Digest Journal of Nanomaterials and Biostructures Vol. 15, No. 4, October-December 2020, p.1009-1015

PREPARATION, CHARACTERIZATION, ANTIOXIDANT ACTIVITY OF FUNCTIONALIZED 2-(FERROCENYLMETHYLAMINO) BENZONITRILE BY ZnO NANOPARTICLE USING 3 AMINOPROPYLTRIETHOXYSILANE(APTES)

S. TRIA[a,b,*], R. AHMEDI[b]
[a]*University of KasdiMerbah Ouargla,Faculty of Mathematics and Material Science, Laboratory of Valuation and Promotion for Saharan Resources(VPRS) , Ghardaia route ,BP511,30000,Ouargla, Algeria.*
[b]*University of El Oued ,(VTRS) Laboratory, B.P.789, 39000, El Oued, Algeria*

The aim of the present study was study the interaction between 2,2-diphenyl-1-picrylhydrazyl radical (DPPH•) and ZNO@APTES@2-(ferrocenylmethylamino)benzonitrile and Galic acide Then determination of binding parameters like binding constant and binding free energy The determination of binding constant and binding free energy is based upon the decrease in absorbance of the electronic absorption spectrum .The ZNs was synthesise according to chemical method. The characterizations of ZnO NPs were measured by FTIR and X-ray diffraction.

(Received March 28, 2020; Accepted October 8, 2020)

Keywords: ZnO@APTES@2-(ferrocenylmethylamino)benzonitrile, DPPH, Binding parameters, Binding free energy, Binding constant

1. Introduction

Nanoparticles are a piece of nanomatrials that are known as a single particles 1–100 nm in diameter from another years nanoparticles have been a common material for the development of new cutting-edge applications in communications, energy[1]

On the other hand Zinc oxide nanoparticles have attracted more care due to their multilateral and promising applications in biological sciences like an antibacterial, antifungal,and antifouling agent [2] As indicated in more reports ZnO is regarded as superior functional material due to the numerous actives sites on its cover wich can be efficiently secure with other materials.[3]

2. Material and method

2.1. Chemicals

The synthesis of ZnO was performed by using zinc acetate $Zn(CH_3COO)_2(H_2O)_2$ and ammonia,Ethanol (Sigma-Aldrich)**,** 3-aminopropyl triethoxysilane (APTES) were obtained from (Sigma-Aldrich**),** 2-(ferrocenylmethylamino)benzonitrile [4]

Acetonitrile (ACN) (HPLC-grade from Sigma-Aldrich) was used as solvent without further purification, 1,1-diphenyl-2-picrylhydrazyl radical (DPPH) (99%), gallic acid (99 %) (GA).

2.2. Preparation ZnO@APTES

ZnO NPS was prepared according to chemical method [5]. Aqueous ammonia (0.2M) was slowly dripped at a rate of 30 mL/ h in a solution of 100 mL of zinc acetate(0.1 M) to pH of 10. This mixture was kept at 60 C for 12 h and then centrifuged for20 min at a speed of 3800 rpm/min.

* Corresponding author: triasafa7@gmail.com

Finally, the solid was rinsed several times with ultrapure water and ethanol by centrifugation and then dried in an oven for 1 h..The prepared ZnO (10 mg) was dissolved in 10 mL ethanol and ultrasonicated for 1h.APTS (10 mL) was added to the solution and sonicated for 1 h to complete the reaction. The amino-functionalized ZnO was separated from the solution via centrifugation, washed with absolute ethanol.

2.3. Unification of ZnO@APTESwith2(ferrocenylmethylamino)benzonitril:

In flask has been put 9mg of 2-(ferrocenylmethylamino)benzonitril with 5 mg of zno@APTES dissolved in 10 ml absolute ethanol under 50c° for 24 h with shake .

2.4. Characteristic measurement

The ultrasonic system used in this study were a VCX 505 sonics. X-ray diffraction(XRD; PROTO) This device works under a wavelength $\lambda_{CuK\alpha1}$ = 1.54 Å was performed at 40Kv voltage and 40mA current. Fourier transform infrared (FT-IR) spectra of the samples were recorded at room temperature (Agilent Technoogies Cary 630 FTIR) in the 300-4000cm^{-1} region.

UV-Vis experiments were performed using a (SP-UV300SRB) and a quartz voltammetric cell with a volumetric capacity of 5 mL. Graphs plot and calculus were carried out using OriginLab software version 2.0 (Integral Software, France).

2.5. Spectrophotometric studies of DPPH-ZnO@APTES@2(ferrocenylmethylamino)benzonitril interaction

The interaction of @APTES@2(ferrocenylmethylamino)benzonitril with DPPH was studied by UV-Vis absorption titration for getting further clues about the mode of interaction and binding strength. Has been calculated the *Binding constant* Depending on the **Benesi-Hildebrand** equation:

$$\frac{A0}{A-A0} = \frac{\varepsilon 0}{\varepsilon - \varepsilon 0} + \frac{\varepsilon 0}{\varepsilon - \varepsilon 0} \frac{1}{K[AS]} \quad (6)$$

where K is the binding constant, *A* 0 and *A* are absorbance of DPPH in the absence and in the presence of antioxidant standards, ε 0and ε are their absorption coefficients respectively, [*AS*] concentration of antioxidant standard.

3. Results and discussion

3.1. X-ray diffraction (XRD)

XRD Spectra provides an insight about the crystallinity of nanoparticles (fig1) is actually zinc oxide [55-3411]. Size of the nanoparticle was calculated using Debye–Scherrer equation. X-ray diffraction peaks obtained at 31.77°,34.42°,36.25°,47.54° ,56.60°,67.95° correspond to the lattice plane of (100),(002),(101),(102),(110),(112). The XRD results evidenced that the particles obtained were nanocrystalline and had a hexagonal Wurtzite structure. Average size of the synthesized nanoparticle was found to be. 91,28 nm (table1)

$$D = \frac{K\lambda}{\beta \cos\theta}$$

where, D- particle size in nm, λ- X-ray wavelength, β- FWHM, θ- Bragg's angle of reflection.

Table 1 represents the FWHM value for every peak assigned for particle size calculation.

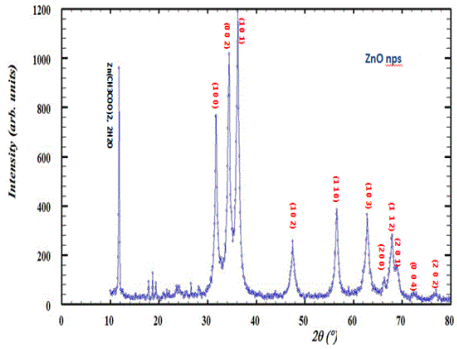

Fig. 1. XDR pattern of Zno NPs:X-axis:2θ(degrees) ;Y-axis:number of strokes.

Table 1. Parameter calculation for average size calculation for nanoparticle.

2θ	hkl	FWHM	D(nm)
31.77	100	0.61	134.91
34.42	002	1.16	71.31
36.25	101	0.97	85.50
47.54	102	1.30	66.31
56.60	110	0.65	136.70
62.85	103	1.63	56.77
67.95	112	1.33	71.95

3.2. FT-IR analysis

Substance-specific vibrations of the molecules lead to the specific signals obtained by IR spectroscopy.FT-IR spectra and fuctional group involved in ZnO NPs synthesis illustrated peak in the rang of 400-550cm^{-1} [7] (fig 2) which is belonged to Zno stretching vibration. After the silane treatment (fig3)several new peak were observed, broak peak obtained at 3350cm^{-1} corresponded to OH stretching vibration[8] and the peak in the rang of 1020-1250cm^{-} corresponded Si-O [9]The peak at 1610 cm^{-} belonged to the NH bond and –NH2 deformation vibration, which proved the presence of NH2 groups[7] . The peak at 687 cm^{-1} can be assigned to Si–C stretching vibration. and the table 2 show the most functional groups.

Such red shift of the FTIR spectrum in ZnO@APTES@2(ferrocenylmethylamino)benzonitril composites are due to the conjugation between ZnO and2(ferrocenylmethylamino)benzonitril surface, the peak at 490cm-^{1} correspond Fe-c and the peak at 2870 correspond C-H aromatic stretch .The bands at 1425 and 1610 cm-^{1} can be attributed to the stretching of N-H groups , the peak at 1358 and 1537 correspond NO stretch . Therefore, the FT-IR spectral features are well matched with reported stretching frequency values and further indicate the intense interaction between ZNO and 2-(ferrocenylmethylamino)benzonitril.

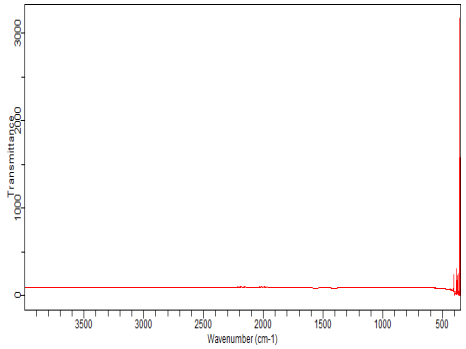

Fig. 2. FTIR by Zno NPs.

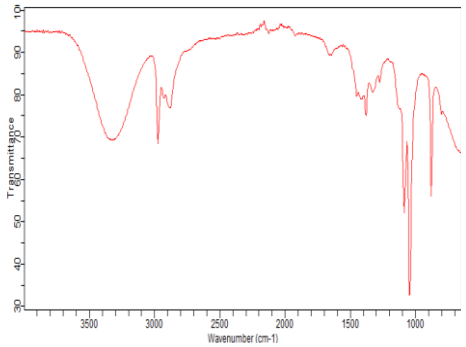

Fig. 3. FTIR peaks for ZnO after treated with APTES.

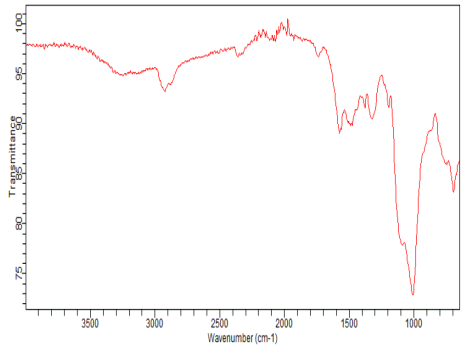

Fig. 4. ZnO@aptes@ and2(ferrocenylmethylamino)benzonitril.

Table 2. Functional group and absorption band of the ZnO after APTES treated.

S.No	Absorption peak(cm^{-1}) In ZnO NPs	Bond/functional groups
1.	3400	OH
2.	2950	$-CH_2$,$-CH_3$ Methylen
3.	2100-2370	Si-H Silanes
4.	1650	C=C
5.	1540	N-H
6.	1200-1300	-Si-C-Silicon-Carbon
7.	1140-1190	-Si-O-C-Silanes
8.	1020-1120	$-C-NH_2$

3.3. Determination of IC_{50}

The addition growing of ontiaxidants to (10^{-4} DPPH Dissolved in ACN) a remarkable overall decrease in absorbance. (table3) And through the equation

$$I\%=((A_0-A_1))/A_0)*100$$

We can calculated Percent of inhibition I%

where I% : Percent of inhibition, *A*0 and *A* are absorbance of DPPH• in the absence and in the presence of antioxidant standards [10]

Table 3. Inhibition values of DPPH%of ZNO@APTES@2-(ferrocenylmethylamino)benzonitril and Galic Acide.

Compound	C(g/l)	A	Percent of inhibition%
G.A	/	1.40	/
	5.10^{-10}	1.12	20
	8.10^{-08}	1.04	25.71
	10^{-07}	1.03	26.42
	8.10^{-05}	1.02	27.14
	5.10^{-04}	0.80	42.85
	8.10^{-02}	0.09	93.57
	0.1	0.06	95.71
ZNO@APTES@2-(ferrocenylmethylamino)benzonitril	/	1.38	/
	8.10^{-10}	1.17	15.59
	7.10^{-09}	1.12	18.94
	9.10^{-06}	1.08	22.28
	8.10^{-05}	1.03	25.36
	7.10^{-04}	0.85	38.95
	8.10^{-03}	0.83	40.20
	9.10^{-02}	0.34	75.36
	10^{-01}	0.25	81.88

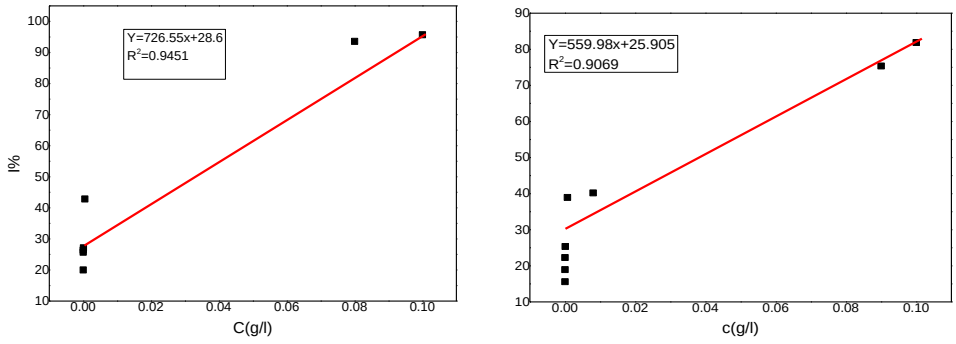

Fig. 5. Curve percentage change inhibition of DPPH in terms of mass concentration of Galic Acid and ZNO@APTES@2-(ferrocenylmethylamino)benzonitril.

Table 4. Results of the evaluation of antioxidant activity.

Compound	The equation	R^2	IC_{50}
G.A	Y=726,55x+28.6	0.9451	$29,45.10^{-03}$
ZNO@APTES@NITRO	Y=559,98x+25.905	0.9069	$43,02.10^{-03}$

We observe when it is IC_{50} small the antioxidant effectiveness it is big and from it we conclude ZNO@APTES@2-(ferrocenylmethylamino)benzonitril has antioxidant effectiveness less than Galic Acide.

3.4. Binding constant

The binding constant and binding free energy were calculated based upon the decrease in absorbance using the equation of Benesi-Hildebrand

Table 5. Values of A and $A_0/A\text{-}A_0$ For each concentration.

Compound	C(mol/l)	C(umol/l)	1/C(umol/l)	A	$A_0/A\text{-}A_0$
G.A	$2.84.10^{-09}$	0.00284	352.1126761	1.12	-5
	$4.54.10^{-07}$	0.454	2.202643172	1.04	-3.8888889
	$5,68.10^{-07}$	0.568	1.76056338	1.03	-3.7837838
	$4,54.10^{-04}$	454	0.002202643	1.02	-3.6842105
	$2.84.10^{-03}$	2840	0.000352113	0.8	-2.3333333
	0.45	450000	2.22222E-06	0.09	-1.0687023
	0.56	560000	1.78571E-06	0.06	-1.0447761
ZnO@APTES@NITRO	$1.31.10^{-12}$	0.00000131	763358.7786	1.17	-3.3823529
	$1.14.10^{-11}$	0.0000114	87719.29825	1.12	-3.2857143
	$1.47.10^{-8}$	0.0147	68.02721088	1.08	-3.0263158
	$1.31.10^{-7}$	0.131	7.633587786	1.03	-2.5555556
	$1.14.10^{-6}$	1.14	0.877192982	0.85	-2.3
	$1.31.10^{-5}$	13.1	0.076335878	0.83	-1.5540541
	0.00014	140	0.007142857	0.34	-1.2365591

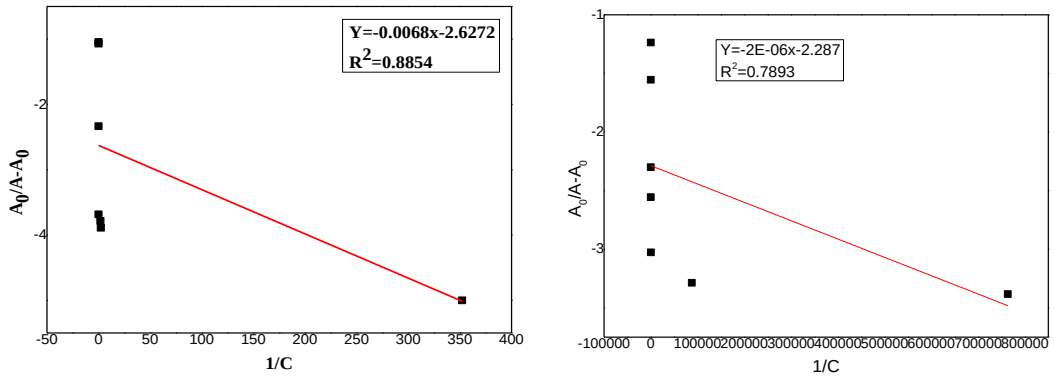

Fig. 5. Linearcurveof1/[OA]intermsof$A_0/A\text{-}A_0$forZNO@APTES@2(ferrocenylmethylamino)benzonitril and Galic Acid.

Table 6. Binding constants and binding free energy values.

Compound	The equation	K	ΔG
A.G	Y=-0.0068x-2.6272	386.35	-49.02
ZnO@APTES@NITRO	$Y=-2^{E}$-06-2.287	1,143E+12	-68,839

Through the values, we observe the compound ZnO@APTES@2-(ferrocenylmethylamino)benzonitril the biggest value of binding constant and this indicates the nature of interaction between free radical $DPPH^{\cdot}$ And ZNO@APTES@2-(ferrocenylmethylamino)benzonitril and it is chemical "interaction chemical" while indicates the small value of the binding constant between G.A and free radical $DPPH^{\cdot}$ That this interaction electrostatic "electrostatic interaction physical"

The negative values of the binding free energy resultant from overlap between free radical $DPPH^{\cdot}$ And Galic Acide ,ZNO@APTES@2-(ferrocenylmethylamino)benzonitril indicate on automatic interaction

4. Conclusion

As a result ,ZNO NPs were successfully synthesized and its treatmeant by 3-aminopropyl triethoxysilane (APTES) then 2-(ferrocenylmethylamino)benzonitril then were successfully determined The binding parameters like binding constant and binding free energy of ZNO@APTES@2-(ferrocenylmethylamino)benzonitril with 1,1-diphenyl-2-picrylhydrazyl (DPPH) The results indicated electrostatic interaction of DPPH radical with ZNO@APTES@2-(ferrocenylmethylamino)benzonitril.

References

[1] M. Zheng, F. Davidson, X. Huang, J. Am. Chem. Soc. **125**, 7790 (2003).
[2] D. Mashitah Mat, J. Jeevanandam, in Nanobiomaterials in Antimicrobial Therapy, (2016).
[3] J. Du, R. Zhao, S. Chen, H. Wang, J. Li, Z. Zhu, ACS Appl Mater Interfaces **7**(10), 5870 (2015).
[4 Lanez, Touhami, Hadia Hemmami, Current Pharmaceutical Analysis **13**(2), 110 (2017).
[5] H. Barrak, T. Saied, P. Chevallier, G. Laroche, A. M'nif, A. H. Hamzaoui, Arabian Journal of Chemistry, (2016).
[6] H. A. Benesi, J. H. Hildebrand, Journal of the American Chemical Society **71**, 2703 (1949).
[7] B. Chang, P. Akil, H. Md, R. Nasir, Journal of Thermoplastic Composite Materials **24**(5), 653 (2011).
[8] S .Yedurkar, C. Maurya, P. Mahanwar, Open J. Synth. Theory Appl. **5**, 1 (2016).
[9] Y. Sun, Z. Zhang, C. P. Wong, Journal of Colloid and Interface Science **292**, 436 (2005).
[10] J. M. Osgerby, P. L. Pauson, J. Chem. Soc., (1958).