

Role of Nanotechnology in Iraq (Synthesis and Characterization): A Review

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ABSTRACT

Nanotechnology has become the focus of attention in all basic sciences such as physics, chemistry biology and others. It concerned with particle size range from 1-100 nanometer. In this review they give a brief description about Nanotechnology in Iraq, Types of synthesis, study the characterization and its application in various fields viz. medicine, industry, agriculture, electronic and in the oil field.

Keywords- Nanotechnology, Characterization, Synthesis, Metal nanoparticles.

I. INTRODUCTION

Nano science that science studies the molecules and compounds which size less than 100 nm. (1). The size of these materials can influence differ significantly properties (optical, electrical and magnetic) when compared with the same bulk materials. These unique features depended on shape, particle size, and high ratio of (surface/volume). In 1959, Richard Feynman wondered what would scientists do if they can control the movement of one atom and rearrange them, as they want. This was the beginning of the nano revolution (2). In 2009 despite all the circumstances, Iraq has managed to establish the first nanotechnology center at the University of Technology. To be the starting point in the field of this science. The center was supported by the Iraqi government. The Nanotechnology Center has directed its research activities towards the necessary needs of Iraqi institutions that have found the science of nanotechnology a useful and effective tool for solving scientific problems and developing research potential (3). In this review, we will study different methods of nanoparticles synthesis, characterizations, and application in different fields. This overview particularly depending on Iraqi Academic Scientific Journals.

II. CLASSIFICATION OF NANOPARTICLES

In general, the nanomaterials vary in source and according to their proportions, such as materials organic or inorganic, natural or synthetic (4). The development of nanotechnology has changed the medical rules used to prevent and diagnose diseases, treatment of cancer, to improve the industrial applications such as in the field of energy, electronics and water treatment (6).

Synthesis of nanoparticles

There are two general methods of producing nanomaterials first, starting from bulk materials then breaking or minimizing them until they reach very small pieces (of nanoscale) using mechanical or chemical methods. This method called top-down process. (5). In contrast, there is the bottom to top method which starting from atoms or molecules to be separated from each other and then aggregated to the nanoscale using chemical reactions or by the exchange of materials (6). Bottom-up method is better than top-down process to synthesize very-small sized particles because it has the possibility of obtaining a uniform size, shape and structure (7). Different methods are used for preparing, depending on building of atoms to get the results wanted. Chemical methods depend on the process of metal reduction such as, sol-gel, hydrothermal, co-precipitation, reduction method, electrochemical, inverse reduction, vapor deposition, and spray pyrolysis. These methods are required high temperature pressure, toxic solvents and non-ecofriendly methods. In physical methods different processes are using to synthesis of nanoparticles such as pulsed laser ablation, arc discharge, and micro wave assisted process. Therefore, the need for clean and environmentally friendly alternative methods has emerged. The use of material like plant extract (leave, bark, peels etc) and microorganism show eco-friendliness, simple, rapid, non-toxic and dependable methods (7-9). Table 1 shows some physical, chemical and biological methods used for synthesis of differ types of metal nanoparticles which are used to produce nanoparticles in scientific researches inside Iraq.

Table 1: Some important physical, chemical and biological methods for synthesizing of metal nanoparticles.

Metal Nanoparticle	Methods			
	Physical	Chemical	Biological	References
Silver	Pulsed laser ablation			12
	Pulsed laser ablation			13
			cinnamon zeylanicum(bark)	15
			Olive leaves	16
			Pleurotusostreatus fungus	17
	Pulsed laser ablation			18
	Pulsed laser ablation			19
		Reduction methods		20
		Reduction methods		22
	Pulsed laser ablation			23
			Lactobacillus spp(bacteria)	24
			Malvaparviflora leaves	25
	Sol-gel			26
			Eucalypyus Bicolor bark	27
		reduction methods		28
		Reduction method		29
	Arc discharge			30
	Electrochemical		31	
		Banana peel extract	32	
		Teucriumpolium (aerial part)	34	
		Trichodermaharizantum(fungus)	35	
		Aspergillusniger(fungus)	36	
Zinc Oxide	Pulsed laser ablation			14
		Sol-gel		33
		Co-precipitation		41
		Hydrothermal		42
	Pulsed laser ablation			43
	Sol-gel		44	
Gold	Pulsed laser ablation			21
	Pulsed laser ablation			37
		Inverse-reduction		46
			Orchid and Gum Arabic	47
		Spray pyrolysis	48	
Iron Oxide	Microwave irradiation			38
		Co-precipitation		39
			Lactobacillus rhamnosus	40
			Lemon	45
Carbon	Arc-discharge			49
		vapor deposition		50
	Pulsed laser ablation			51
	Pulsed laser ablation			52
	Pulsed laser ablation			53

III. DESCRIPTION TECHNIQUES

Different techniques were used to study the nanoparticles of the prepared materials. Some of these techniques are Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), Scanning Electron

Microscopy (SEM) Transmission Electron Microscopy (TEM), Atomic Force Microscope (AFM) and UV-Visible spectrophotometer.

Fourier Transform IR Spectroscopy:

Fourier Transform Infrared Spectroscopy (FTIR) is an important technique to study and understand

nanoparticle surfaces. This technique is used to determine the effective groups aggregates on the surface of nanoparticles by measuring the vibrational frequencies of chemical bonds. An example the FTIR spectrum of zinc oxide nanostructures are shown in figure (1). Bands of 417, 437, and 740 cm^{-1} spectra of ZnO and 1540.1, 1492.9, 1357, 1043.49, 833.25 a companion with expansion oscillation of crystalline hexagonal ZnO expansion vacillation (44). Another example figure (2)

shows the FT-IR spectrum of the prepared Fe_3O_4 coated with oleic acid (OA). The two new bands at 1639 and 1541 cm^{-1} were assigned to the asymmetric (COO^-) and symmetric (COO^-) stretching vibrations. This indicates that oleic acid has been both physically and co-ordinatively adsorbed on the surface of magnetite nanoparticles. The absorption peak observed at 584 cm^{-1} identical to the Fe-O stretching vibration related to the magnetic phase (38).

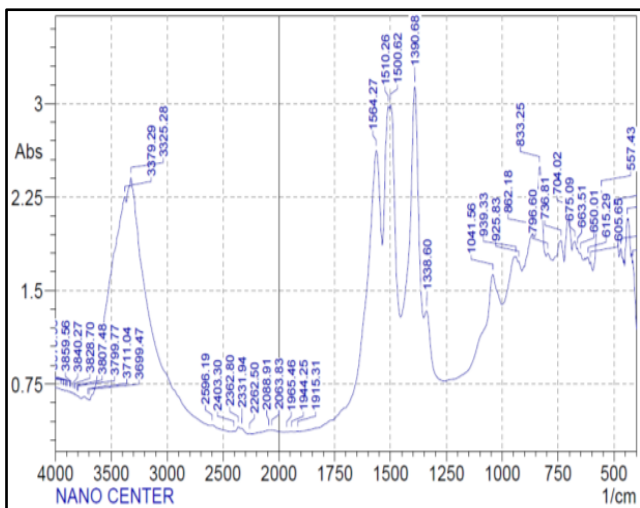


Figure 1: Spectra of FTIR for ZnONPs (Ref. 44)

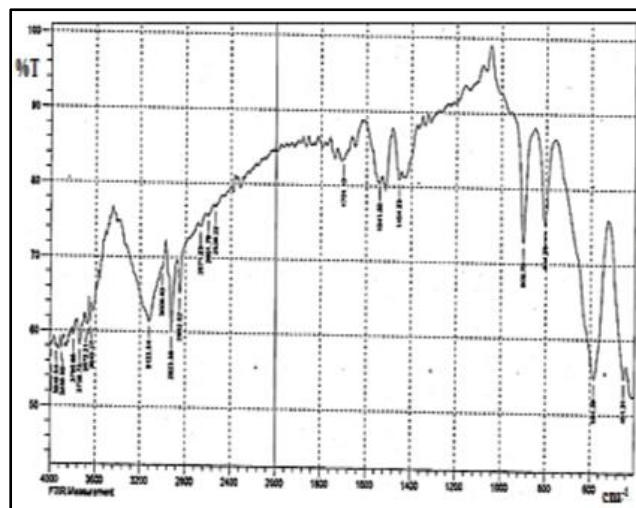


Figure 2: Spectra of FTIR for Fe_3O_4 NPs (Ref. 38)

X-ray Diffraction:

X-Ray Diffraction (XRD) is one of the most important techniques in studying the size, shape and arrangement of nanoparticles. The particles size can be determined from the width of the X-ray peaks using the Scherer equation. The diffracted patterns explain whether the sample materials are pure or contain impurities. An example, the XRD pattern of Fe_3O_4 nanoparticles obtained using solve-hydrothermal reaction assisted by microwave irradiation method showed five main

diffraction peaks were observed at $2\theta = 30^\circ, 35.6^\circ, 43.3^\circ, 54^\circ, 57.1^\circ$, correspond respectively to the planes (220, 311, 400, 422, and 511 respectively) of Fe_3O_4 nanostructures figure (3). The calculated crystal average size is (25.5) nm (38). Another example figure (4) the diffraction peaks of gold NPs gold observed at $38.14^\circ, 44.06^\circ, 64.92^\circ$ and 77.7° , representing the index as (111), (200), (220) and (311), respectively, which verified the polycrystalline face-centered cubic structure (21).

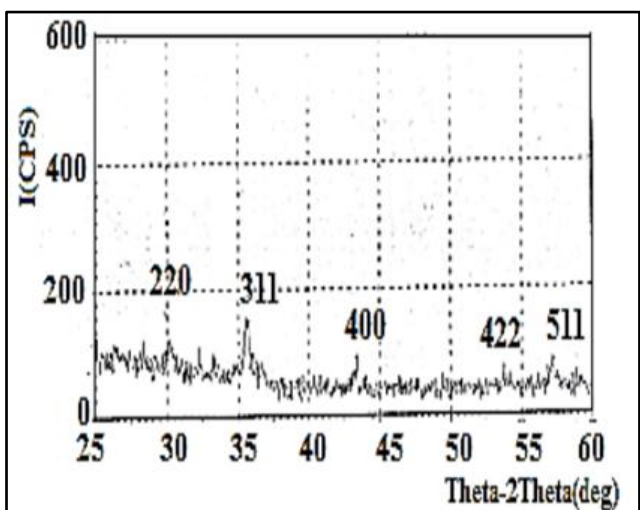


Figure 3: XRD patterns of the Fe_3O_4 NPs (Ref. 38)

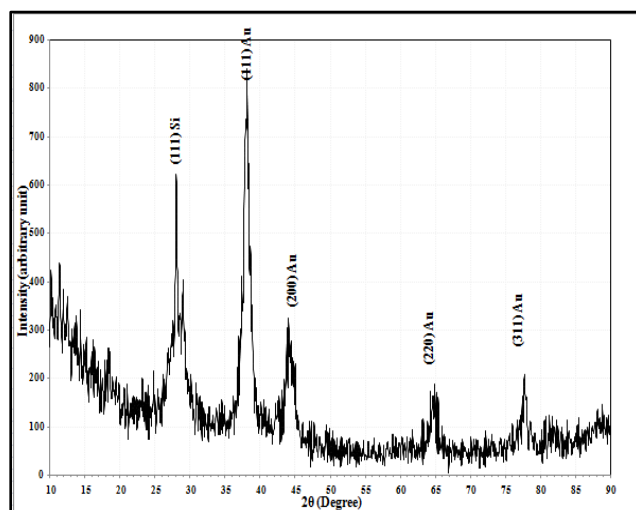


Figure 4: XRD patterns of the AuNPs (Ref. 21)

Scanning electron microscopy:

It is another technique giving structural examination with two-dimension imagination. It has the ability to analyze different sizes of nanoparticles, size distributions, shapes, and the surface morphology of the synthesized particles at the micro scales. So that SEM may offer, better performance for surface and shape for nanoparticles analysis. Figure 5 shows the SEM images of the prepared AgNPs at different reaction temperatures. Figure 5 (a) citrate-AgNPs have prepared by 0,005M of AgNO₃ reduction at T=100C for 2h. It was observed that the particles with a size ranging from (80.7 to 413.2) nm with mean average of 202 nm. From Figure5 (b) it has

noted that the agglomerations of nanoparticles have the biggest. Figure 5 (c) shows SEM micrograph at temperature 200C for 2h with the same concentration silver nitrate. The image observed spherical and irregular particles with a size ranging from 22.3 to 99.5 nm (20). Another example figure (6) shows SEM micrograph with different enlargement Fe₃O₄. It is obvious from the shapes that there are dense chips of particles that appear irregularly and gather irregular particles to form a large part of them. There are other smaller ones with irregular sizes shown by the image that there is agglomerate. The shape of the nanoparticles was either spherical or semi-spherical or possessed other forms (45).

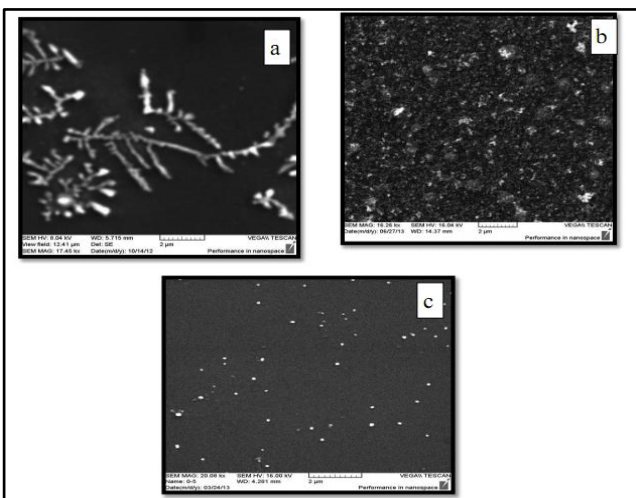


Figure 5: SEM images of AgNPs (Ref. 20)

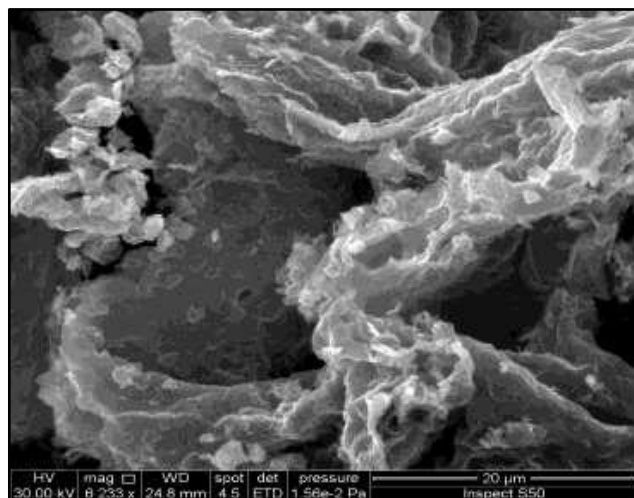


Figure 6: SEM image of Fe₃O₄NPs (Ref. 45)

Transmission Electron Microscopy (TEM):

Transmission Electron Microscopy is one of the methods that used to determine nanomaterials size, distribution and morphology. Particles as small as a few angstroms (10–10 m), which is near atomic levels can be viewed in TEM. Figure 7 display the size of the gold nanoparticle was 44 nm with different particles formats

(clusters, spherical, branched chain) and the average size between (20 - 50) nm (47). Another example figure (8) shows TEM image colloidal silver nanoparticles prepared by electrochemical method. Average size of the particles is (a) (10-12) nm (b) 15 nm, (c) (15-20) nm, (d) (30-44) nm. (31).

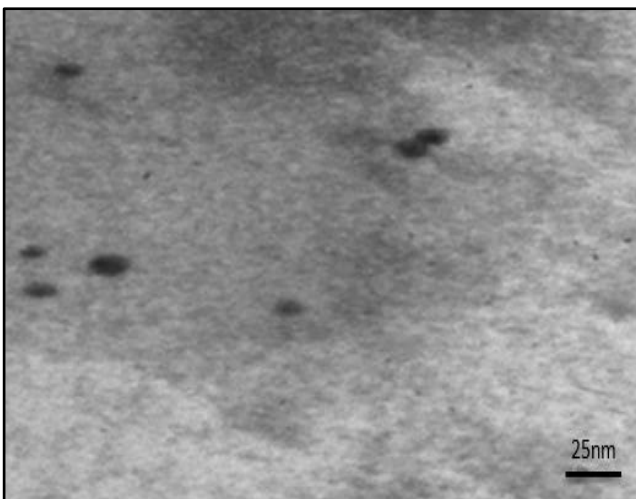


Figure 7: TEM images of AuNPs (Ref. 47)

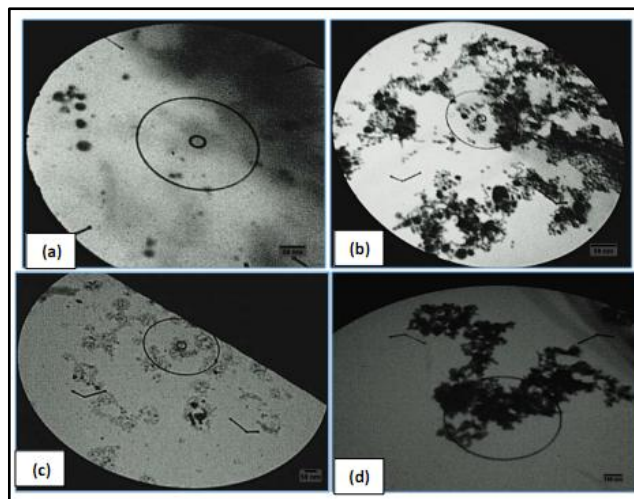


Figure 8: TEM images of AgNPs (Ref. 31)

Atomic Force Microscope (AFM):

It is another technique used to image the surface of nanoparticles on a nm and to measure surface forces. The surface is scanned according to the force between tip of sample and the vibration to study the surface characteristics of the sample. Figure 9 shows an example of AuNPs which have grossness surface large particles diameter distribution and the mean particle size was (68

nm) (47). Another example Figure10 shows the 2D and 3D AFM images of zinc oxide colloidal NPs. The micrographs obviously show that zinc oxide nanoparticles have spherical shape and grain size in the range of (5-39) nm in diameter. A root mean square (RMS) roughness of nanoparticles was 2.97 nm with average size 24,6 nm (25).

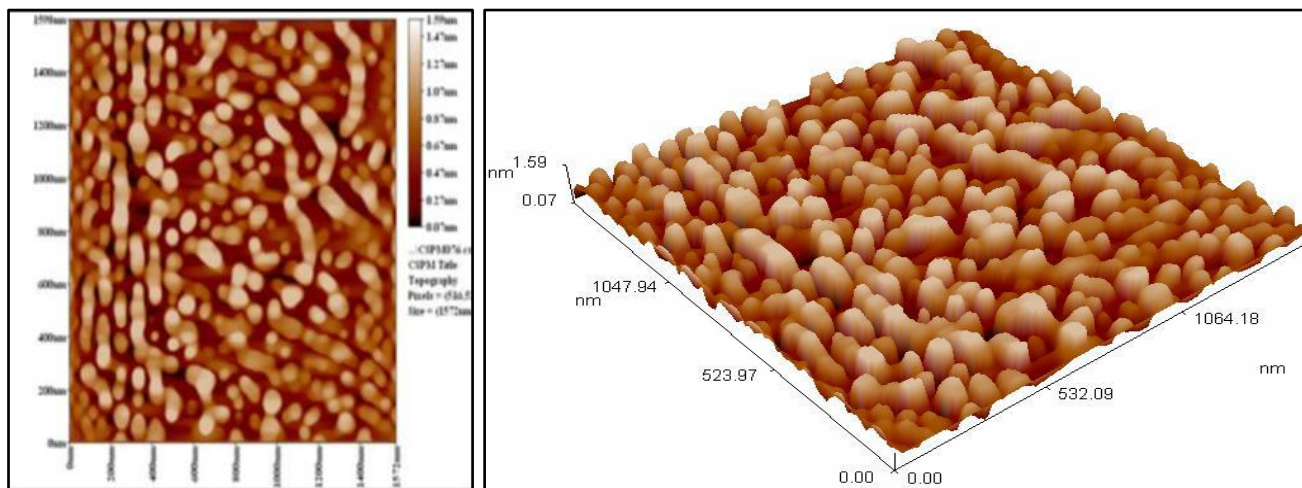


Figure 9: AFM image of GNPs 2D, 3D by using orchid as reducing agent (Ref. 47)

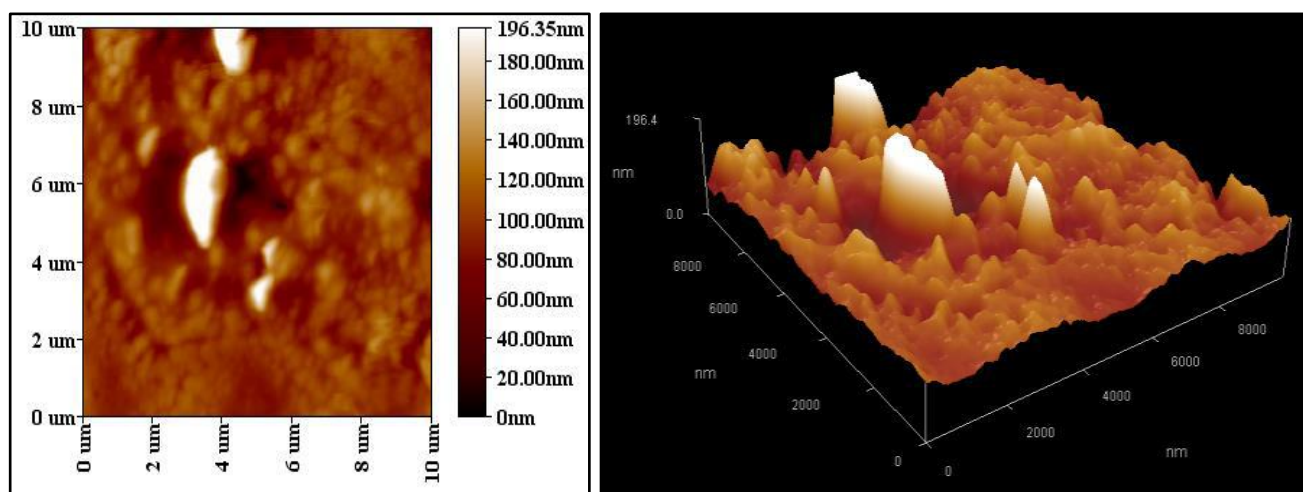


Figure 10: 2D and 3D AFM images of ZnONPs using laser ablation (25)

UV-Vis Spectroscopy:

In particular, metal such as noble metals Plasmon resonance is an optical property of the nanoparticles. This SPR peak is shown in UV absorption spectra. The magnitude of peak, wavelength and spectral bandwidth associated with nanoparticles are dependent on size, shape and material composition (54). Due to Mie, theory one band of SPR means spherical metal nanoparticles (55). For example, figure (11) three UV-Vis spectra for AuNPs were piloted in different time intervals and observed that the color changed (no color-yellow-ruby red) of the gold nanoparticles with a time. The peaks shifted not much with time from (552.50 nm

to (550.00 nm) with increase in absorbance from (0.694) to (1.490) were revealed a linked point between the more reduction reaction and formation nanoparticles (56). The figure(12) has shown the UV-vis spectra of silver nanoparticles recorded at temperature of 100- 200°C. The absorbance band was broadened and positioned at 442.28, 423.5 nm and 421.41 nm at the temperature of 100 C, 150 C and 200 C, respectively for showing that silver nanoparticles have produced at a low temperature. By temperature increasing, the strongest absorption bands gradually shift to a higher wavelength. Then, it has concluded that the nanoparticles size has decreased with increasing of reaction temperature(22).

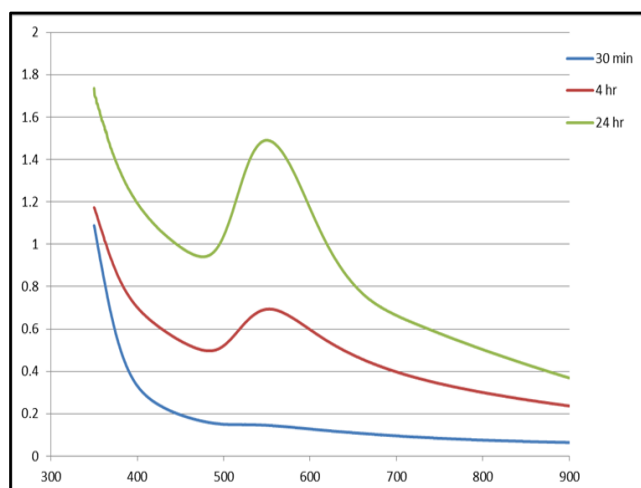


Figure 11: UV-Vis spectra of AuNPs (Ref. 56)

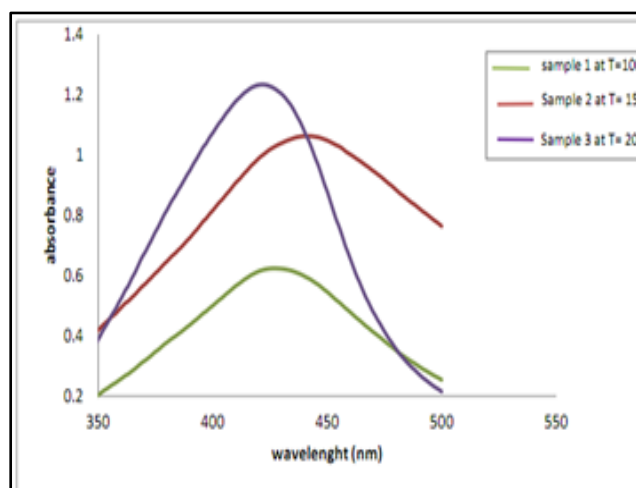


Figure 12: UV-Vis spectra of a AgNPs (Ref. 22)

Shape of nanoparticles:

Several shapes of nanoparticles were synthesized such as spherical (57), Quantum Dots (58), thin films (59), nanoporous (60), nanowires (61) and nanotube (52, 53).

IV. APPLICATION OF NANOPARTICLES

Nanoparticles have much consideration to researchers in the field of medicine, agriculture, electronic, and industry due to their optical, physical and chemical properties gained when compared with the basic materials.

Silver nanoparticles (AgNPs):

Many studies have begun to investigate their therapeutic efficacy as inhibitors for the growth of parasitic pathogens, fungal pathogens, and bacteria pathogens. Silver nanoparticles showed anti-parasitic activity against *E. histolytica* trophozoite where it causes millions of cases of dysentery and liver abscess each year. (62). In Iraq the Cutaneous leishmaniasis (CL) is the most widespread disease in Iraq. Macrophages are the main inhabitant cell for *Leishmania*; they phagocyte and allow parasite multiplying. To elimination, the effect of *Leishmania* parasites phagocytosis is the main factor. Ag NPs has the ability to activate the macrophages and enhanced inhibitory effects on *L. tropica* promastigotes and amastigotes in vitro following the infection after 48 hrs. of treatments (63). The powerful bioactivity of Ag NPs leads towards the clinical use as antifungal (35,64).

Silver nanoparticles showed high antibacterial activity and for that reason it has get a great probability in the preparation of drugs used against different type of bacteria diseases (65). The increasing of acquired infections in hospital and community, present antibiotic therapies are not effective, silver and silver nanoparticles showed strong effect against microbial (66-73).

Silver nanoparticles effect on the weights of the testes, epididymides and effect on the characteristics of sperm in male albinomice (74). It also observed

histological change on the ovary of female albino mice (75). Ahistological change on liver of *Coturnix coturni* after exposure to different concentration of silver nanoparticles (76). Silver nanoparticles had positive effect in enhance burn healing when it's applied locally (77).

The central nervous system is the most important system; it includes brain and spinal cord. It is very sensitive to any accidental infection during ontogenesis. The cerebellum is the second largest part of the brain after cerebrum and it's very sensitive to the abnormal changes during the embryological development. Silver nanoparticles at concentration range (2-20) mg/kg/day can produce many histological toxicities to the embryo's hindbrain and cerebellum when administrated to the dams during pregnancy period (78).

Silver nanoparticles have a significant effect on increasing the activity of lymphocytes, cytokines levels in mice, IgG concentration and phagocytes. It can be used as an effective adjuvant to improve the immune protection (79).

Acid phosphatase enzymes has been used in the detection of prostatic carcinoma. The activity of enzyme decreases by using nanoparticles like silver and gold. The inhibition of enzyme activity increased by increasing nanoparticles concentration (80).

Nanoparticles genotoxicity is a subject have got a great attention as a result of wide application of nanotechnology in many sections which in contact with human health. The genotoxicity of silver nanoparticles in the treated animals showed that the spleen cells were the less DNA damaged cells while the lymphocytes and bone marrow cells more effective manner (81).

In multiple myeloma plasma cells fight the germs by making antibodies that recognize and attack it. By using silver nanoparticles the phagocyte of cells increase which indicate that nanoparticles of silver do something like immune modulators and then the process of ingesting bacteria increases (82).

AgNPs act as an anti-oxidant factor by inhibition the formation of free radicals and scavenging all species of (ROS) from the irradiation water samples in certain range of concentration of Ag NPs (83).

Gold nanoparticles (AuNPs):

AuNPs have certain to be strong tools in various nanomedicine applications such as in drug delivery, diagnosis and therapeutics. AuNPs promoting radiotherapy treatment of ovary cancer cells (84) and brain cancer (85).

Colloidal Au and Ag nanoparticles interact with functional groups of GGT enzyme, resulting in protein denaturation and inactivate it. Gold nanoparticles was more interact with enzyme and inhibited it than silver nanoparticles, so that using of gold nanoparticles for detection and therapy of cancer is better than silver nanoparticles (86).

Zinc oxidenanoparticles (ZnONPs):

Zinc oxide nanoparticles ZnO showed the ability toward Mice Mammary Adenocarcinoma cancer cells, this toxicity correlated directly with ZnO nanoparticles concentrations. This toxicity correlated directly with ZnO nanoparticles elevated concentrations (87).

One of the most important challenges to treating diseases is the apperence of new strains that are resistant to antibiotics. ZnONPs combination with some antibiotics showed interactive and hostile effect for different bacterial isolate (32). Zinc oxide Nanoparticles was synthesized to act as antifungal agents to overcome the developed of fungi resistance to many conventional fungicides (33)

Zinc oxide nanoparticles were used to reduce acidity and maintain soil temperature (88).

Carbon nanoparticles:

In electronics, the Nano electronic device, which is formed from carbon nano tube, proved that it is better than ordinary devices. These Nano devices have some advantages compared to complementary metal oxide semiconductor transistors for example higher ability to move electrons, smaller size, and lower power consumption (89).

To increase drilling efficiency, multi wall carbon nanotube and silicon oxide nanoparticles were used in drilling fluids to make drilling smooth and efficient. Nano particles can work to activate other characteristics of digging fluids, like viscosity, gel strength, filter loss control, and friction reduction (90).

Aluminum oxide nanoparticles (AL₂O₃NPs)

The nanoparticle shows a good catalyst when blended with fuel diesel. Nanoparticles of AL₂O₃ increase the surface to volume ratio and increase the calorific value, that's leading to reduction in ignition delay and extra completely combustion so blended diesel fuel with nanoparticles of AL₂O₃ show reduction in Brake Specific Fuel Consumption (BSFC) and enhancement in thermal efficiency and when increase the ratio of nanoparticle shows more reduction in BSFC and thermal efficiency (91).

Steel structures are exposed to external erosion due to soil components. The repair of defects in the structures was repaired by using alumina nanomaterials, which prolonged the life of the carbon steel structures when compared to the use of red paint as an anti-corrosion (92).

Al₂O₃ nanoparticles and polypropylene fiber were used to get better properties of denture base material such as roughness and hardness of the surface, thermal properties and Power of influence (93).

Iron oxide nanoparticles (Fe₂O₃NPs)

Fe₂O₃ nanoparticles could be considered as promising killing agents in antimicrobials system. Also, biosynthesis of iron oxide nanoparticles had antibacterial effect against some pathogenic bacteria (94,95).

Nanotechnology for cancer had get a great attention for diagnosis, treatment, and monitoring the different type of cancer. Iron oxide nanoparticles induced cell cytotoxicity at all concentration when exposed to (Hela, RD and AMN3) cancer cell lines against REF normal cell line. Dose dependent effects of iron oxide nanoparticles have been confirmed with different cell types (96).

Corrosion processes are responsible for severe losses in the oil industry. Although organic and inorganic materials and mixed materials inhibitors have been used for a long time to control or reduce corrosion. Nano materials are good corrosion inhibitors because they have many advantages such as high efficiency of inhibition, low cost, minimum toxicity and effortless production. Zinc and nickel ferrite nano materials (ZnFe₂O₄, Zn_{0.6}Ni_{0.4}Fe₂O₄) have been act an efficient corrosion inhibitors of carbon steel in local Iraqi bentonite mud as a source of the corrosion (97).

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