

**Synthesis and Characterization of Novel Nano Dithiocarbamate
Complexes Derived From GO-benzimidazole**

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*Department of Chemistry, Collage of Education for women, University of Tikrit.

**Department of Chemistry, College of science, University of Tikrit.

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Abstract

The first attempt to produce nano dithiocarbamate complexes has been done by the use of graphene oxide nano particles as a base material. The ligand of the type GO-benzimidazole dithiocarbamate coordinate with metal ions {Pd(II), Co(II), Ni(II)} through two sulfur atoms (bidentate) to form nano square planer complexes of the formula $[M(L)_2]_x$. These materials have been characterized by infra red spectra (IR), X-ray diffraction (XRD) and Atomic force microscopy (AFM).

Key words: - Dithiocarbamate, Graphene oxide, Nanoparticles, X-Ray diffraction, Atomic Force Microscopy.

**تحضير وتشخيص معقدات نانوية جديدة لثنائي ثايوكارباميت مشتقة من أوكسيد الجرافين –
بنزايמידازول**

مصطفى عبد الغفور الهيتي، أ.م.د مظهر يونس محمد* و أ.م.د أحمد خلف جبر**

*قسم الكيمياء، كلية التربية للبنات، جامعة تكريت.

**قسم الكيمياء، كلية العلوم، جامعة تكريت.

المخلص

المبادرة الأولى لتحضير معقدات نانوية جديدة لثنائي ثايوكارباميت قد تمت باستخدام دقائق أوكسيد الجرافين النانوية كمادة أساس. إن الليكاند $L =$ أوكسيد الجرافين – بنزايמידازول ثنائي ثايوكارباميت يتناسق مع ذرات الفلزات الأتية $\{Co(II), Ni(II) \text{ and } Pd(II)\}$ من خلال ذرتي الكبريت (ثنائي السن) ليكون معقدات نانوية ذات ترتيب مربع مستوي والتي تمتلك الصيغة $[M(L)_2]_x$. كما وقد تم تشخيص هذه المركبات المحضرة باستخدام طيف الأشعة تحت الحمراء ، حيود الأشعة السينية والتصوير المجهر باستخدام مجهر القوى الذرية.

الكلمات المفتاحية: - ثنائي ثايوكارباميت، أوكسيد الجرافين، دقائق النانوية، حيود الأشعة السينية، مجهر القوى الذرية.

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Introduction

Nanotechnology has recently a lot of attention, particularly in the research and industrial communities. It offers many unprecedented opportunities for advancing our ability to impact not only our day to day lives, but the environment in which we live. The ability to design, synthesize and manipulate specific nano structured materials lies at heart of the future promise of nanotechnology.^(1,2) Dithiocarbamate (dtc) formation reactions have many points which encourages us to choose it:-

- i- Is best done at lower temperature.
- ii- It gives a High percentage of the product.
- iii- Usually proceed cleanly (without side product).
- iv- High basicity of dithiocarbamate ligands toward metal ion⁽³⁾.
- v- They are able to stabilize transition metals in a variety of oxidation states^(3,4).

In nature, the transition metal sulphur coordination compounds are known and found. Such compounds are structurally and electronically interesting ⁽⁵⁾ and the chemistry of sulphur containing compounds become very important in the industries, technology and biology.^(6,7)

Carbon nanostructures have been extensively studied due to their excellent properties and numerous applications ⁽⁸⁻¹⁰⁾.

Graphene oxide is similar to structure of graphite layer, but the plane of carbon atoms in graphene oxide is heavily decorated by oxygen-containing groups ⁽¹¹⁾, addition; GO exhibits an increased inter layer spacing (d) (from 0.34 nm in graphite to ~0.6 (in dried hummer's GO)-1.3 (in liquid water) nm in GO)^(12,13)

GO have many exogenous functional groups such as epoxy (bridging oxygen atoms), hydroxy in the basal plane , carboxyl and carbonyl moieties lining the nanosheet edge ⁽¹⁴⁾.

Experimental

Chemicals:

Reagent grade Carbon disulphide was obtained from Sharlau, ortho-Phenylenediamine and potassium permanganate were obtained from BDH, Graphite from Merck, while Nickel

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chloride dihydrate , Cobalt chloride hexahydrate, Sodium hydroxide, and Sodium nitrate were obtained from HI-MEDIA , Palladium chloride from Sigma- Aldrich, Sulphuric acid was available from Riedel-de Haen.

Instrumentation:

All infrared spectra of nanomaterials were recorded in WQF-510 spectrophotometer at a range between ($400-4000\text{ cm}^{-1}$) KBr discs, X-ray diffraction measurements were recorded for nano materials by using (Shemadzu – XR – 6000) device with Nickel - Copper filter for the x-ray radiation ($\text{Cu K}\alpha$, $\lambda = 1.5406\text{ \AA}$) , Atomic Force Microscope (AFM images) were recorded by using atomic force microscope type PHYW.

Syntheses of nano materials:

Graphene oxide:

Graphene oxide was prepared according to Hummers' method⁽¹⁵⁾, 1 g of graphite was added to cool 50 ml concentrated H_2SO_4 and stirred in an ice bath for 15 minutes. 4 g of sodium nitrate and 6 g of potassium permanganate were added to above solution and stirred in an ice bath for 6 hours . The ice-bath removed and the temperature of the mixture was kept at 35°C in water path for 30 minutes. After that, the mixture became pasty (deep red- brown in color). 50 ml of deionized water was then added to above mixture. The temperature then raised to $90-98^\circ\text{C}$. The above mixture was diluted by addition 250 ml warm deionized water. Following this, 30% H_2O_2 (~ 30 ml) was added till the solution turned bright yellow. The graphite oxide powder was dried at 40°C for 24 h. All those steps found in the diagram 1

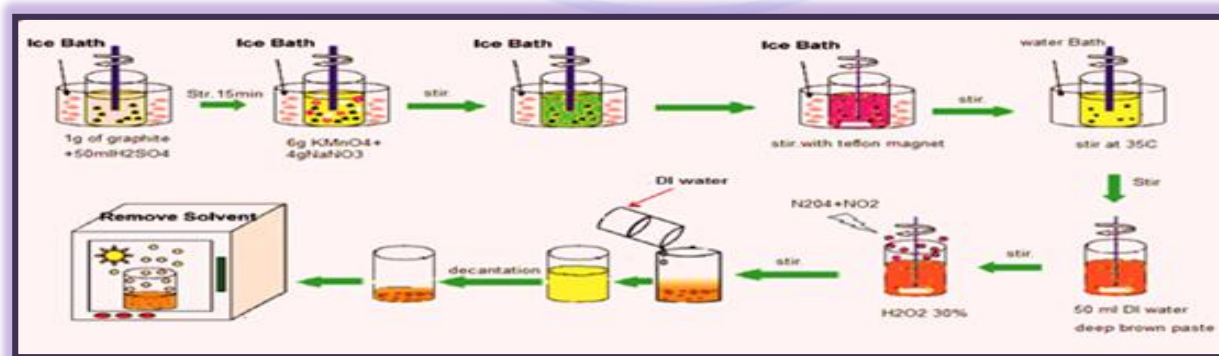


Diagram (1): preparation's steps of GO

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Preparation of GO -benzimidazole

Typically, 1 g GO was dispersed in 300ml DI water, 6 g o-phenylenediamine (o-PD) was dispersed in (100 ml) ethanol by ultrasonication, Then, o-PD solution was added into the GO solution. Small amount of poly phosphoric acid was added to this mixture, and the mixture was ultrasonicated for 1hour. The solution was then sealed in a 500 ml Pyrex beaker and stirred for 7 days at room temperature and 5 hours at 180 °C. The mixture was then naturally cooled to room temperature, filtered, washed for several times by distilled water and dried at 60°C for 12 hours. ^(16,17)

Preparation of GO-Benzimidazole dithiocarbamate:-

The dithiocarbamate derived from GO-oPD) material was produced by mixing of excess amount of (0.2 mol,10 ml) CS₂ with dispersed 0.4g of (GO-benzimidazole), in 100 ml DMSO by ultrasonicator in a 200ml Pyrex beaker. The mixture was maintained at 0 –7 °C using a water-ice bath and maintained to continuous stirring for 2 hours. An aqueous solution of (0.2 mol, 8 g) sodium hydroxide were added to the reaction mixture. The final reaction mixture was stirred for further 8 hours at 0 -10 °C and 7 days at room temperature. Solid obtained was then filtered, washed by ethanol and dried in oven at 60 °C for 24 hours.

Preparation of Co(II), Ni (II), and Pd (II) complexes with GO-Benzimidazole dithiocarbamate:-

The complexes were prepared by using (1:5) ligands –to- metal weight ratio. (10 mg ligand/1ml DI water) was dispersed by ultrasonicator in a Pyrex beaker, aqueous solution (50 mg/1ml) of (MCl₂.nH₂O), was added dropwise and slowly under vigorous stirring. The reaction mixture was stirred for 2 days at room temperature, after that the mixture was refluxed for 4 hours in water path. The resulting colored precipitate was filtered, washed several times by: ethanol and water and dried at 60°C for 24 hours.

Results and Discussion

The Dithiocarbamate ligand and its Co(II), Ni(II), and Pd(II) complexes have been synthesized and characterized by IR spectra, X-ray diffraction. They are found to be air

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stable; in addition to good yield percentage (Table1). The ligand is soluble in water and all complexes are dispersed in DMSO.

IR Spectra:

Graphene oxide:

For the Graphene Oxide (GO), the characteristic peaks are observed at 1178 cm^{-1} C-O attributed to epoxy groups, 1570 cm^{-1} is attributed to skeletal vibrations of unoxidized graphitic domains,, 1385 cm^{-1} C-OH bending, 1718 cm^{-1} assigned to C=O (stretching vibration); and 3428 cm^{-1} peak can be attributed to the O-H stretching vibrations of the C-OH groups, these peaks indicate that graphite converts to graphene oxide^{(11,12) (18,19)} Figure 1

GO-benzimidazol:

In the spectrum of GO-benzimidazol, the peaks at 1707 and 1220 cm^{-1} disappear, moreover, the new peaks at $1574,1544\text{ cm}^{-1}$ are attributed to the skeletal stretching vibration mode of quinoid and benzoid rings in phenazine. The peaks at $1630,1257\text{ cm}^{-1}$ can be attributed to the stretching of C-N and C-N, respectively the other one at 767 cm^{-1} in the fingerprint spectrum region also can be assigned to the characteristic peaks of phenazine. These results suggest that GO has been successfully functionalized through formation of benzimidazole by using o-phenylenediamine as the functionalizing reagents, respectively. ^(16,17) Figure 2

GO-benzimidazol dithiocarbamate:

The infrared absorption spectra for the prepared ligand founds at $(1078,933)\text{ cm}^{-1}$ for GO-benzimidazol dithiocarbamate, which are attributed to stretching vibration of C-S group, (Table 1) . The second important band is 1489 , which assigned to stretching vibration of C-N group of GO-benzimidazol dthc. Figure 3.

Infrared spectra of nano complexes:

The coordination mode of the ligand to the metal ions have been investigated by comparing the infrared spectra of the free ligand with its metal complexes (Table 1).

The bands of $\nu(\text{C-N})$ was appeared at 1489 cm^{-1} in free ligand and shifted towards high values at rang $(1510-1516)\text{ cm}^{-1}$ in the spectrum of the complexes. ^(20,21).

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The band of ν (C..S) of dithiocarbamate ligand appeared at 1078 cm^{-1} and , Shifted towards lower values at range $(1033-1055)\text{cm}^{-1}$ in the complexes spectra as shown in (Table 1). This results indicating the coordination of two sulfur atoms of these dithiocarbamate with metal ion^{(22),(23)}. The silver nitrate was used and gives negative results In nano complexes that's mean no chloride ion was coordinate to metal ion.

X-Ray Diffraction

X-Ray Diffraction of Graphene oxide :

X-ray diffraction pattern of GO powder shows a large interlayer spacing than that found in graphite (GO, major peak at $2\theta = 10.8^\circ$ corresponding to an interlayer spacing of 8.12 \AA).

The XRD pattern of the graphene oxide powder shows other two peaks at ($2\theta = 22.5^\circ$) attributed to the intermediate and peak at ($2\theta = 42.7$) which is in agreement with the values reported in literature ⁽²⁴⁾ Figure 4-a

X-Ray Diffraction of GO-benzimidazol:

GO-benzimidazole show a slightly high angle of reflection at 12.4° with a reduced interlayer distance of 7.16 \AA for GO-benzimidazole. This decreased of interlayer distance can be explained by the formation of benzoxazole and benzimidazole rings on the edges of GO after covalent functionalization, because the introduced aromatic molecules will weaken the electrostatic repulsion between the GO sheets and thus induce a smaller interlayer distance. Additionally, peaks at $20-25^\circ$, corresponding to the chemically converted graphene are observed in GO-benzimidazole, indicating the partial reduction and re-stacking of GO occurring during the functionalization process.⁽¹⁷⁾ Figure 4

X-ray measurements of the GO-benzimidazol dtc:

In the case of nano ligand; the ligand (GO-benzimidazol dtc) shows peak at 9.25° with increase of inter layer spacing that equal 8.98 \AA . This increased of interlayer distance can be explained by the formation of dithiocarbamate on the edges of benzimidazole- graphene oxide. Figure 4

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X-ray measurements of some prepared complexes:

The differences between of XRD pattern of nano palladium complexes and ligands indicated to the formation of complexes. From X-ray measurements pattern it seems that the smallest peaks of complexes demonstrate that an partial complex formation occurred. Figure 4

Atomic force microscopy (AFM) measurements:

AFM image demonstrate 2D and 3D AFM images of (GO-benzimidazol dtc) with scanning area of $2.229 \mu\text{m} \times 2.229 \mu\text{m}$, average grain size 67.17 nm and height 1.4 nm. AFM image of the complexes nanoparticle with scanning area of $2 \mu\text{m} \times 2 \mu\text{m}$. The average grain size of complexes (89 -117 nm) in diameter and its height around (0.85-3.34) nm. It can be noticed from AFM images that complexe and ligand particles have different morphologies between ligand and complexe nanoparticles. From AFM image, the complexes are agglomerated from many complexe nanoparticles, the nanoparticles combine and pack together to form sub-microparticles⁽²⁵⁾. (Table 2) shows height and average grain size of the prepared GO-benzimidazole dithiocarbamate and its complexes. Figures (5 – 8)

Table (1): C_u-N, and C_u-S stretching vibration (cm⁻¹) and some physical properties of the Prepared nano ligand and Complexes

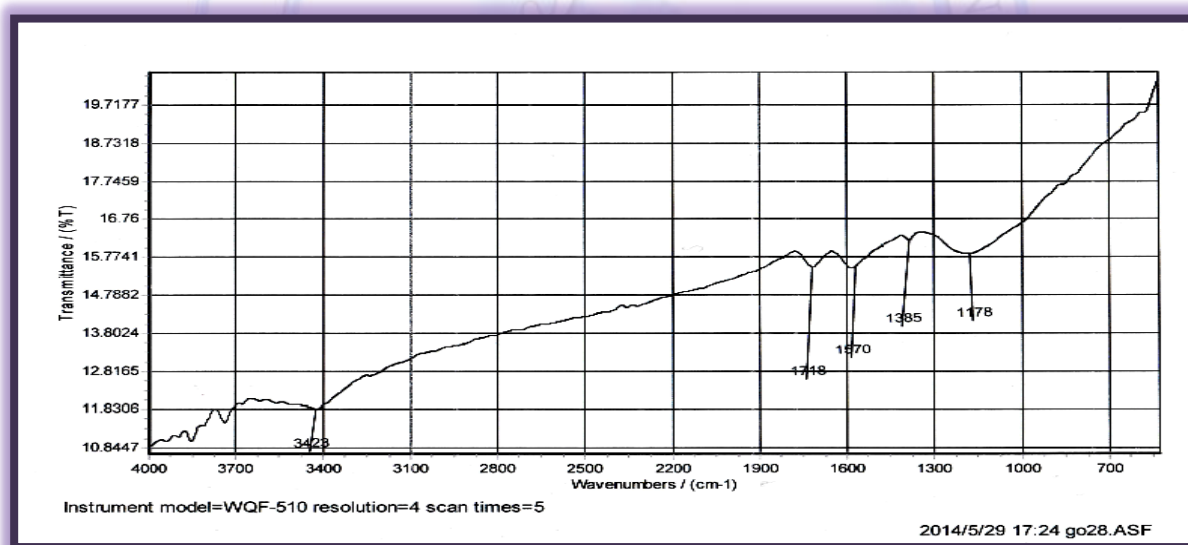
Complex	ν (C _u -N)	ν (C _u -S)	Yield %	Color
GO-benzimidazole dtc	1489 (w)	1078 (w)	67	grey
		933(s)		
[Ni(GO-benzimidazole dtc) ₂] _x	1512 (w)	1038 (w)	67	Deep brown
[Co(GO-benzimidazole dtc) ₂] _x	1510 (w)	1055 (w)	80	Black
[Pd(GO-benzimidazole dtc) ₂] _x	1516 (m)	1033 (w)	82	brown

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**Table (2): Height and average grain size of the prepared GO-benzimidazole
dithiocarbamate and its complexes**

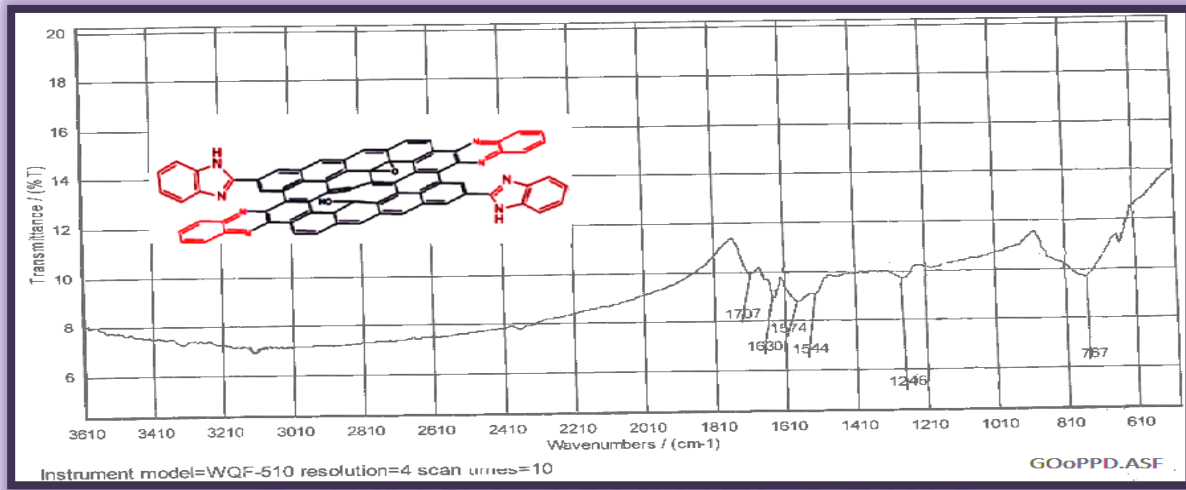
Comp. no	compound	Height(nm)	Average grain size(nm)
1	(GO-benzimidazole dtc)	1.40	67.17
2	[Ni(GO-benzimidazole dtc) ₂] _x	2.30	89.85
3	[Co(GO-benzimidazole dtc) ₂] _x	1.61	99.03
4	[Pd(GO-benzimidazole dtc) ₂] _x	2.91	94.37



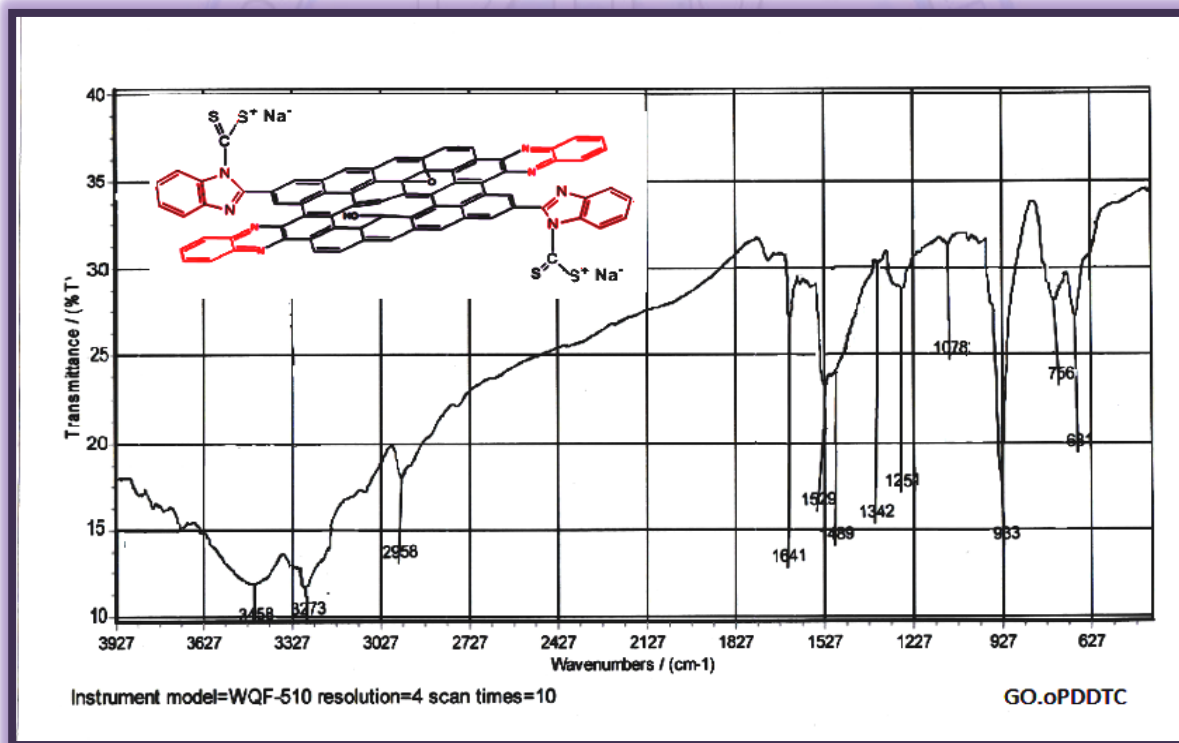
Figure(1): infrared spectra of Graphene oxide

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Figure(2): infrared spectra of Go-benzimidazole



Figure(3):Infrared spectra of GO-benzimidazole dtc.

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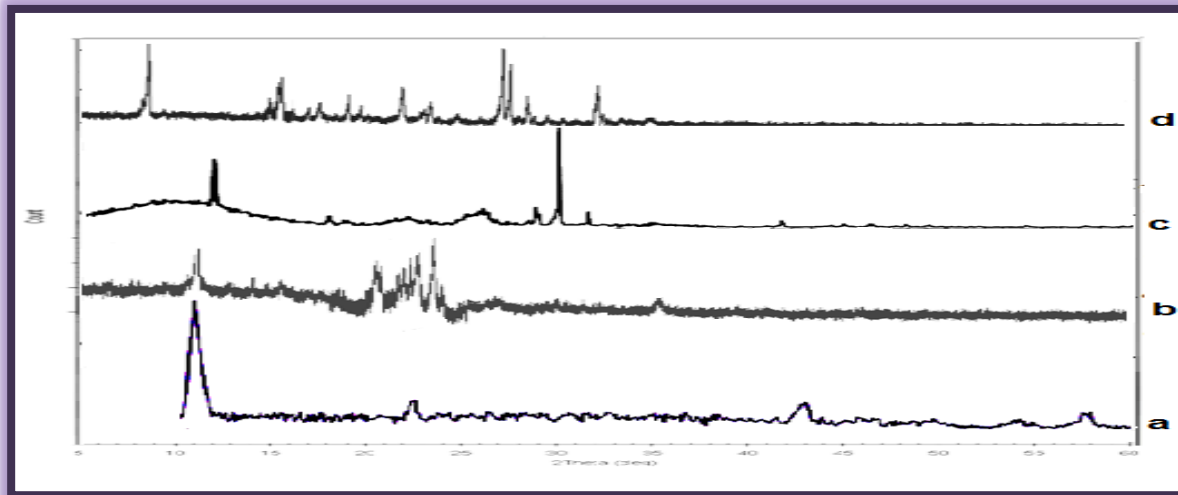


Figure (4): XRD pattern of a: Graphene oxide, b: GO-benzimidazole, c: GO-benzimidazole dithiocarbamate , and d: $[Pd(GO-benzimidazole\ dtc)_2]_x$

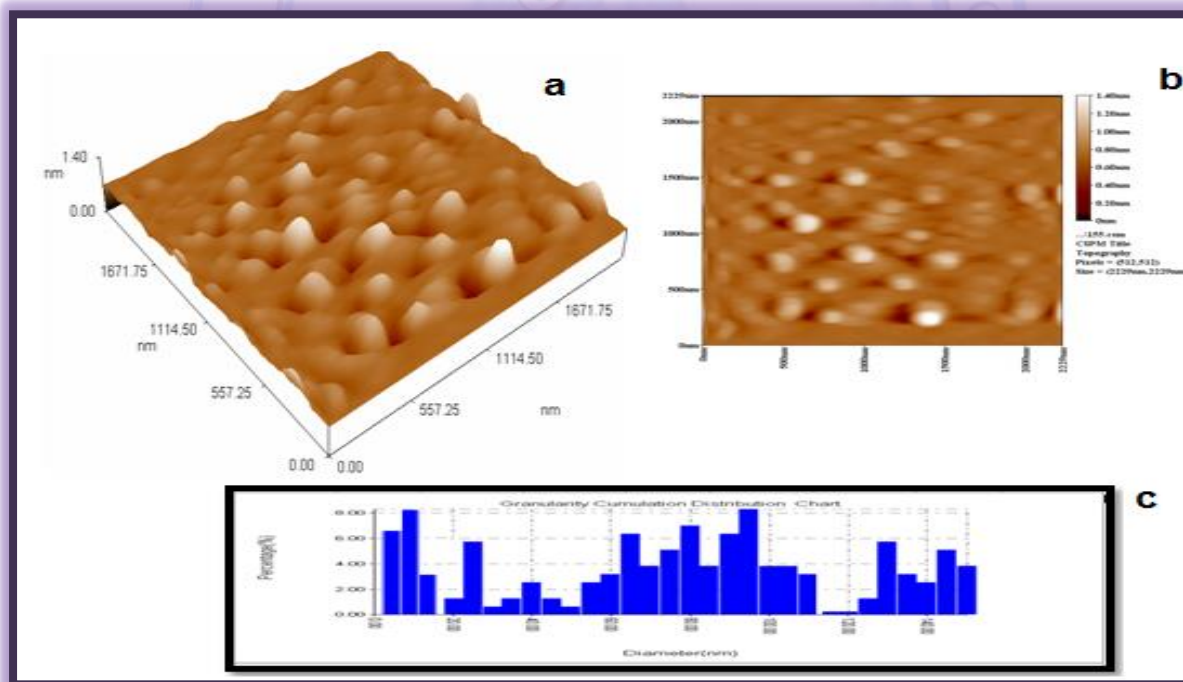
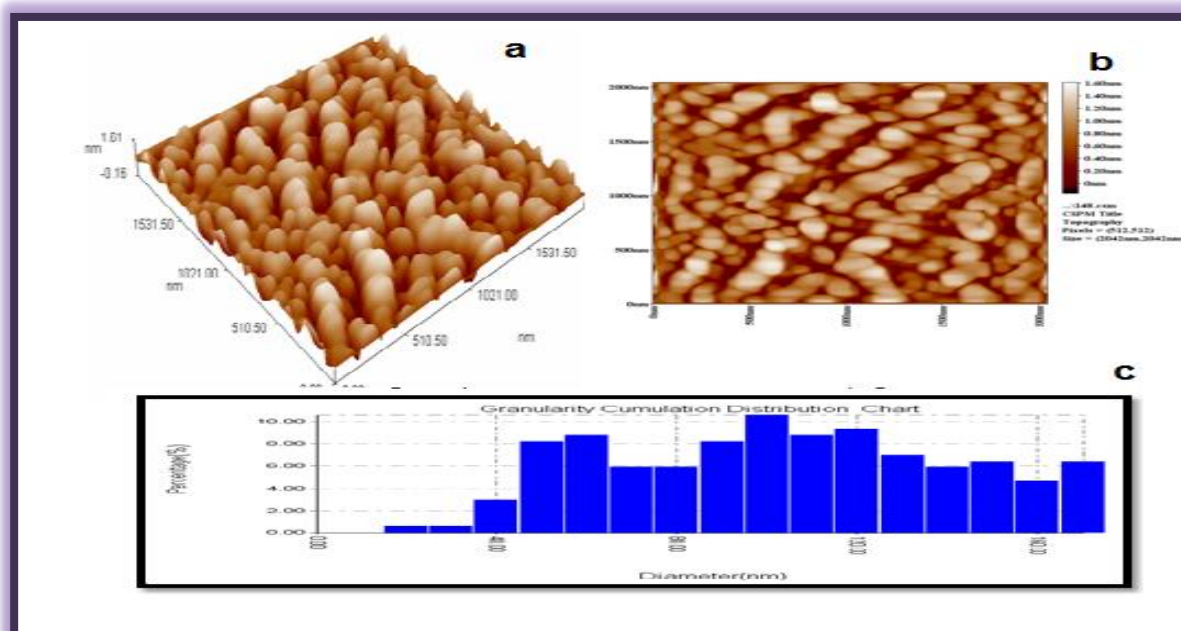


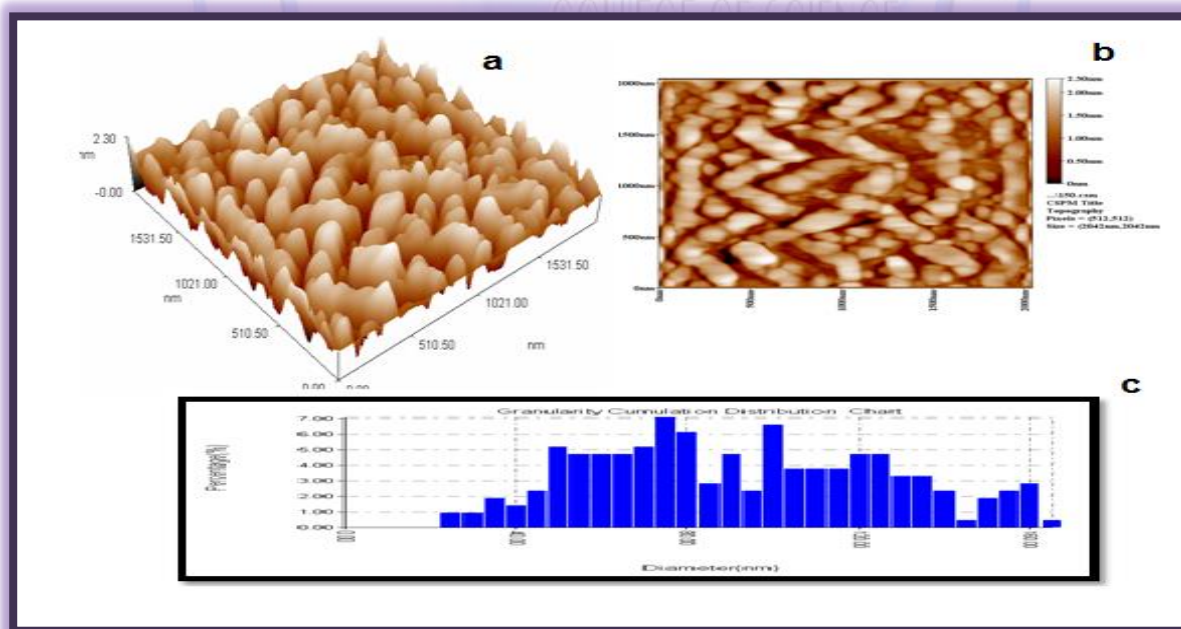
Figure (5): XRD pattern of a: Graphene oxide, b: GO-benzimidazole, c: GO-benzimidazole dithiocarbamate , and d: $[Pd(GO-benzimidazol\ dtc)_2]_x$

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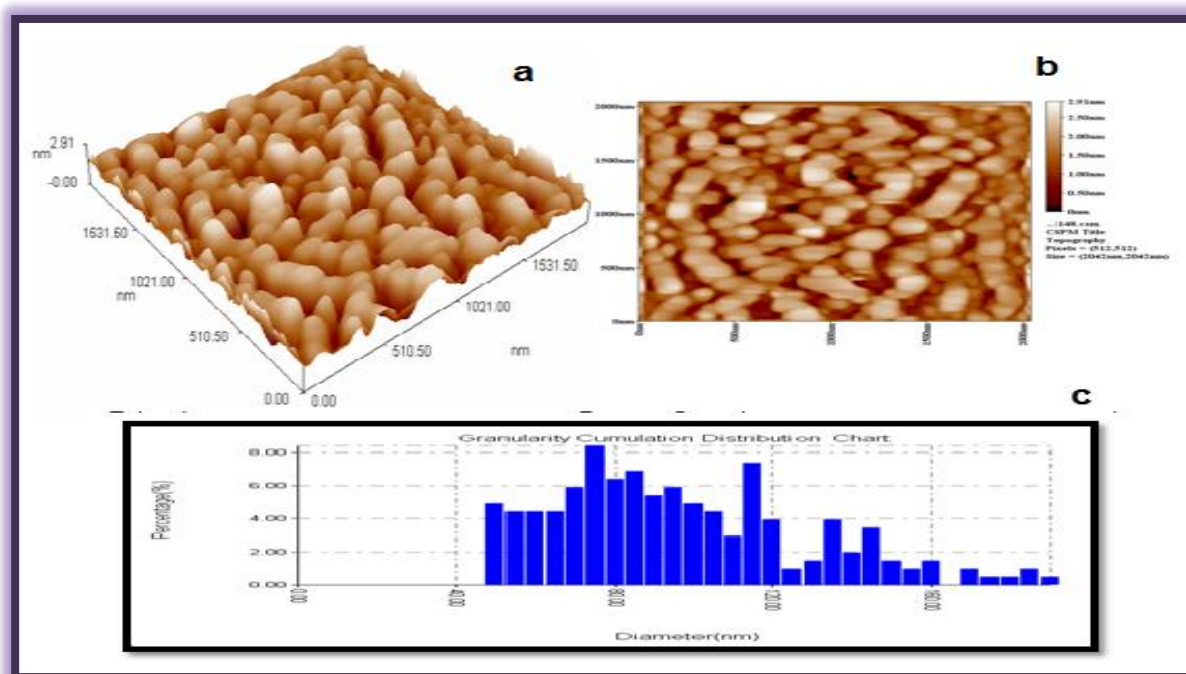
Figure(6): a: 3D , b: 2D AFM image ,and c: Granularity distribution chart of $[Ni (GO-benzimidazol dtc)_2]_x$



Figure(7): a: 3D , b: 2D AFM image ,and c: Granularity distribution chart of $[Co(GO-benzimidazole dtc)_2]_x$

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Figure(8): a: 3D , b: 2D AFM image ,and c: Granularity distribution chart of $[Pd(GO-benzimidazole dtc)_2]_x$

Conclusion

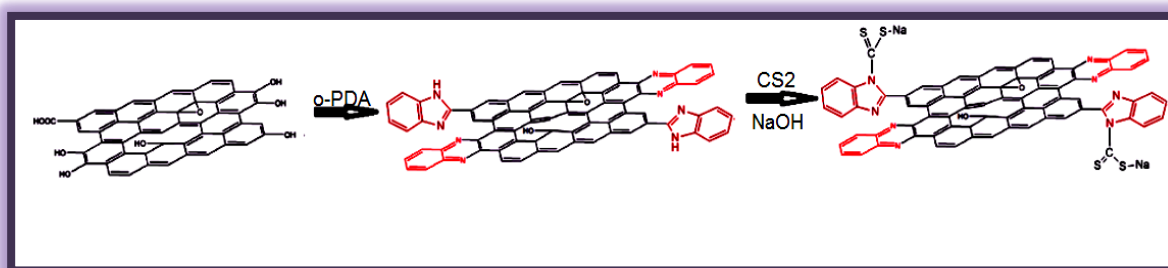
1- GO is activated by poly phosphoric acid (PPA) through the formation of GO-phosphoric anhydride. After that, the amino groups of ortho-phenylenediamine(o-PD) are protonated and some hydroxyl groups are converted to phosphate ester, The free hydroxyl portion reacts with the GO-phosphoric anhydride to generate an ester. It then undergoes quick acyl migration, along with ring closure to form benzimidazole on GO with the aid of acid.

Figure 9 shows a preparation pathway of GO-benzimidazole dithiocarbamate.

2- GO-Benzimidazole exhibit a high solubility in most organic solvents, such as (DMF) and DMSO but the GO-Benzimidazole dithiocarbamate has a high solubility in water.

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Figure(9): pathway of GO-benzimidazole dithiocarbamate preparation.

3- GO-benzimidazole dithiocarbamate coordinate with metal ions {Pd(II), Co(II), Ni(II)} through two sulfur atoms as bidentate to form compounds of the formula $[M(L)_2]_x$. As shown in figure 10

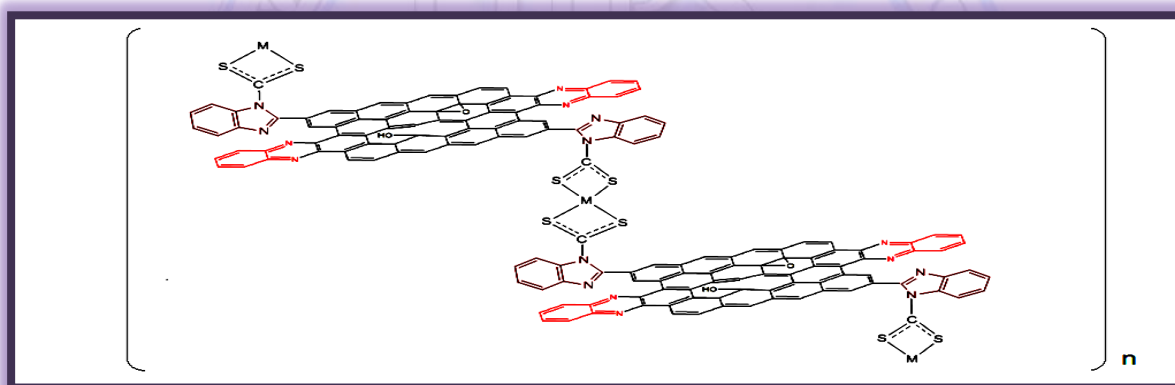


Figure (10): $[M(\text{GO-benzimidazole dtc})_2]_x$

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