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Characterization of Alumina Nanoparticles Prepared Via Green Synthesis Method

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ABSTRACT

The green synthesis method of nanoparticles attracts the attention of researchers in various scientific specializations as it is easy, environmentally friendly, and low-cost. It is one of the important methods for preparing alumina nanoparticles, which has wide applications in various fields. In this work, alumina nanoparticles were prepared by this technique using an aluminum salt with a plant extract in the manner used in previous studies. The resulting nanoparticles were then characterized structurally and optically using several techniques. The results of X-ray diffraction (XRD) measurement proved the formation of alumina nanoparticles with a hexagonal phase through the peaks appearing in the diffraction pattern belonging to these nanoparticles, and it was found that their average particle size is equal to (61 nm). As for the scanning electron microscope images (SEM), it was shown that their diameters average range between (35 - 55 nm) and that their shapes are not arranged between spherical and rod-like, with the formation of aggregations of them. The results of measuring the UV-Vis spectrophotometer through the absorption spectrum showed that the surface plasmon resonance (SPR) of these nanoparticles at the wavelength (~300 nm). Fourier-transform infrared spectroscopy (FTIR) analysis distinguished the appearance of bonds belonging to alumina and within the range (~ 400 - 1100 cm^{-1}).

Introduction

All science fields are implicated in nanotechnology, including materials science, physics, chemistry, biology, engineering, and computer science, where nanotechnology is a modern specialization of research [1-5]. Nanoparticles (NPs) have a large surface area, magnetic, and mechanical properties, better surface-to-volume ratios, as well as outstanding chemical stability in high temperatures and severe environments [6-10]. NPs can be fabricated from different materials and can be synthesized using various techniques that are based on biological, chemical, or physical [1-6]. Green synthesis using plant extracts to prepare nanoparticles is an environmentally friendly, economical, and effective biological method that attracts the attention of researchers, it is an important technique in preparing metal oxide NPs [11-13].

Recently, metal oxide NPs have attracted a big interest, they are being fundamentally used as heterogeneous nanocatalysts in a variety of organic transformations due to their high surface area, and small sizes which affect particular biological and catalytical applications [14,15]. One of the important metal oxides NPs is alumina NPs (Al_2O_3 NPs) which have been widely used in a wide range of industries, foods, personal care, medicine, biosensors, water treatment, high-risk pollutants detection, solar cell devices, capacitors, and photonic crystals. They are water-insoluble and have variable dimensions according to the preparation method [16-20]. In this work, Al_2O_3 NPs were prepared via green synthesis, using an aqueous extract of red onion peels, and then their structural and optical properties were characterized using some structural and optical measurement techniques. This technology was adopted in this work because it is a development of clean technologies that are safe for environmental and human health and encourages the replacement of current products with new environmentally friendly nanoproducts, which are made using microorganisms or plant extracts. The red onion

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plant extract was used in this work. As the plants contain organic compounds such as flavonoids, amino and carboxylic acids, ketones, phenols, and proteins, which contribute an important role in the recovery of mineral salts and the production of NPs.

Materials and Methods

Preparation of Plant Extract

The plant extract was prepared by collecting the peels of red onions available in the markets. The peels were collected and washed several times with distilled water to get rid of dust and dirt. Then they were dried under the shade and ground using an electric grinder. Then (200 ml) of distilled water was added to (5 gm) of this resulting powder in a glass baker, stirring the mixture using a magnetic stirrer and heating it at (80 ℃) for (30 min), where a red-brown extract was obtained. The extract was then cooled to room temperature, and the product was filtered and collected for use in the next step.

Preparation of Aluminum Chloride Solution

M) of aluminum chloride was prepared by dissolving (2.5 gm) of aqueous aluminum chloride ($AlCl_3.6H_2O$) in (100 ml) of distilled water while stirring using a magnetic stirrer until a clear solution was obtained. The required weight of ($AlCl_3.6H_2O$) was calculated using equation (1) [21]:

$$M = \frac{n}{V} \quad = \frac{W}{V} \times \frac{1}{MW} \qquad (1)$$

Where n represents the number of moles, M represents the molar concentration in units of (mol/L), W represents the weight to be dissolved, MW represents the molecular weight, and V represents the volume of solvent.

Preparation of Alumina Nanoparticles

(20 ml) of plant extract was added to the saline solution gradually using a burette, with continuous stirring and maintaining the temperature between (60-80 ℃). The acidity was then adjusted by adding sodium hydroxide (NaOH) at a concentration of (1 M), which resulted in a brown precipitate that was cooled to room temperature and left until the next day, where it was collected and dried in a convection oven at (100 ℃). Finally, the product was burned in an incineration oven at (450 ℃) for (2 hours), and thus a white powder of aluminum oxide nanoparticles was obtained.

The above three preparation steps represent the protocol followed in most previous studies to prepare metal oxide nanoparticles using the green synthesis technique, as in [8], and Figure (1) represents an illustrative diagram of the steps for preparing alumina nanoparticles by green synthesis.

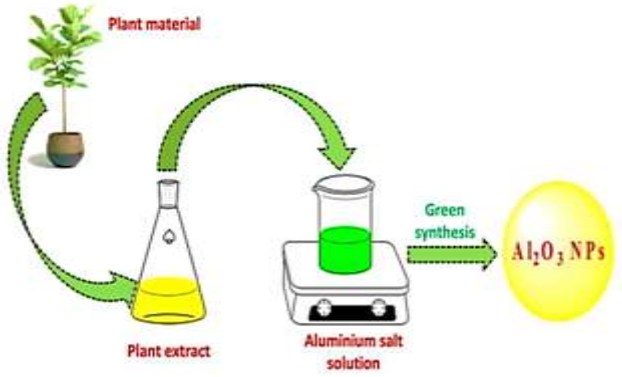

Figure 1. Schematic diagram of green synthesis of Al_2O_3 NPs [8]

Results and discussion

XRD Analysis

Analysis of the data obtained from the XRD measurement proved that the resulting particles are alumina NPs by the appearance of diffraction peaks belonging to this material, as shown in Figure (2), which shows the Miller indexes related to the diffraction angles shown in the figure, which matched with the JCPDS Card (71-1123) with the formation of the hexagonal phase. Using equation (2) [9], which represents the Scherrer equation, the average crystalline size of the nanoparticles was calculated and it was equal to (61 nm).

$$D = \frac{K\lambda}{\beta \cos\theta} \qquad (2)$$

Where K represents the shape factor constant with value (0.9), λ denotes X-ray wavelength, β is the full width at half maximum (FWHM) of the X-ray peaks, and θ denotes the diffraction angle. Table (1) shows a summary of the most important results obtained from the XRD pattern, which include diffraction angles, FWHM, spacing between planes (d), and Miller coefficients, in addition to crystalline size.

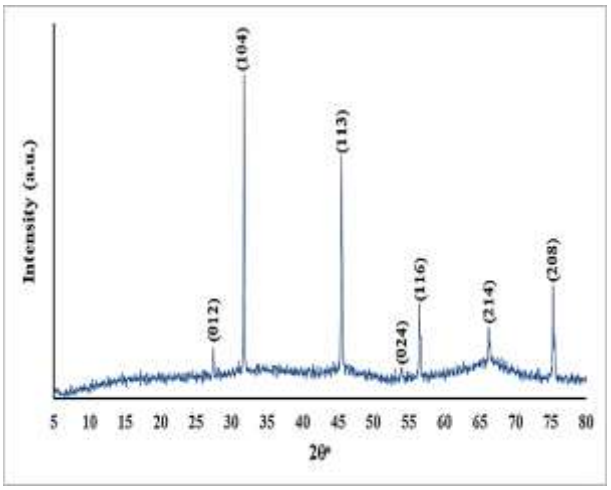

Figure 2. XRD pattern of alumina NPs

Table 1: XRD diffraction analysis results of the prepared NPs

Pos.(°2Th.)	β(°2Th.)	d(Å)	hkl	D(nm)
27.473070	0.178069	3.24394	012	45.86337676
31.793710	0.126904	2.81227	104	64.9381684
45.528410	0.136240	1.99075	113	63.09077784
53.955030	0.160837	1.69804	024	55.17072809
56.545450	0.147129	1.62624	116	61.12975463
66.281130	0.145668	1.40901	214	65.00253637
75.337840	0.134038	1.26052	208	74.67775767

SEM Analysis

Figure (3) represents SEM images of the prepared NPs. The images showed the formation of spherical and rod-like shapes for the Alumina nanoparticles, so they appear to be an assembly of differently shaped structures. This result is consistent with [14], where the Alumina NPs formed small aggregates as stated in [20]. The diameters average of these nanoparticles ranged between (35 – 55 nm).

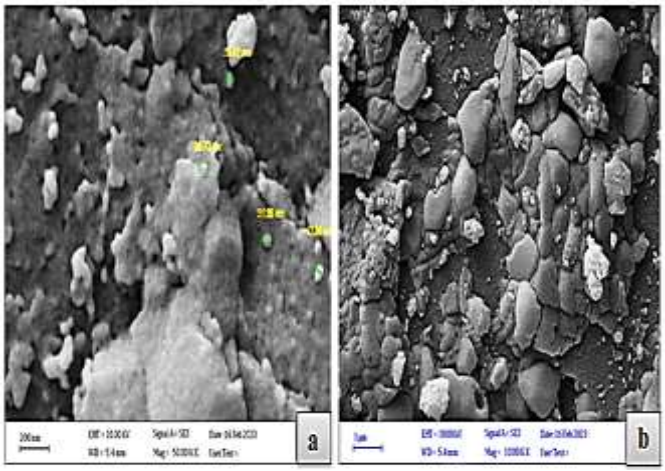

Figure 3. SEM images of alumina NPs at two scales: a) 200 nm, b) 1 µm

UV-Vis Spectrophotometer Analysis

The absorption spectrum of materials is one of the main indicators of the formation of nanoparticles, as the absorption spectrum of nanoparticles differs from that in the case of bulk materials, as it is characterized by the appearance of a peak representing the surface plasmon resonance (SPR), which is a distinctive characteristic of every nanomaterial in its absorption spectrum, as it is responsible for changing the color of the nano solution [10]. Figure (4) shows the absorbance spectra of the prepared colloidal solution and it is found that the SPR is about (300 nm) which agrees with previous studies [1,12, and 14]. On the other hand, the transmittance spectrum of this material can be observed in Figure (5), where the behavior of the curve is opposite to the behavior of the curve of the absorbance spectrum. The higher the absorbance value, the lower the transmittance of the material, and vice versa. As for the direct energy gap of aluminum oxide nanoparticles, it was calculated using the Tauc relationship as shown in Figure (6), which represents the square of the product of the absorption coefficient (α) multiplied by the photon energy ($h\upsilon$) as a function of the photon energy (where h represents Planck constant and υ represents the frequency of the photon), and its value was (2.4 eV).

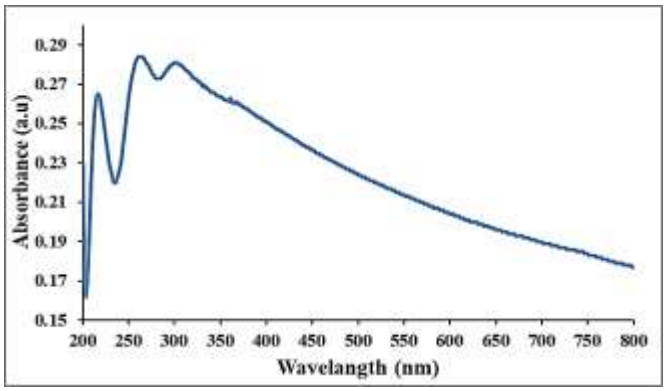

Figure 4. Absorbance spectra of alumina NPs

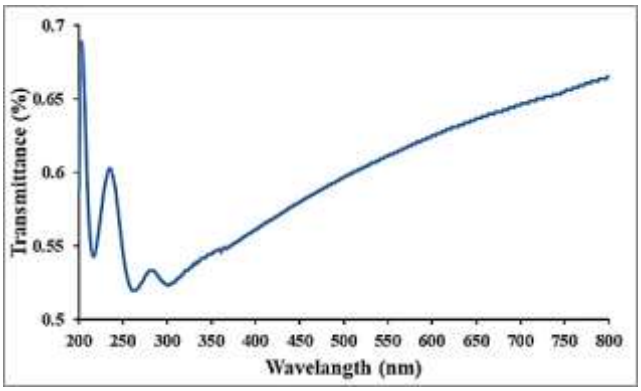

Figure 5. Transmittance spectra of alumina NPs

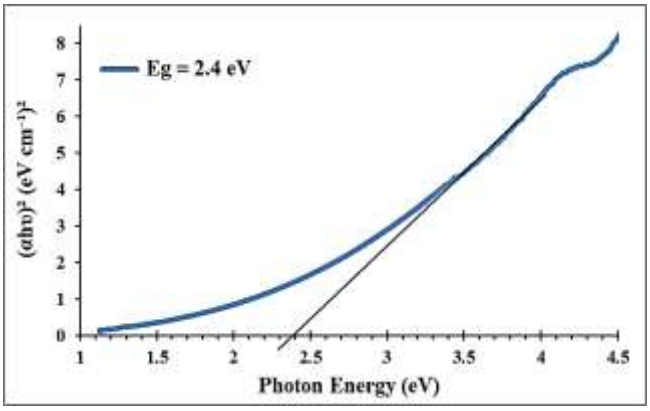

Figure 6. Band gap energy of alumina NPs

FTIR Analysis

This technique was used to obtain an infrared spectrum of emission of the prepared NPs. In addition to the bonds and active groups belonging to the alkanes, alkynes, carboxyl, and hydroxyl, alumina bonds are the important bonds in which the current study is interested, thus, IR spectroscopy in the range about (400 - 1100 cm^{-1}) can be used as a fast and easy tool to distinguish the presence of transition alumina phases as in [22]. Figure (7) represents FTIR transmission spectra of the prepared NPs, the absorption peaks about (500 cm^{-1}) assigned to amorphous aluminum oxide, where this figure shows the peaks which are related to the stretching vibrations mode of the (Al–O) band in alumina. Also, it distinguished the peaks around (1000 cm^{-1}) related to the symmetric bending of the (Al–O–H) bond, this agrees with the previous study [23].

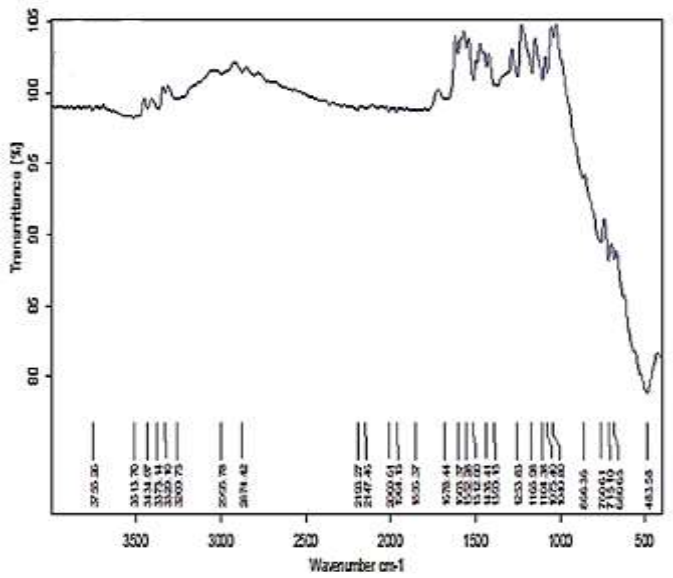

Figure 7. FTIR spectra of alumina NPs

Conclusion

Alumina nanoparticles can be prepared by an environmentally friendly, rapid, and low-cost green synthesis method. Through the characterization of the resulting particles prepared in this method, it becomes clear that they are hexagonal in composition, with sizes and diameters on the nanoscale, and their shapes range between spherical and rod-like, with the appearance of a distinct peak within the curve of their absorption spectrum, which represents surface plasmon resonance. In short, this represents a quick, simplified description of the resulting nanoparticles, which can benefit from one of their applications in the biological or industrial field.

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توصيف جسيمات الالومينا النانوية المحضرة بطريقة التوليف الاخضر

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الخلاصة:

تعد طريقة التوليف الاخضر للجسيمات النانوية جاذبة لاهتمام الباحثين بمختلف تخصصاتهم العلمية كونها سهلة وصديقة للبيئة وذات تكلفة قليلة، وهي احدى الطرق المهمة لتحضير جسيمات الالومينا النانوية والتي لها تطبيقات واسعة بمختلف المجالات. ففي هذا العمل تم تحضير جسيمات الالومينا النانوية بهذه التقنية باستخدام احد املاح الالمنيوم مع مستخلص نباتي بالطريقة المتبعة في الدراسات السابقة، ثم تم توصيف الجسيمات النانوية الناتجة تركيبيا وبصريا باستخدام عدة تقنيات. اثبتت نتائج قياس حيود الاشعة السينية (XRD) تكون جسيمات الالومينا النانوية ذات الطور السداسي من خلال القمم الظاهرة في نمط الحيود والعائدة لهذه الجسيمات وتبين ان معدل الحجم الحبيبي لها مساويا لـ (61 nm)، اما صور المجهر الالكتروني الماسح (SEM) فقد بيت ان معدلات اقطارها تتراوح بين (55 nm – 35) وان اشكالها غير منتظمة تتراوح بين الكروي والعصوي مع تكون تكتلات لهذه الجسيمات. وقد بينت نتائج قياس مطياف الاشعة فوق البنفسجية - المرئية من خلال طيف الامتصاص ان رنين البلازمون السطحي لهذه الجسيمات قد تكون عند الطول الموجي (300 nm~). ميز التحليل الطيفي للأشعة تحت الحمراء لتحويل فوريه (FTIR) الروابط التي تنتمي إلى الألومينا وضمن النطاق (cm^{-1} 1100 - 400 ~).

الكلمات المفتاحية: جسيمات الالومينا النانوية، التوليف الاخضر، اكاسيد المعادن النانوية، رنين البلازمون السطحي.