \dots\dots\dots\dots(4)$$

Where (As) is the specified surface area (m^2/g) and the theoretical density of ZrO_2/Nps is 5.68 g/cm^3. The Size and severity determine the distribution of volume ratio and volume statistical ratio. The density of the zirconium nanoparticles was calculated using a cyclometer (pycnometer). This instrument measures density using ISO: 1183 & ASTM:854 standards. It is a bottle with a glass stopper and a capillary tube to remove air bubbles and improve accuracy. The empty bottle's weight W(pyc) was measured first. Then, water was added and measure its new weight W(pyc,wat). Next, the bottle was dried and powder was added, and its weight was measured again. Finally, water was added to the powder and the bottle's weight was measured again W(pyc,wat,pow) [29].

$$\rho = \frac{W_{pow}}{W_{(pyc,wat)} - \left(W_{(pyc,wat,pow)} - W_{(pow)}\right)} \quad \ldots\ldots(5)$$

3. Results and discussion

The tetragonal phase of zirconia nanoparticles can be stabilized at room temperature [30,31]. studied the composition and nature of ZrO_2/Nps using X-ray diffraction pattern. Figure (2) shows intense high peaks at 2θ (28.22°, 30.41°, 35.29°, 50.63°, 60.19°, 70.87°). These peaks correspond to (111), (002), (102), (122), (230), (223). They also match the defined JCPDS (ZrO_2) of the file No.00-013-0307 [26]. There is a noticeable peak at 2θ=30.41° related to the 002 plane. The larger peaks in the ZrO_2/Nps formula showed a small crystal size of about 27.97nm based on calculations using Scherrer formula.

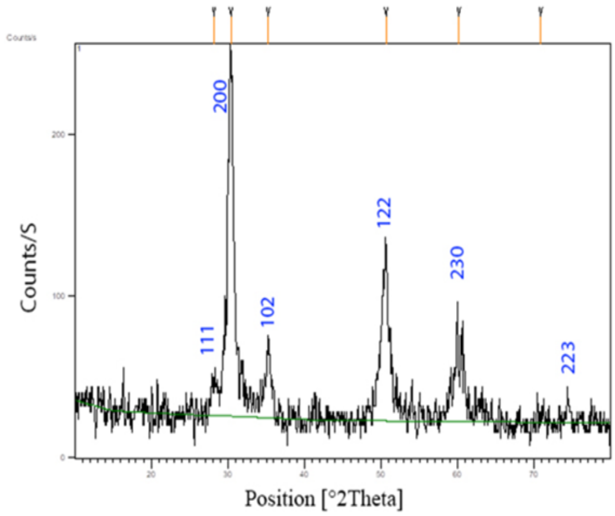

Fig.2, The XRD spectrum of (ZrO_2/Nps).

Table.1, Particle size analysis of (ZrO_2/Nps).

Position [°2Th]	(hkl)	d (A°)	D crystal size (nm)	<L> nm	Constant of lattice a°
28.22	111	3.158	21.728	28.97	5.4700
30.41	200	2.935	54.588	72.78	5.8715
35.29	102	2.540	22.112	29.48	5.6801
50.63	122	1.800	46.623	62.16	5.4013
60.19	230	1.535	12.177	16.23	5.5365
70.87	223	1.328	10.604	14.13	5.4756

A machine called Nicole Magna-IR 550 was used to check the purity of the washed powders. The machine recorded the absorption spectrum. The spectrum from 400 to 4000 cm^{-1} was recorded. Figure (3) shows us the (FTIR) spectra of the powder obtained by the co-precipitation method. Table (1) displays the binding sites for ZrO_2/Nps. The band spans from 600 cm^{-1} to 446 cm^{-1}. It shows the Zr-O vibration in the hexagonal structure of the Nano crystal ZrO_2 powder. Water molecules oscillate for a long time. The oscillations were ranged from 3909cm^{-1} to 3500cm^{-1}. Water absorbed and broken oscillate at 1620.88cm^{-1}. This suggests the hydrated molecules may be hydroxyl groups.

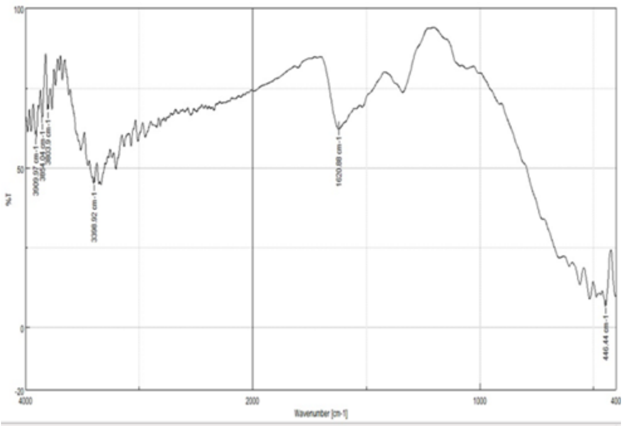

Fig.3, FTIR for ZrO_2/Nps.

Table.2, The (FTIR) an absorption spectrum of ZrO_2/Nps [25,32-34].

Wave number cm^{-1}.	Functional group
407	Zr–O stretching modes
500	Zr–O stretching vibration
613	Zr–O–Zr stretching
635-706	distinctive for Zr-O-Zr vibration
683	Zr–O tetragonal structure vibration and the broadness of the band indicates that the ZrO2 powders are Nanocrystal
757	Zr–O2–Zr asymmetric
819	Zr–O–Zr bending mode vibration
1173 and 1380	stretching vibrations of Zr-O terminal groups
2360	stretching the vibration of hydroxyl zirconium (Zr–OH) bond

A scanning electron microscope (SEM) was used to observe the shape, size, and surface of the nanoparticles obtained. Figure (4) shows the SEM image of the ZrO_2/Np preparation. In Figure 4B, the researchers found tiny particles that were 40nm in size and spread out. Another study by N. Al-Zaqri also observed similar particle shapes. [11]. On average, the J-imaging program finds 200 particles in the zirconia nanoparticles. The average ZrO_2/Nps value is 74.03nm. Figure 5 shows the particle size distribution. There is a peak in the region between 40 and 50 nm, and the distribution appears to be good.

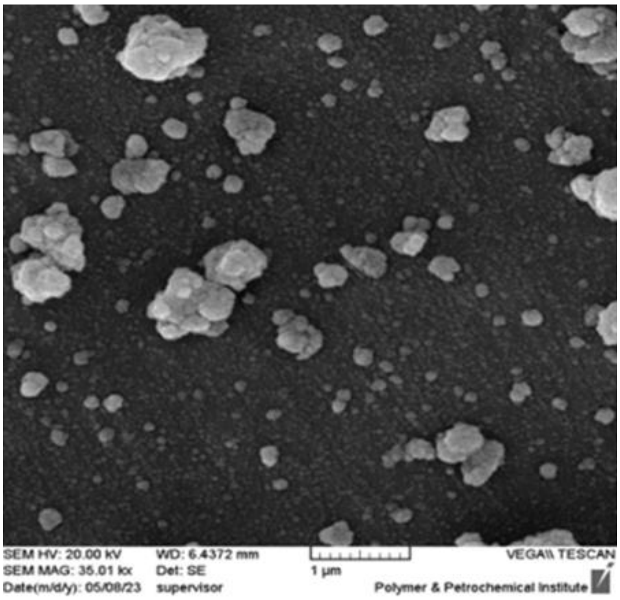

Fig.4A, The SEM image of ZrO_2/Nps.

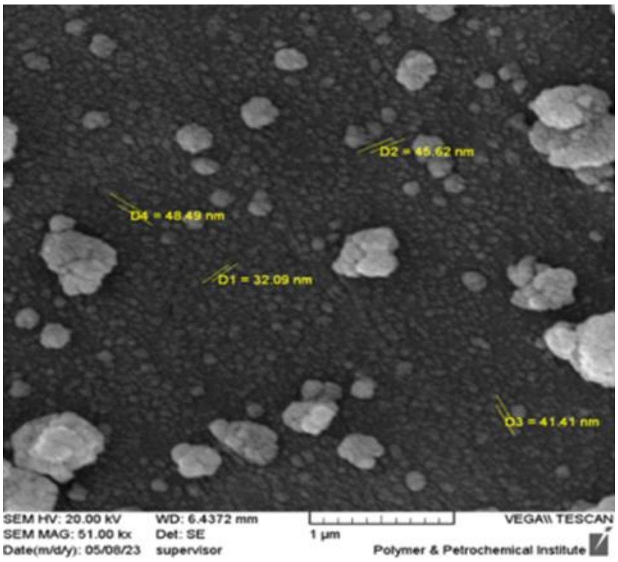

Fig.4B, The SEM image of ZrO_2/Nps.

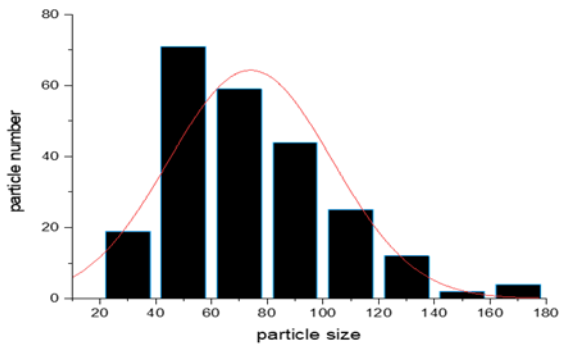

Fig.5, The particle size distribution of (ZrO_2)/Nps.

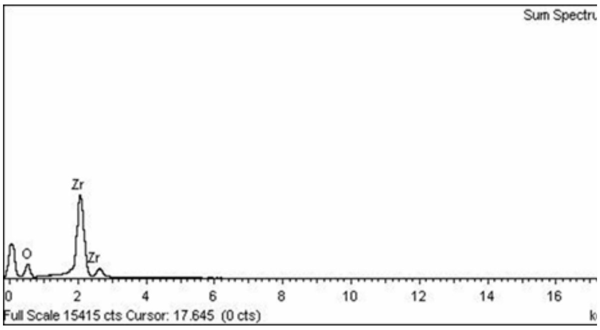

Fig.6, EDX image of ZrO_2/Nps.

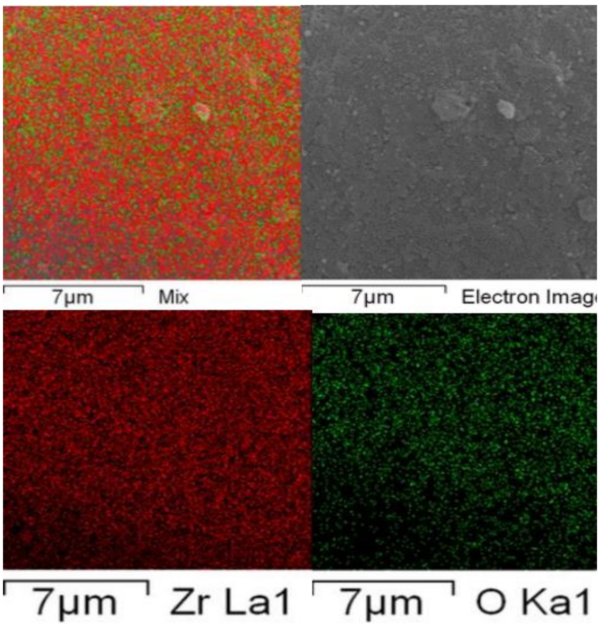

Fig.7, Spectral analysis (EDX) of ZrO_2/Nps.

Figure (6) shows the base mapping of ZrO_2/Nps. EDX microanalysis on the particles was performed to confirm this. The average ratio of zirconium to oxygen was calculated using the peak quantification. It gave a value of 43.69% zirconium to 56.31% oxygen. The peaks are only from Zr and O_2, with no unclear signal. This shows that ZrO_2 is pure and formed well. Also, a strong peak signal at 2 keV, was observed which represents the ideal level for ZrO_2/NP absorption. Figure 7 presents the chemical composition of the nanoparticles obtained. The composition shows good homogeneity between two elements.

In this study, it was necessary to calculate the Brunauer–Emmett–Teller (BET) surface area for ZrO_2/Np. BET measurements of ZrO_2/Np showed a specified surface area of 21.67 m^2/g. This is important for dental restorative applications. So this dependent on the size of a particle ≈ (48 nm) according to the equation (1). The zirconium nanoparticles have a lower density (5.169±0.12 g/cm3) than solid zirconium (5.68 g/cm3). The decrease happened because the particles became less dense and smaller, or had a bigger surface area [35].

4. Conclusion

The ZrO_2 nanocrystals were prepared successfully by co-precipitation methods, which were identified by physio-chemical characterization (XRD, SEM, EDX, FTIR, and BET) besides to densitometry which showed that the obtained NPs are single phased with homogeneous chemical. The co-precipitation method used in this study is useful for purity and nano particles is smaller. It was observed through the test conducted on the prepared ZrO_2 nanocrystals that they have physical properties that enable them to be an effective material in dental restoration according to international specifications.

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