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Characterization of Cr_2O_3 Nanoparticles Prepared Using Cauliflower Extract by Two Methods

Saja Q.Ali, Wisam J. Aziz, Raad S. Sabry
Department of Physics, College of Science, Mustansiriayah University, Baghdad, Iraq

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ABSTRACT

Chromium oxide nanoparticles were synthesized using cauliflower extract by two methods: simple chemical method and the sol-gel method. These technologies are new, environmentally friendly and cheap. Cauliflower contains plant materials and biomolecules (chromium, phenols, alkalis, vitamins, amino acids, quinones, etc .)that convert chromium chloride hexahydrate ($CrCl_3.6H_2O$) into chromium nanoparticles. The plant extracts also act as diluents, stabilizers and anti-caking agents. X-ray diffraction (XRD) analysis showed that the size of the crystals decreased from (36.1 to 57.8) nm using the simple chemical method to (13.31 to 20.68) nm of Cr_2O_3 using sol-gel. The scanning electron microscopy (SEM) showed that Cr_2O_3 NPs of the simple chemical method were Nano layers with (130.3) nm, while the Cr_2O_3 NPs of the sol-gel method were spherical or semispherical in shape with a particle size of (14.89 to 39.08) nm. The results obtained have no matches in the reported literature.. Ultraviolet-visible (UV-Vis) showed that the band gap energy of Cr_2O_3 NPs of the simple chemical method was 2.5 eV, while it was 3.4 eV for Cr_2O_3 NPs of the sol gel method . Cr_2O_3 NPs of high purity , small particle size, and large energy gap were obtained from the sol-gel method This means that the NPs from the sol gel method were better than those of the simple chemical method. The study revealed that the Chromium oxide nanoparticles synthesized using cauliflower extracts could be used as antibacterial agent for human pathogenic bacteria

Keywords: Cr_2O_3 NPs, plant extracts, green chemistry, Antimicrobial activity

توصيف الجسيمات النانوية لأوكسيد الكروم الثلاثي المحضرة باستخدام مستخلص القرنابيط بطريقتين

سجى قيس علي، وسام جعفر عزيز، رعد سعدون صبري
قسم الفيزياء، كية العلوم، الجامعه المستنصريه، بغداد، العراق

الخلاصه

تم تصنيع الجسيمات النانوية من أكسيد الكروم باستخدام مستخلص القرنبيط بطريقتين ، الأولى بطريقة كيميائية بسيطة والثانية بطريقة سول–جل. هذه التقنيات جديدة وصديقة للبيئة ورخيصة. يحتوي القرنبيط على مواد نباتية وجزيئات حيوية (الكروم ، الفينولات ، القلويات ، الفيتامينات ، الأحماض الأمينية ، الكينونات ، إلخ. (التي تحول هيكساهيدرات كلوريد الكروم (CrCl3.6H2O) إلى جزيئات الكروم النانوية. تعمل المستخلصات النباتية أيضًا كمخففات ومثبتات وعوامل مانعة للتكتل. أظهر تحليل حيود الأشعة السينية (XRD)أن حجم البلورات انخفض من (36.1 إلى 57.8) نانومتر بالطريقة الكيميائية البسيطة إلى (13.31

*Email: saja.qais90@gmail.com

إلى 20.68) نانومتر من Cr2O3 باستخدام هلام سول. أظهر الفحص المجهري الإلكتروني (SEM) أن الجسيمات النانوية لـ Cr2O3 NPs كانت (طبقات نانو) مع (130.3) نانومتر بطريقة كيميائية بسيطة بينما أظهر (SEM) أن الجسيمات النانوية لـ Cr2O3 NPs باستخدام مستخلص القرنبيط كروية أو شبه كروية في الشكل) بحجم جسيم من (14.89 إلى 39.08) نانومتر بطريقة سول–جل ، النتائج التي تم الحصول عليها لم تتطابق مع أي بحث آخر. أظهرت الأشعة فوق البنفسجية المرئية (UV–Vis) قيمة فجوة النطاق من 2.5 فولت من Cr2O3 NPs بطريقة كيميائية بسيطة ، بينما في طريقة sol–gel لـ Cr2O3 NPs كانت 3.4 فولت. في هذا البحث تم الحصول على نقاوة عالية ، وحجم جزيئات صغير ، وفجوة طاقة كبيرة لأكسيد الكروم NPsفي طريقة sol–gel أفضل من أكسيد الكروم NPs بطريقة كيميائية بسيطة. كشفت الدراسة أن جزيئات أكسيد الكروم النانوية المصنعة باستخدام مستخلصات القرنبيط يمكن استخدامها كعامل مضاد للجراثيم للبكتيريا الممرضة للإنسان.

1. Introduction

The study of fine and ultrafine particles has received in-creasing interest due to the new properties that the material may show when the grain size is reduced [1]. During the past decades, considerable progress in the synthesis of nano- particles has been achieved. Nanomaterials, particularly transition-metal oxides play an important role in many areas of chemistry, physics and material science [2]. Nanotechnology is one of the most active areas of research in modern materials science; nanotechnology has become a form of the pioneering and exciting field in chemistry, physics, and biology. The study of nanoparticles has received increasing attention due to the material's novel qualities that may emerge as particle size is lowered .Nanotechnology can describe the fabrication and characterization of nanomaterials, (1-100) nanometers, for the development of science [2].Nanotechnology is an enormously powerful technology, which holds a huge promise for the design and development of many types of novel products with its potential medical applications on early disease detection, treatment, and prevention. Nanoparticles are shown new (improved) properties based on specific characteristics such as size, distribution, and morphology [3]. The nanoscale dimension is important because quantum mechanical properties of electronics, photons and atoms are shown at this scale. In addition, nanostructures allow controlling the correction of materials without changing the chemical state. In general, nanotechnology plays an important role in the specialized qualities of the most innovative scientific field. Nanotechnology. It is mainly involved in the manufacture of nuclear plants in various sizes, shapes, chemical compositions, chemical compositions [4,5]. The major benefits of NPs over larger particles are high surface-to-image ratio. In the last two decades, nanostructured materials have undergone extensive study due to their unique specialization and applications in the many fields [6]. Nanotechnologies involved in the fabrication of nano materials may be classified as top-down or bottom-up approaches. Top-down (physical methods) or bottom-up (chemical and biological methods) is a measure of the level of advancement of nanotechnology. The NPs which can be synthesized by both top-down (physical) and bottom-up (chemical methods and via a green pathway as in this research) [7]. In technological applications, conventional metal oxides are used in the manufacture of electronic circuits, motorcycles, fuel cells, and coatings to protect the surface from corrosion, and as a catalyst [8]. The development of nanomaterials has garnered great interest, especially in the physical, chemical and biological sciences for their performance in the manufacture of microelectronics, transistors, and light emitting diodes as well as in cancer treatment[9].

2. Experimental

2.1 Materials

All the chemicals used were of highest purity available and were used as received without further purification or distillation: [$CrCl_3.6H_2O$] (99.5%, Sigma-Aldrich), sodium hydroxide (NaOH) (99%, Fluka), cauliflower extract; its source was from local market.

2.2 Preparation of Plant extracts

In a simple chemical method, small parts of the cauliflower plant were purified from impurities, and cut into small pieces and left in the sun for two days. After that it was grounded to fine powder with a solid metal electric mixer. The plant extracts were made from a mixture of 5 g of powder in 100 ml of deionized water. The solution was heated at 70 ° C for 30 min on a magnetic stirrer. The resulting aqueous solution was cooled at room temperature and purified during Whitman's filtration Figure 1 an explanation of the steps for converting a fresh plant into an extract. In the sol - gel method.

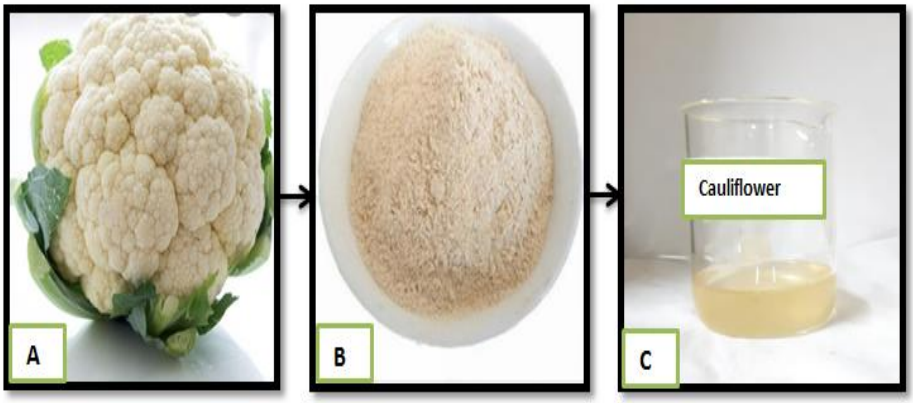


Figure1 -Stages of converting fresh plant into extract (cauliflower), A) Plant, B) powder, C) extract.

2.2.1 Preparation of chromium oxide NPs by the simple chemical method

Non-synthesized Cr_2O_3 NPs (50 mL, 1 M) and chromium chloride hexahydrate ($CrCl_3.6H_2O$) were added to 100 mL of the prepared cauliflower extract.. This prepared solution was placed on a magnetic stirrer at 70 ° C for 30 min.After that, the solution was left to cool to room temperature. 25 mL of Cr_2O_3 was placed in a ceramic oven at 200 ° C for two hours to obtain a nano-base. The Cr_2O_3 NPs powder was stored in sealed labeling serum tubes. Figure 2 shows the stages to prepare NPs using cauliflower extracts.

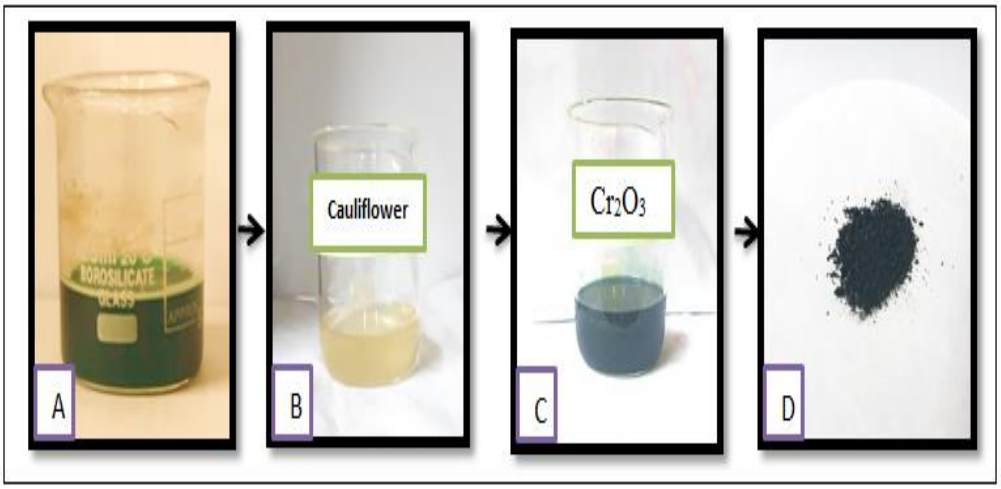


Figure 2-The stages of preparation of chromium oxide NPs (A) chromium chloride hexahydrate ($CrCl_3.6H_2O$) solution, (B) cauliflower extract, (C) Cr_2O_3 solution, (D) Cr_2O_3 NPs powders.

2.2.2 Preparation of chromium oxide NPs by the sol-gel method

5 grams of ***(Cauliflower)*** powder was used in 100 ml of distilled water and putted on the magnetic stirrer for two hours at 70 °C, 13 grams of chromium sulfate is taken with 50 ml of distilled water for 10 minutes on the magnetic stirrer and then filtered using filter paper and then after filtering, a centrifuge is used at 15,000 cycles for 10 minutes Then, $CrCl_3$ is added over the plant extract for half an hour on the magnetic stirrer, and then it is placed on to turn it into a gel After that, and place on the magnetic stirrer. Then several drops of sodium hydroxide were add to the solution until it attained pH = 7. The temperature was increased to 90°C and left to turn into liquid (Gel). Thus it was allowed to stay for one and the half hour after which the temperature was increased to (120°C) and left to become dry gel (Xerogel) , then lifted and left to cool down. The powder was collected and placed in a container of porcelain and inserted into the oven 25 ml of the solution is taken and placed in a ceramic eyelid and placed in an oven at (200)°C for two hours. After turning off the oven, the sample is left inside for 24 hours to obtain a Nano powder.

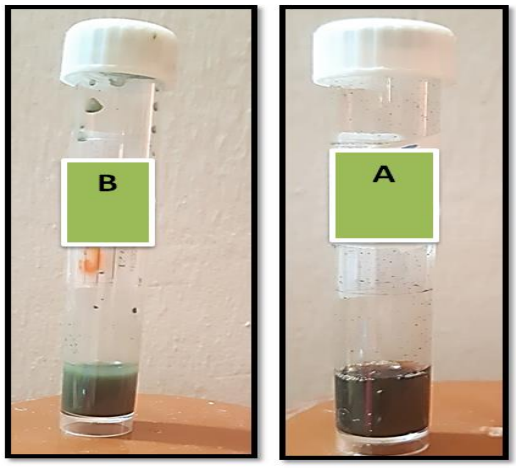


Figure 3-explains of fresh chromium oxide NPs using cauliflower extract (A) a simple chemical method, and (B) in the sol-gel method

3. Results and Discussions

3.1 X-ray Diffraction (XRD) of chromium oxide NPs prepared *by the simple chemical method.*

XRD is an important technique that is commonly used to investigate the structural properties to ascertain the crystalline nature and phase identification of chromium oxide nanocrystalline films.From Figure 4, it is noticed that the 012 and 104 peaks are the preferred orientations of prepared (**Cr_2O_3**) NPs using cauliflower plant. Table (1) shows the XRD results of **Cr_2O_3** NPs . The crystallite size (D) was estimated by the following Scherrer's Equation (1).

$$\boldsymbol{D(nm) = \frac{K\lambda}{\beta \mathrm{Cos}\theta}} \quad \textbf{(1)}$$

Where k is called shape factor (0.9), λ is the wavelength (0.15418) β is full width at half maximum (FWHM), and θ is a diffraction angle.

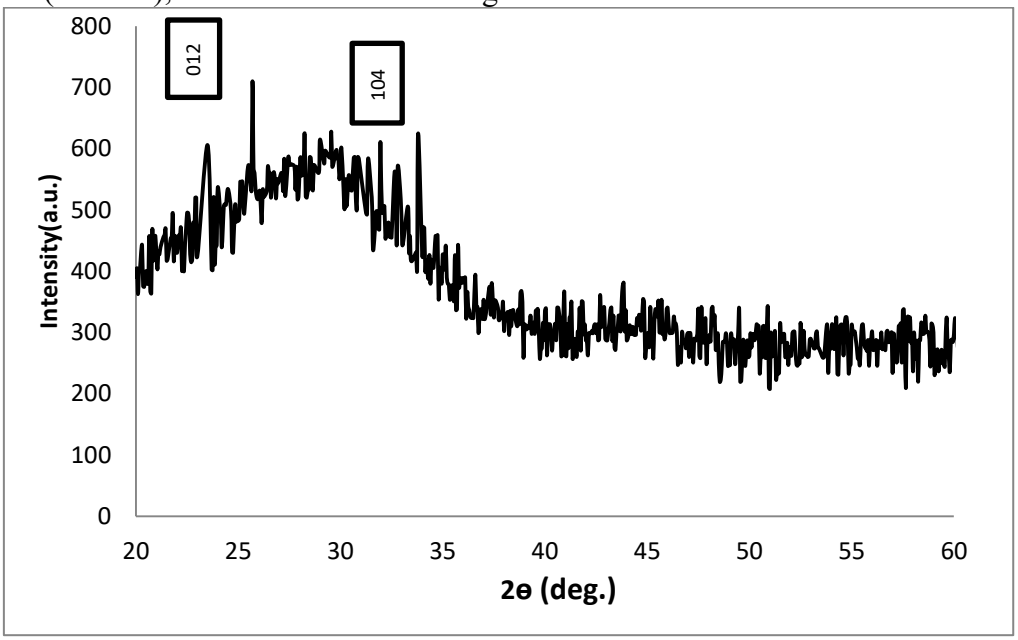


Figure 4-XRD pattern of Cr_2O_3 NPs prepared by the simple chemical method using cauliflower extract.

Table 1-XRD results of Cr_2O_3 NPs prepared by the simple chemical method using cauliflower extract.

Plant Extract	Material	FWHM (deg.)	2θ Exp. (deg.)	(hkl)	2θ JCPDS (deg.)	Crystallite size D (nm)
cauliflower	Cr_2O_3	0.14	25.7	(012)	25.1	57.818888818
		0.22	33.8	(104)	33	36.1

3.2 X-ray Diffraction XRD for chromium oxide NPs by the sol-gel method.

It is noticed from Figure 5 that the peaks (012),(104),(110),(202) and (122) are the preferred orientation of $\mathbf{Cr_2O_3}$ NPs.

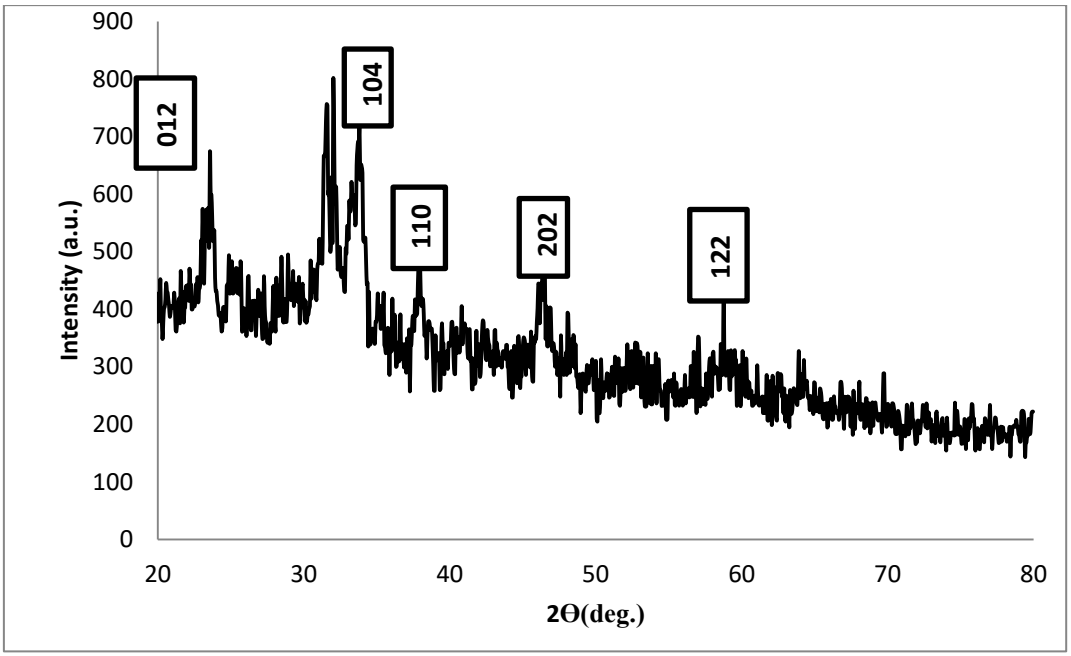


Figure 5-XRD Patterns of Cr_2O_3 nanoparticles prepared by the sol-gel method using cauliflower extract.

Table 2-XRD results of Cr_2O_3 nanoparticles prepared by the sol-gel method using cauliflower extract.

Plant Extract	Material	FWHM (deg.)	2θ Exp. (deg.)	(hkl)	2θ JCPDS (deg.)	Crystallite Size D(nm)
cauliflower	Cr_2O_3	0.393	23.51	(012)	23.1	20.68
		0.49	33.82	(104)	33.2	16.14
		0.59	37.86	(110)	37.5	13.31
		0.49	46.4	(202)	45.5	15.5
		0.36	58.75	(122)	59.2	20

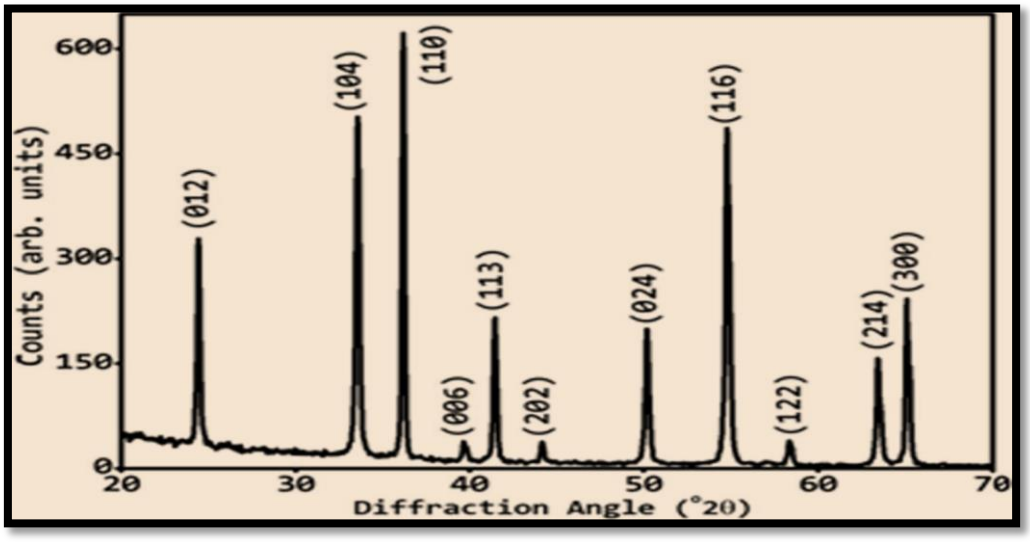


Figure 4-1- XRD patterns of Cr2O3 NPs (JCPD) Card no, 96-210-4123[10].

3.3 Scanning Electron Microscopy (SEM) of chromium oxide NPs prepared by the simple chemical method at 200 °C.

SEM image measurements were performed to determine the surface morphology of chromium oxide NPs using cauliflower extract prepared by the simple chemical method. Figure 6 (A-D) shows the shape and average size of **Cr_2O_3** NPs. It is seen as e (Nano layers).

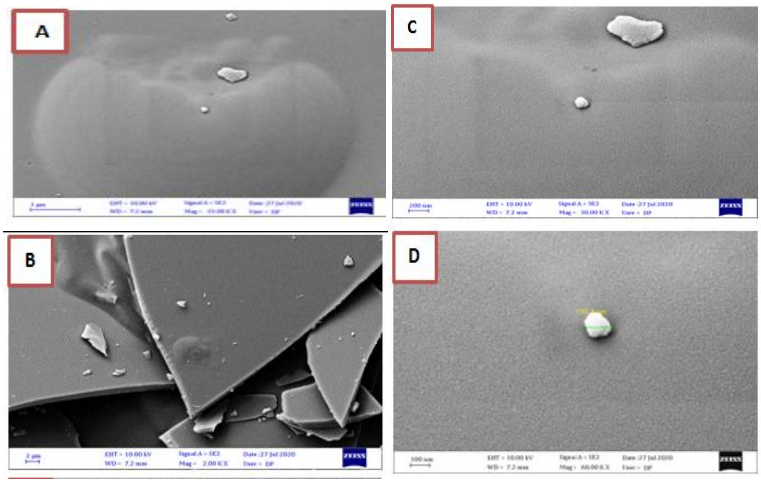


Figure 6-SEM analysis of Cr_2O_3 NPs prepared by the simple chemical method using cauliflower extract at 200°C.

3.4 Scanning Electron Microscopy (SEM) of chromium oxide NPs prepared *by the sol-gel method at 200°C.*

Figure 7 (A-D) are the SEM images of the (**Cr_2O_3**) NPs prepared by the sol-gel method using cauliflower extract. It shows that the nanoparticles are spherical or semispherical in shape with a particle size of (14.89 to 39.08) nm.

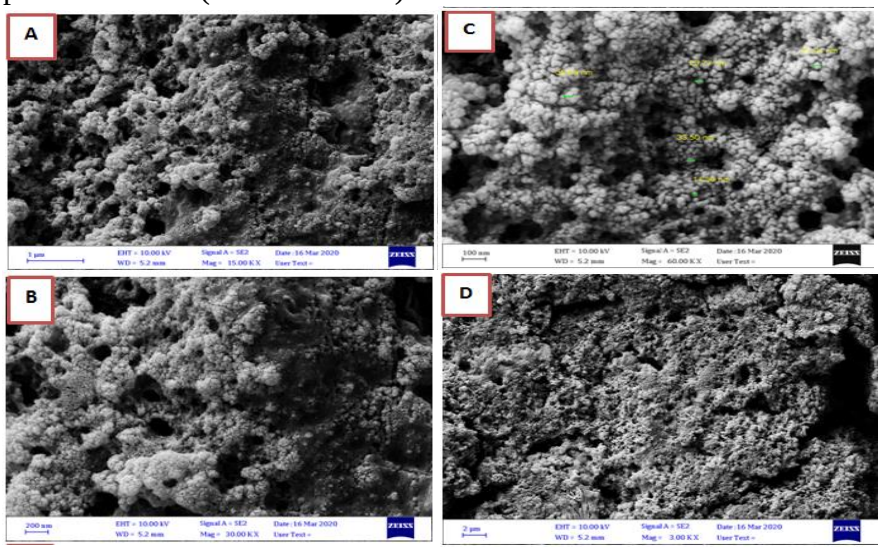


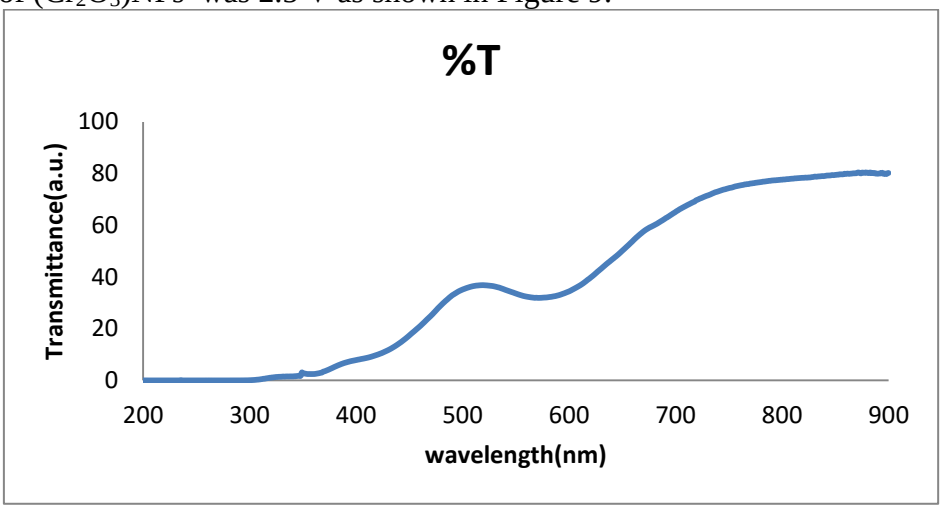
Figure 7-SEM analysis of Cr_2O_3 NPs prepared by the sol-gel method using cauliflower extract at 200°C.

3.5 UV-Vis properties of chromium oxide NPs prepared by the simple chemical method

The samples were examined by UV-Vis spectroscopy to determine the absorbance of the Cr_2O_3 NPs cauliflower extract. Figure 8 shows the optical transmittance spectra of (Cr_2O_3) NPs prepared by the simple chemical method(as shown in Figure 8. The spectrum, at the spectral range of (200-900) nm, shows a low transmittance at 400 nm resulting in strong absorption of (Cr_2O_3) in this region.

The energy gap of the (Cr_2O_3) NPs was estimated by plotting $(\alpha h\upsilon)^2$ against the photon energy ($h\upsilon$). The intercept of the extrapolation of the linear part of the graph with the $h\upsilon$ axis

gives the energy gap value. The gap depends on the energy band, the crystal structure of the film and the arrangement and distribution of the atoms in the crystal lattice. The optical band gap value of (Cr_2O_3)NPs was 2.5 V as shown in Figure 9.



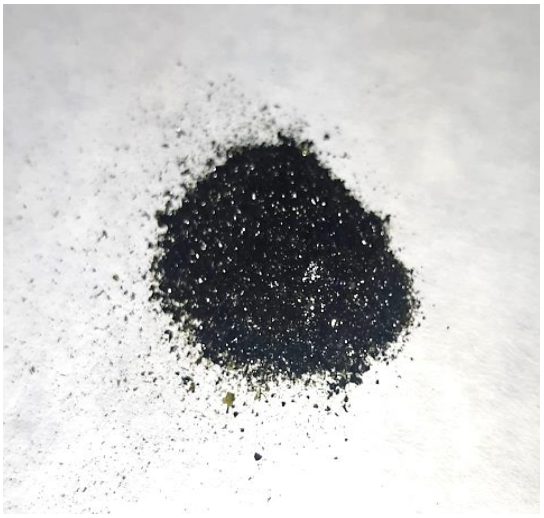


Figure 8-UV-Vis transmission spectra of Cr_2O_3 NPs prepared by the simple chemical method using cauliflower extract.

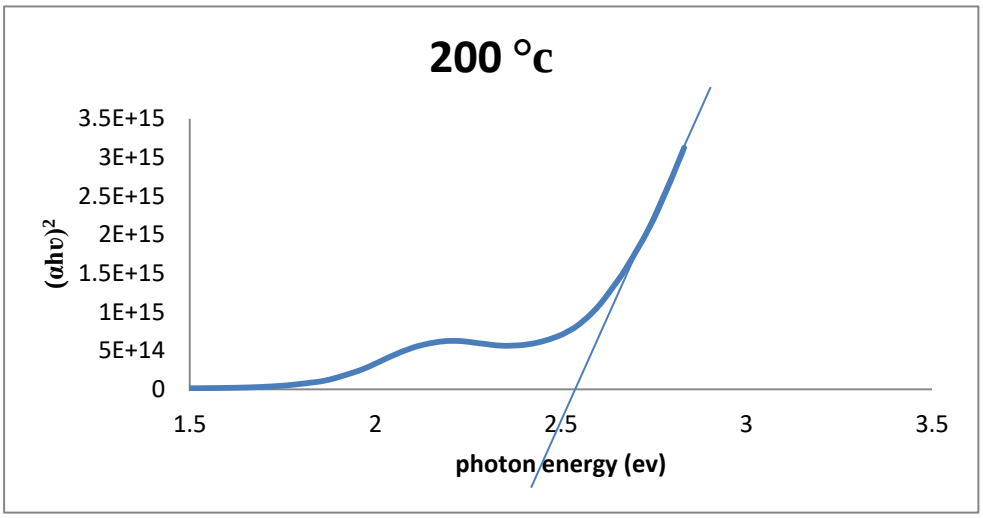


Figure 9-Energy band gap of Cr_2O_3 NPs prepared by the simple chemical method using cauliflower extract.

3.6 UV-Vis properties of chromium oxide NPs prepared by the sol-gel method.

Figure 10 shows a high transmittance percentage above 400 nm indicating the strong absorbance of **Cr_2O_3** in this region. All films showed increase in transmittance at the wavelengths longer than 400 nm.

The optical band gap of chromium oxide NPs was calculated by plotting $(\alpha h\nu)^2$ versus $h\upsilon$ and by extrapolating the straight line of the curve to the $h\upsilon = 0$ as shown in Figure 11. It was found that the **Cr_2O_3** NPs have direct transition type and the bandgap has increased from 2.5 eV to 3.4 eV with the
sol-gel method. Increase of the optical energy gap of chromium NPs with the sol-gel method can be ascribed to the formation of smaller chromium oxide NPs.

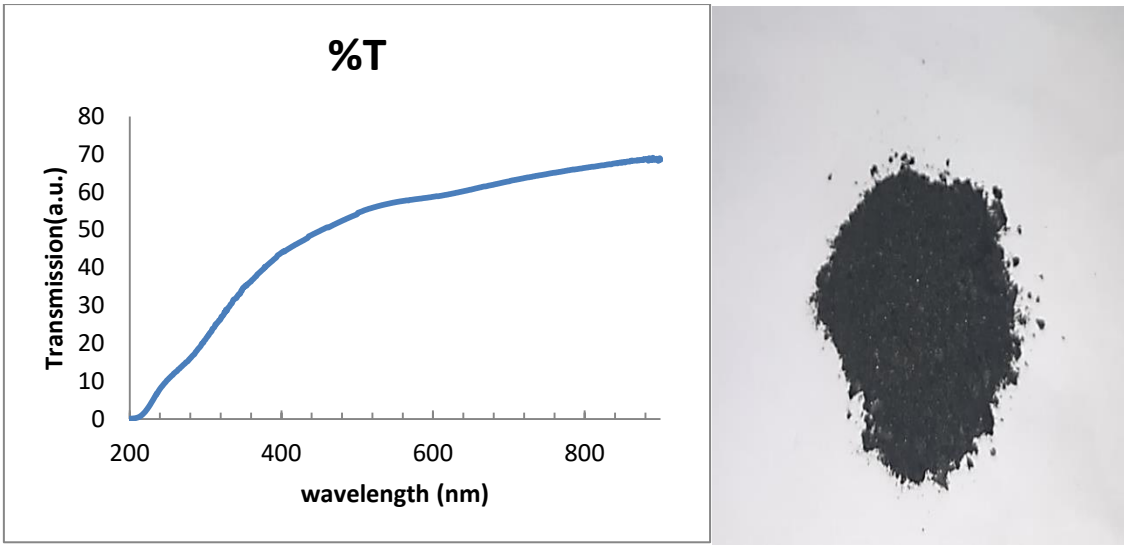


Figure 10-UV-Vis transmission spectra of Cr_2O_3NPs prepared by the sol-gel method using cauliflower extract.

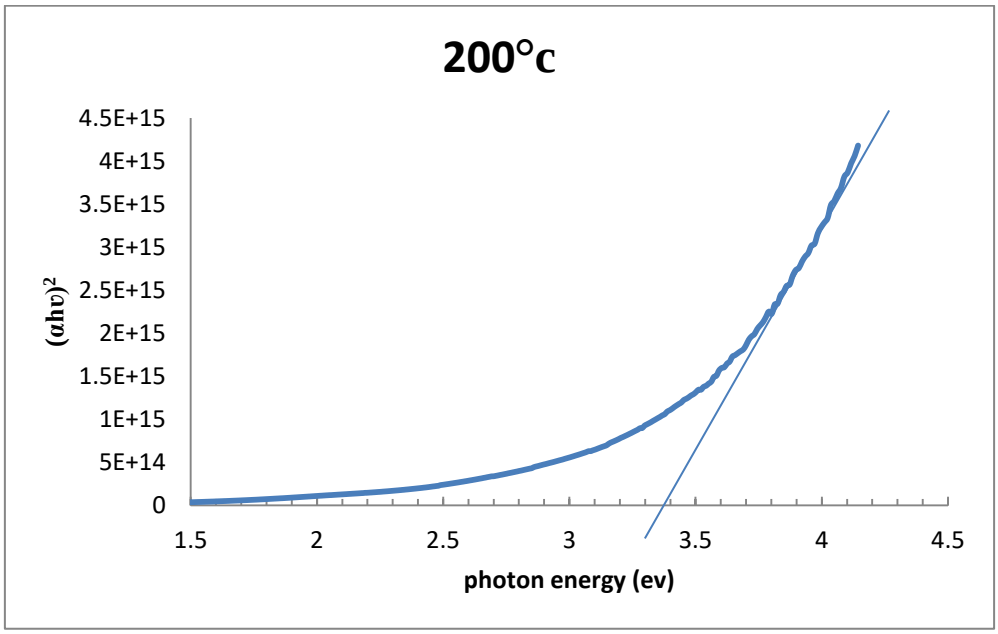


Figure 11-Energy band gap of Cr_2O_3 NPsprepared by the sol-gel method using cauliflower extract.

3.7 Comparison between chromium oxide NPs prepared by the simple chemical method and the sol-gel method.

It was noted that chromium oxide NPs prepared by the simple chemical method were less pure and were not completely good, but when the result using the sol-gel method was excellent. An increase in purity, a decrease in the particles size and an increase in the energy gap were noted. . Table (3) shows the results of chromium oxide NPs from the two methods.

Table 3-The results of chromium oxide NPs in two methods

Plant Extract	Material in a simple chemical method	Crystallite size D(nm)	Particle size (nm)	Energy gap (ev)
cauliflower		36.1	130.3	2.5
		57.8		
	In a sol-gel method	**Crystallite size D(nm)**	**Particle size (nm)**	**Energy gap (ev)**
		20.68	14.89	3.4
		16.14	39.08	
		15.5		
		20		

Antibacterial Activity of Cr_2O_3 NPs

The antimicrobial activity of Cr2O3 NPs synthesize have been examined against bacterial cultures Gram-positive (Bacillus subtilis), Gram-negative (Escherichia coli), and against fungal cultures (Candida albicans) using agar well diffusion method[11].

Table 4-The antibacterial activity of the Chromium oxide nanoparticles prepared using cauliflower extract against the tested bacteria as demonstrated by diameters of the inhibition zone (mm)*.

	Inhibition zone	
	Cr2O3 nanoparticles synthesized by	
Isolated bacteria	***Cauliflower extract (simple chemical method)***	***Cauliflower extract (sol-gel method)***
Staphylococcus aureus +	***21***	***16***
Staphylococcus epidermidies +	***22***	***20***
Escherichia coil -	***22***	***19***
Klebsiella up -	**21**	**17**
Candida albicons	***18***	***16***

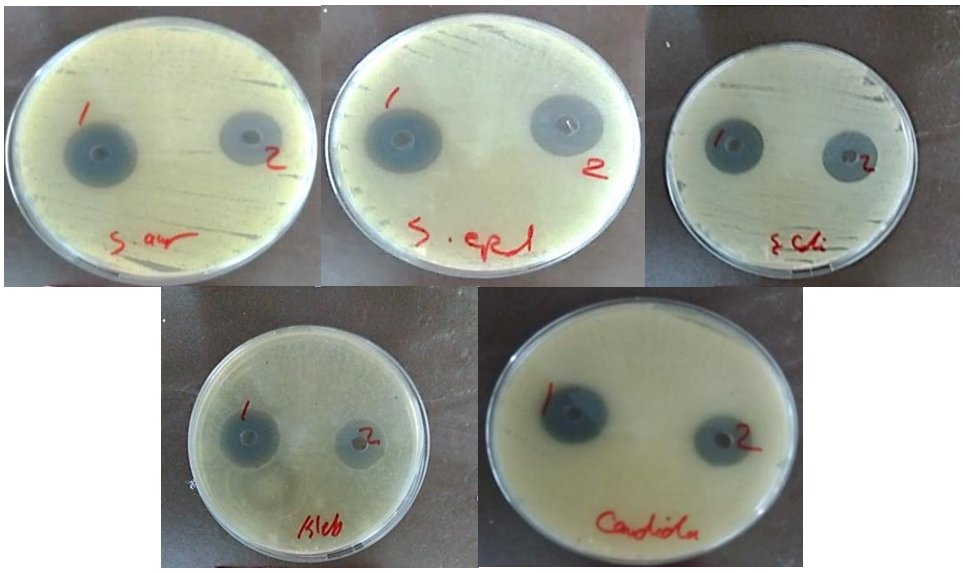


Figure 12-The antibacterial activity of Cr_2O_3 NPs synthesized by cauliflower extract on different Gram- negative and Gram positive bacteria. (1) Simple chemical method and (2) sol-gel method.

4. Conclusion

This work succeeded in the biosynthesis of chromium oxide nanoparticles using cauliflower extract by the simple chemical and sol-gel methods. The cauliflower extract has succeeded in converting $CrCl_3.6H_2O$ into chromium oxide nanoparticles. Also, the cauliflower extract acted as a reducing, stabilizing and anti-agglomeration agent. It was noted that the results of the sol-gel method are better than those of the simple chemical method. This was noticed by an increase in purity, a decrease in the size of particles and an increase in the energy gap. The prepared powders were characterized using XRD, SEM, and UV-Visible spectroscopy. No similar results was found in the literature on chromium oxide nanoparticles prepared using cauliflower extract.The study also revealed that chromium oxide nanoparticles repared using cauliflowerextract could be an antibacterial agent for human pathogenic bacteria.

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