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Preparation and Characterization of Tiopronin Gold Nanoparticles

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Abstract: *Characterization of gold nanoparticles is significant to appreciate and control nanoparticles synthesis and applications. The present work aims to study the characterization of tiopronin gold nanoparticles ,by TEM, SEM, UV-visble, and NMR.The results shows a rough doped shape of nanoparticleswhich due to tiopronin molecules attached on gold surface.The average particle size of prepared (Tio Au NPs) by chemical method was (48) nm which range between (15-75) nm. The $\lambda_{em}$was (700nm) which means that the effective crystalline size of Tio Au NPs was about (1.6nm).*

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Keywords: *Tiopronin, Gold nanoparticles, SEM, TEM, NMR, UV-visible, EDX and FTIR.*

I. Introduction

Nanotechnology can be defined as the synthesis, design, and application of materials and devices whose shape and size have been engineered at the nano scale (Donaldson *et al*., 2004).Gold nanoparticles are different from its bulk yellow solid and it is inert in nature while gold nanoparticles are wine red solution and are reported to be anti-oxidant. Inter particle interactions and assembly of gold nanoparticles networks play key role in the determination of properties of these nanoparticles (Deb *et al*., 2011). Characterization of gold nanoparticles is significant to appreciate and control nanoparticles synthesis and applications. Nanoparticles characterization is executed using a range of diverse techniques like scanning and transmission electron microscopy (SEM, TEM), Fourier transform infrared spectroscopy (FTIR) and UV– Vis spectroscopy. These techniques are helpful to resolve diverse parameters such as particle size, shape, crystallinity, fractal dimensions, pore size and surface area. Additionally, orientation, intercalation and dispersion of nanoparticles and nanotubes in nanocomposite materials could be decided by these techniques. (Arun *et al*., 2013).Tiopronin was a drug molecule for modulating cysteine precipitation and excretion in cystinuria (Fengshou *et. al*., 2015) .Tiopronin is also sometimes used as a stabilizing agent for metal nanoparticles. The thiol group binds to the nanoparticles, preventing coagulation(Jennifer *et al*., 2007).Tiopronin protected gold clusters are alkane thiolate nanoparticles in which the presence of a carboxylic and amino group of tiopronin allows to modify the charge of the nanoparticles as function of the pH of the medium (Rafael Prado-Gotor and EliaGrueso, 2011). The present work aims to study the characterization of gold nanoparticles coated with tiopronin.

II. Materials and Methods

Tiopronin monolayer-protected gold nanoparticles (Tio Au Nps) were prepared using chemical methods of Temple et al.(Templeton *et al*., 1999), A mixture of $HAuCl_4.3H_2o$ (0.8 mmole) & N-(2-mercapto propoinal) Glycine (2.4mmole) was dissolved in 35ml of methanol /acetic acid 6:1 (v/v) in around bottom flask resulting a ruby red solution. Sodium borohydrate ($NaBH_4$) (16mmole) was added quickly in 15ml of Double Distilled Water (D.D.W).The solution of the second step was added to the components of the first step gradually with constant stirring and temperature changed from 22^{o}C to 44^o C for a period of 15 min. The pH changing from 1.2 to 5.1was checked, note that the color changed from dark red to black suspension solution, the solution stirred for 30 min then it is left to cool. The solvent was removed by Vacuum using section pump. The final solution was purified by dialysis in which the pH of the crude product which dissolved in 20ml of double distilled water and adjusted to 1 by dropwise addition of concentrated hydrochloric acid . The last solution was loaded into 15 cm segments of seamless cellulose ester dialysis membrane, and placed in 4L of deionized water in a beaker with gentle stirring. The beaker was recharged with fresh water every 10 h over the

course of 72 h. The dark brown (Tio Au Nps) solution was collected from the dialysis tubes. A nuclear magnetic resonance (NMR) spectrum was used in order to see that tiopronin was not free but bound to the gold.

Transmission electron microscopy (TEM) was performed with a Philips CM 200 electron microscopy working at 200 KV; a small drop from solution of (Tio Au NPs) was deposited on a microscopy grid (copper support covered with carbon) dried and slowly in an open air.(Ali, *et al*., 2013)

Scanning Electron Microscopy (SEM)A droplet of solution (Tio AuNPs) was deposited on glass cover slid (2×2) cm^2 to dry the sample before scanning, it should be used furnace (at low temperature) to accelerate the drying process.(Anna *et al*., 2016)

UV-Visible plasma absorption measurements were carried out at room temperature on Shimadzu 1800 UV-Visible spectrophotometer using a quartz cell with 1 cm path length and Lambda 40, (Perkin Elmer,USA) in the wavelength range of 200-800 nm. The deionized water was used as the blank. (Umesh and Nayak, 2012)

Nuclear magnetic resonance (NMR) spectra for (Tio Au NPs) were obtained with a Bruker 400 MHZ spectrometer at room temperature. (Sondes *et al*., 2014)

Energy Dispersive X-Ray Analysis (EDX)

Energy Dispersive X-Ray Analysis (EDX) is generally coupled with either an SEM or a TEM. During EDX analysis, the sample is bombarded with an electron beam inside the electron microscope and the bombarding electrons collide with the sample atom, freeing them in the process. A position vacated by an ejected inner shell electron is eventually occupied by a higher energy electron from an outer shell but for this to happen; the transferring outer electron must give up some of its energy by emitting an X-ray,EDX was carried out using a Hitachi SU70 Analytical SEM. It is equipped with an Oxford Instruments 50mm^2 X-Max silicon drift EDS detector. (Anne, 2013)

Fourier Transform Infrared spectroscopy (FTIR)

A droplet of solution is deposited on glass cover to dry sample before measurement; it should be left over night in dust protected environment. (Ojea-Jimenez *et al*., 2012)

III. Results and Discussion

Transmission Electron Microscopy

Figure (1) shows the transmission electron microscopy image of gold nanoparticles capped with troponin (Tio Au NPs). In comparison to TEM image of gold nanoparticles (Au NPs) in previous study of (Rasha, 2014) .The results indicated that gold nanoparticles have a clear and smooth circular shape as shown in figure (B) while figure (A) shows a rough doped shape that means, the black points on (Au NPs) is due to tiopronin molecules attached on gold surface, also it was found that the gold nanoparticles in (A) was attache each other by like a viscous surface it was tiopronin effect.

The average particle size of prepared (Tio Au NPs) by chemical method was (48) nmwhich range between (15-75) nm, while the average particle size of prepared gold nanoparticles (Au NPs) using laser ablation was (25) nm.

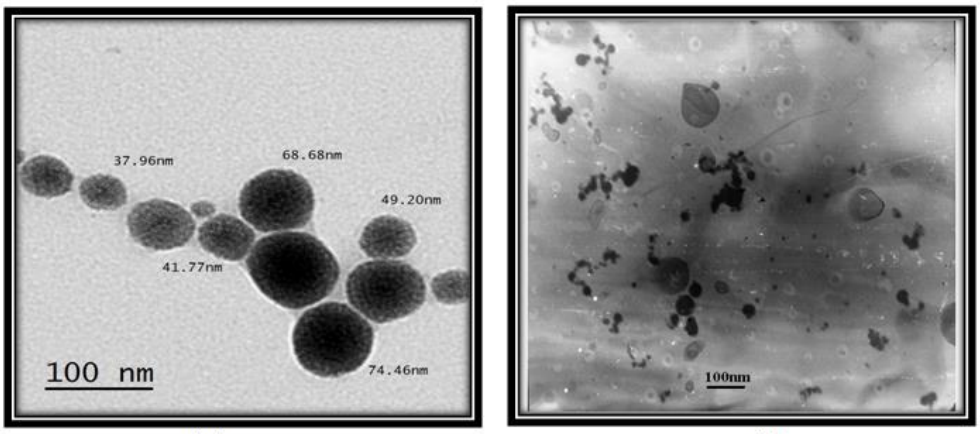


Figure (1): TEM Image of the (A) Tiopronin Gold Nanoparticles (TioAu NPs), (B) Gold Nanoparticles.

Scanning Electron Microscopy

Figure (2) shows scanning electron microscope image of tiopronin gold nanoparticles (Tio Au NPs), the particle size of nanoparticles was ranged (15-70) nm, and gold nanoparticles have clear and smooth circular surfaces.

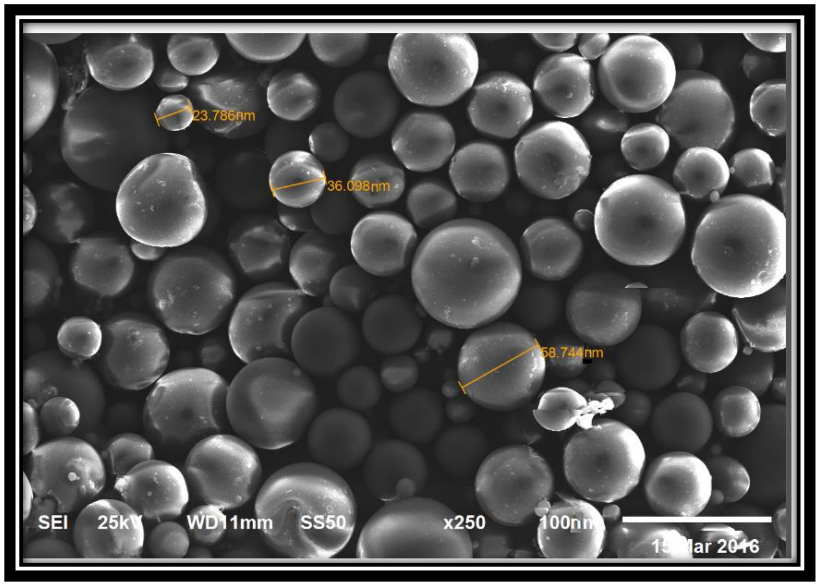


Figure (2): Scanning Electron Microscope Image oftiopronin gold nanoparticles (Tio Au NPs).

UV- Visible Spectra

Employment of UV-Visible Spectra in the investigation of the surface Plasmon resonance of binding process of gold nanoparticles with tiopronin, tiopronin capped nanoparticles solution has tanned color which results of light scattering by the clusters, which inhibit surface Plasmon resonance (SPR) absorption (500-600)nm. From the UV-Visible spectra obtained in figure (3), the absence of (SPR) peak is consistent with the solution color (Hostetler *et al*., 1998).while this result was disagreement with that of (Prado-Grater *et al*, 2014) which showed a slight detectable surface Plasmon band.

The gold monolayer protected nanocluster investigated in this work gave UV-visible spectra agree with that for Au_{144} (thiol) $_{60}$ which reported in the reference (Farrag *et al*., 2013). Figure (4) shows the UV-visible spectra published in the reference (Farrag *et al*., 2013) it gives the relationship between the sizes selected gold cluster protected by thiol ligand and the shape of the absorbance curve, it is clear that the peak will decreases as the cluster size increases. (Farrag *et al*., 2013)

UV-visible technique is sensitive to change of metal core clusters. So the stability of the prepared clusters was examined by UV-visible spectroscopy, the determined spectra shows no change which means that gold clusters are stable in air for a many months in refrigerated environment.(Farrag *et al*, 2013)

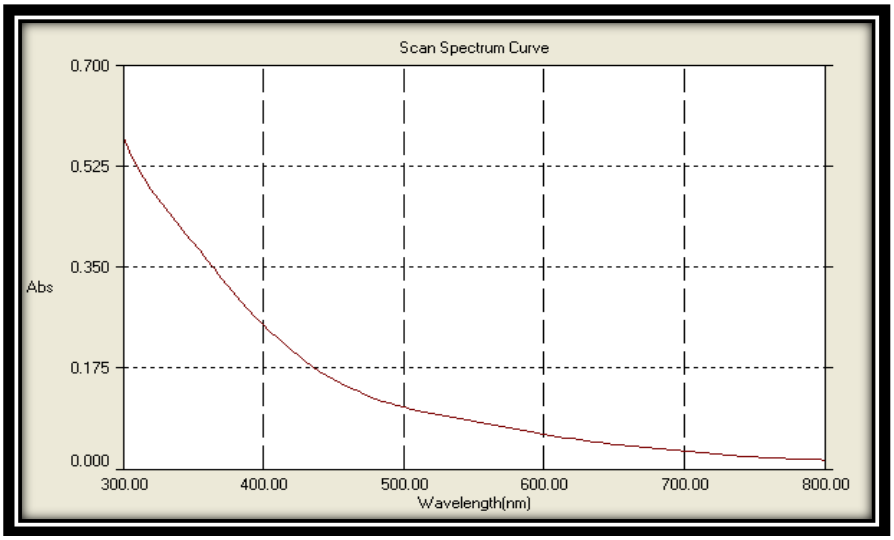


Figure (3) UV-visible spectra for (Tio Au NPs).

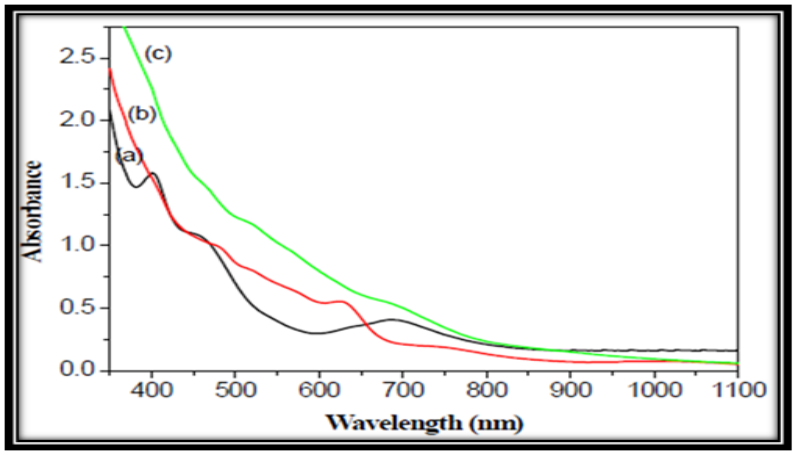


Figure (4)UV- visible spectra for some size selected gold clusters.

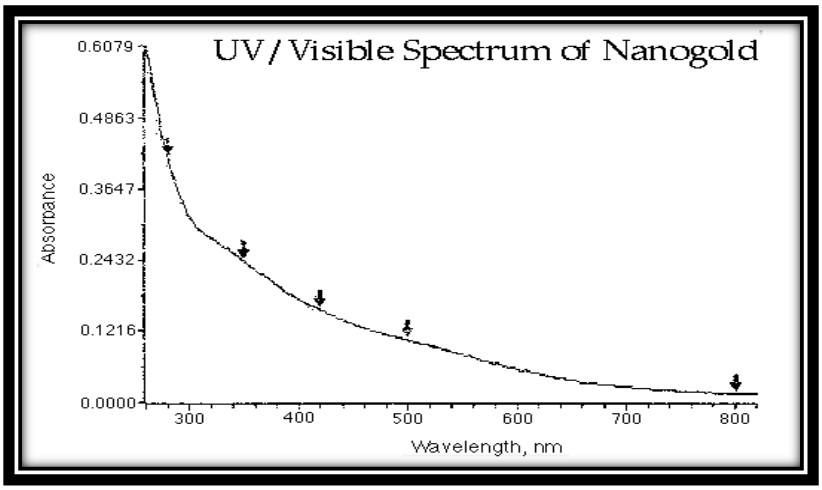
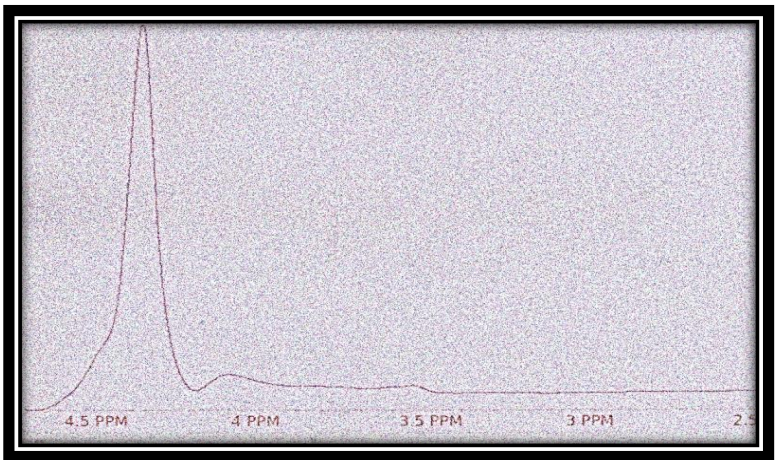


Figure (5) UV-visible spectra for (Au NPs).

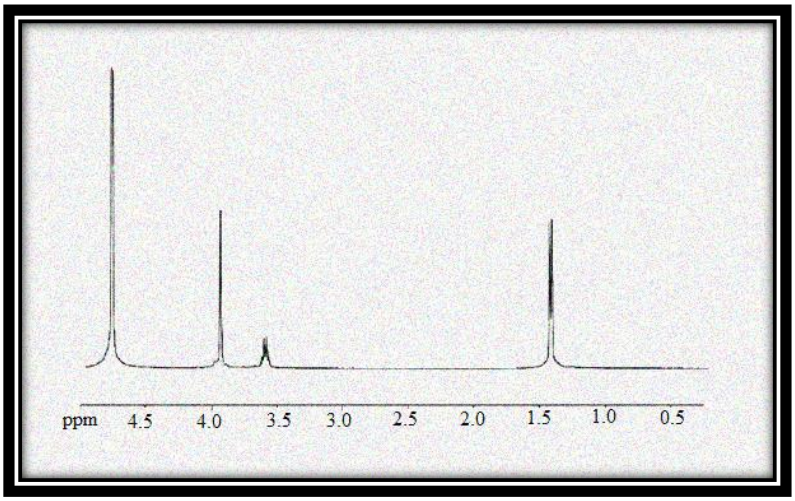
Nuclear Magnetic Resonance

The successful attachment of tiopronin ligands to the surface of the gold nanoparticles was clearly demonstrated by the nuclear magnetic resonance spectra (Figure6). There are brood peak appears in the spectra of gold nanoparticles capped with tiopronin (fig 6 A), these broad peaks appearing at chemical shifts similar to that of free tiopronin which are sharp peaks. (Fig 6 B)

Disappearance of the S-H peak at chemical shift 1.5 was observed in comparison between (Fig. A&B) that is due to the binding of nanoparticles, with thiol group of tiopronin. (Leff, *et al.*; 1996)



(A)



(B)

Figure (6) Nuclear magnetic resonance (NMR) for (A) gold nanoparticles binding with tiopronin and (B) tiopronin

Energy Dispersive X-Ray Analysis (EDX)

Figure (7) and tables (1) show elemental composition studies by Electron Dispersive X-ray analysis. In figure (7) Au-Tiopronin main elements were Wt% of Au equal to 59.30%, carbon equal to 15.41% and both nitrogen and oxygen had the same Wt% equal to10 %. (Anne, 2013)

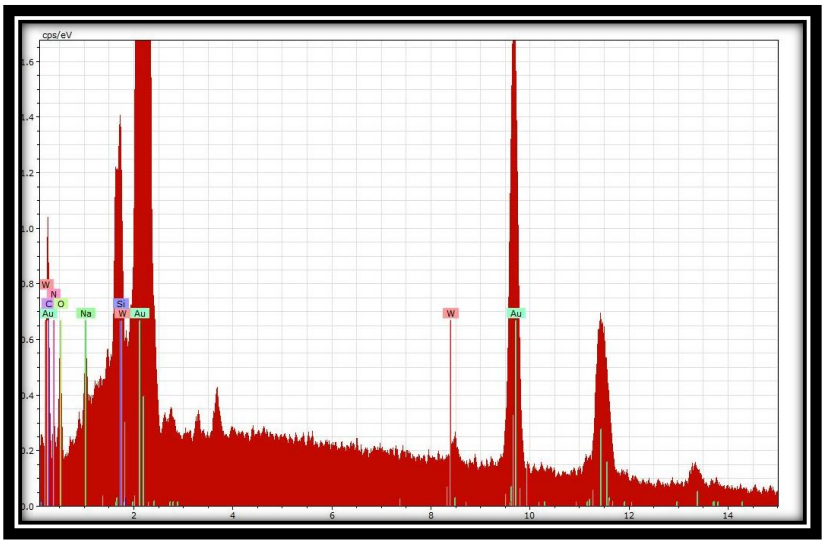


Figure (7) Energy Dispersive X-Ray Analysis (EDX) for Au-Tiopronin

Tables (1) Energy Dispersive X-Ray Analysis (EDX) for Au-Tiopronin

Spectrum: Acquisition 1236

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Au	79	L-series	40.77	59.30	9.69	1.06
C	6	K-series	10.60	15.41	41.30	2.09
N	7	K-series	7.24	10.53	24.20	1.78
O	8	K-series	7.16	10.41	20.95	1.51
W	74	L-series	1.08	1.57	0.27	0.07
Na	11	K-series	1.06	1.54	2.16	0.12
Si	14	K-series	0.85	1.24	1.42	0.07
		Total:	68.75	100.00	100.00	

Fourier Transform Infrared spectroscopy (FTIR)

In this workfourier transform infrared spectroscopy of gold cluster capped by tiopronin ligand, have been studies. Fig (8) shows the infrared spectra of the tiopronin and Au- Tiopronin clusters. As usual the S-H stretching vibration band (2535-2564 cm^{-1}) is visible only in the spectrum of the ligand Fig (8) and disappears after binding with Au cluster Fig (9).(Ruddon, 1990)

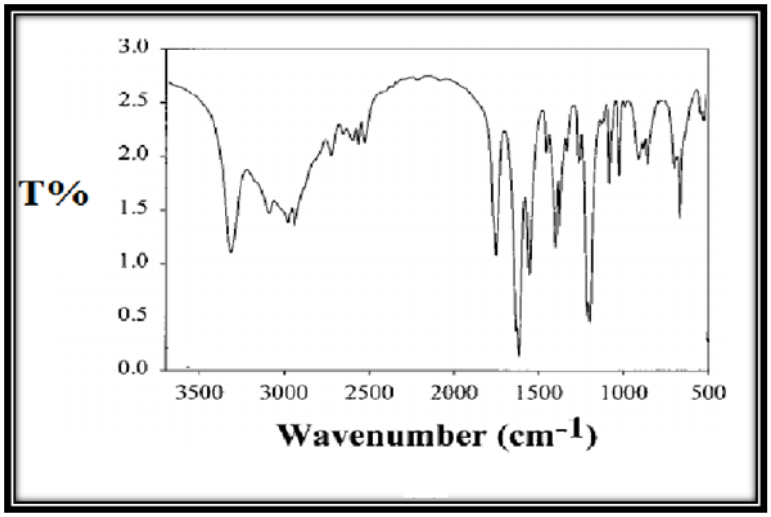


Figure (8) Fourier Transform Infrared spectroscopy (FTIR) for Tiopronin

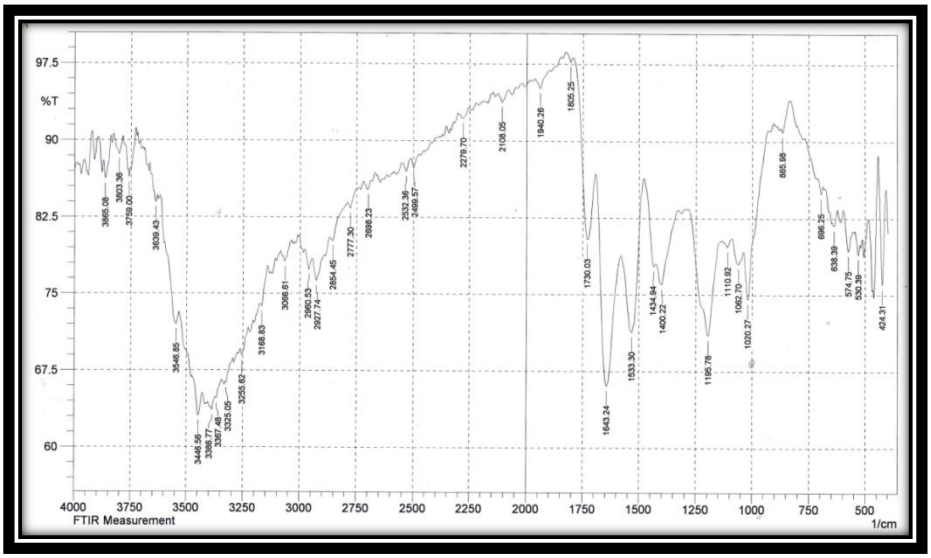


Figure (9) Fourier Transform Infrared spectroscopy (FTIR) for Au- tiopronin.

IV. Conclusions

The interaction of gold nanoparticles capped with tiopronin was investigated by using different techniques: TEM, SEM, UV-visible and NMR

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