

DOI: <http://dx.doi.org/10.21123/bsj.2017.14.2.0379>

Synthesis of Pure Nano semiconductor Oxide ZnO with Different AgNO₃ Concentrations

Assist. Prof. Dr. Ali S. Al-Taie

Hiba S. Abd Alwahab

Department of Mathematics, College of Science for Women, University of Baghdad, Baghdad, Iraq.

Received 26/1 /2015

Accepted 18/ 5/2015



This work is licensed under a [Creative Commons Attribution 4.0 International License](https://creativecommons.org/licenses/by/4.0/)

Abstract:

Zinc oxide nanoparticles sample is prepared by the precipitation method. This method involves using zinc nitrate and urea in aqueous solution, then (AgNO₃) Solution with different concentrations is added. The obtained precipitated compound is structurally characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), Atomic force microscopy (AFM) and Fourier transform infrared spectroscopy (FTIR). The average particle size of nanoparticles is around 28nm in pure, the average particle size reaches 26nm with adding AgNO₃ (0.05g in100ml =0.002 M) (0.1g in100ml=0.0058M), AgNO₃ (0.2g in 100ml=0.01M) was 25nm. The FTIR result shows the existence of -CO, -CO₂, -OH, and -NO₂⁻ groups in sample and oxides (ZnO, Ag₂O).and used an atomic force microscope and microscope scanning electron to model the record.

Key words: Nanoparticles ZnO, Doped (AgNO₃), XRD, SEM .AFM.

Introduction:

Zinc oxide is one of the semiconductor inorganic compounds with the formula ZnO. It usually appears as a white powder nearly insoluble in water, which is widely used as an additive into numerous materials and products including, paints, glass, cement, ceramics, rubber lubricants, plastics, ointments, adhesives, pigments, sealants, and foods batteries. ZnO exists in the earth crust; however, much of the ZnO used commercially is produced synthetically. Due to a wide band gap of ZnO oxide with an energy gap of 3.37eV at room temperature which has been used considerably in photochemical properties [1-4]. ZnO nanostructures have a great advantage in

the process of catalytic reaction due to their large surface area and high catalytic activity [5] Nanoscience is the study of phenomena on a nanometer scale. Atoms are a few tenths of a nanometer in diameter and molecules are typically a few nanometers in size. Nanometer is a magical point on the length scale for this is the point where the smallest man-made devices meet the atoms and molecules of the natural world. Typically, nano means 10⁻⁹, so a nanometer is one billionth of a meter and is the unit of length that is generally most appropriate for describing the size of single molecule. Nanometer objects are too small to be seen with check eye. If one wants to see a 10 nm sized marble in his hand, his eye would have to be smaller than a human hair. Anyhow, the

rough definition of Nanoscience could be anything which has at least one dimension less than 100 nanometer [6].

Material and Methods:

Apparatus

1. Fourier Transforms Infrared Spectrophotometer (FTIR) model himadzu (Japan) has been used to determine the IR-spectra of ZnO in the range (400-4000) cm^{-1} .

2. Atomic Force Microscope AA 3000, scanning probe microscope, Angstrom advanced Inc., (USA), has been used to study the topography of the prepared Nanoparticles ZnO.

3. X-Ray Diffraction analysis achieved in the Ministry of Science and Technology –materials research department by using SHIMADZU (XRD -7000) diffractometer /Japan , measure the particle size and morphology of the synthesized nanoparticles.

4. SEM model Tescan veg III (czech), determine the morphology of the sample.

Methods:

Urea ($\text{CO}(\text{NH}_2)_2$)99%, BDH, Zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) 99%, BDH, Silver nitrate (AgNO_3)99%, BDH, and Double distilled water are used as starting material for the preparation of samples. At the outset, 4.7g of Zinc nitrate is dissolved in 50 ml of distilled water stirring for 30 minutes. At the same time 3.0g of urea is dissolved in another 50ml of distilled water, also under stirring for 30 minutes. Then the urea solution is added drop by drop to

zinc nitrate solution with strong stirring at 70 ° C for 2 hours to allow full growth of nanoparticles. When adding the urea solution to the zinc is complete, different concentrations of silver nitrate as a dopping material are added .The white precursor product is centrifuged at 8000 rpm for 10 min and washed with distilled water to remove any impurities or possible absorbed ions. The obtained product is calcined at 500 °C in air atmosphere for 3 hr. using burning furnace. [7]

Results and Discussion:

Structural Characterization

1. X-ray Diffraction (XRD) Studies

The powder XRD for the synthesized compound (calcined at 500 °C for 3 hr) obtained from direct precipitation method of 3.0 g Urea and 4.7 g zinc nitrate is shown in Figure 2a, while the synthesized ZnO dopped with 0.05,0.1,0.2 gm of AgNO_3 is shown in Figures.2b,c,d respectively .The XRD peaks in the wide angle range of 2θ from 10° to 70.° The peaks appear at 2θ range of 31.79°, 34.45°, 36.27°, 47.55°, 56.60° and 62.87°. The peaks appear at 2θ range of ZnO and 0.05 AgNO_3 27.80°, 31.79°, 32.24°, 34.03°, 34.43°, 36.26° shown Figure2a,b. And the peaks appear at 2θ range of ZnO and 0.1 AgNO_3 31.82, 34.47, 36.30, 47.58, 56.37, 56.63 as shown Figure.2c. The peaks appeared at 2θ range of ZnO and 0.2 AgNO_3 27.81°, 31.80°, 32.24°, 34.45°, 36.27°, and 46.21° show Fig.2d .The average crystallite sizes (τ) are calculated by using the Debye - Scherrer equation as shown in Table(1) :

$$\tau = \frac{K\lambda}{\beta \cos \theta} \dots\dots\dots [8]$$

Table 1: The Corners of the Zinc Oxide and by Adding the Doped

ZnO pure	ZnO,0.05AgNO ₃	ZnO,0.1AgNO ₃	ZnO ,0.2 AgNO ₃
31.79°	27.80°	31.82°	27.81°
34.45°	31.79°	34.47°	31.80°
36.27°	32.24°	36.30°	32.24°
47.55°	34.03°	47.58°	34.45°
56.60°	34.43°	56.37°	36.27°
62.87°	36.26°	56.63°	46.21°

The shape factor is K (the typical value is 0.89), λ is the wavelength of incident beam, β is the broadening of the diffraction line measured in radians at half of its maximum intensity (FWHM) and θ is the Bragg's angle. From the

XRD data, the average crystallite sizes are found to be 28 nm for pure ZnO and the average size of ZnO doped with 0.05, 0.1, 0.2 AgNO₃ are sequentially (26, 26, 25 nm).

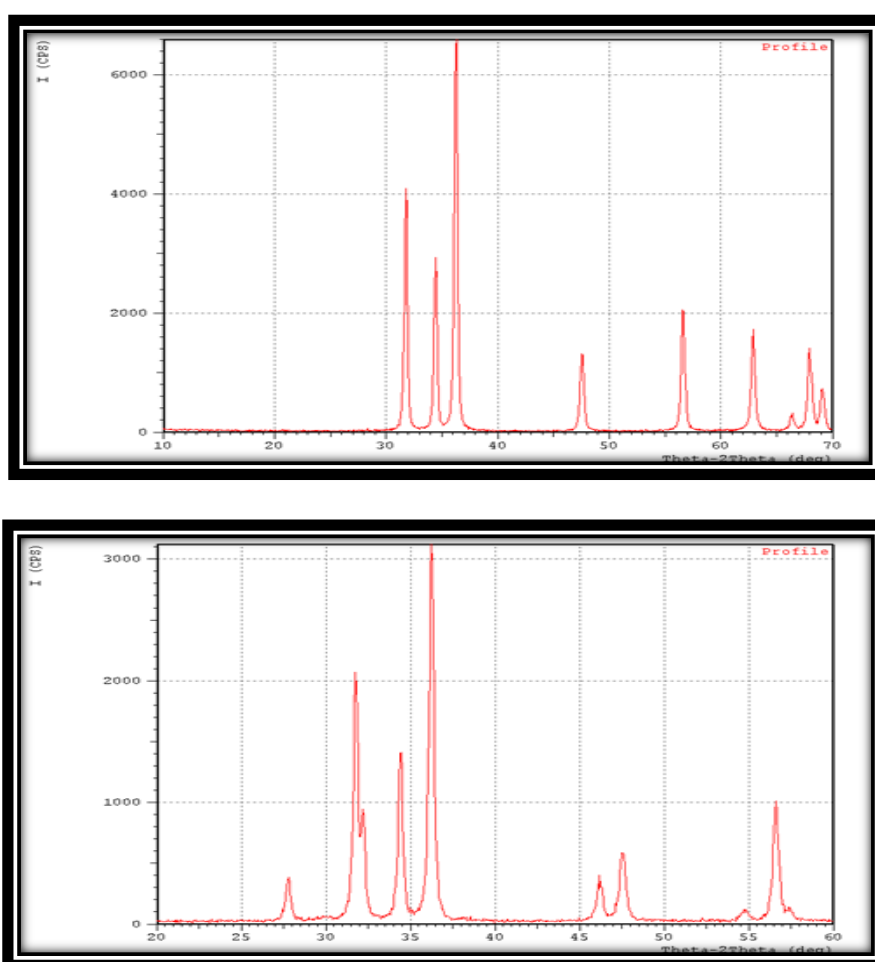


Fig (2a.) X-Ray Diffraction Patterns of Zinc Oxide, (2b) ZnO Doped with 2.94g/mol AgNO₃

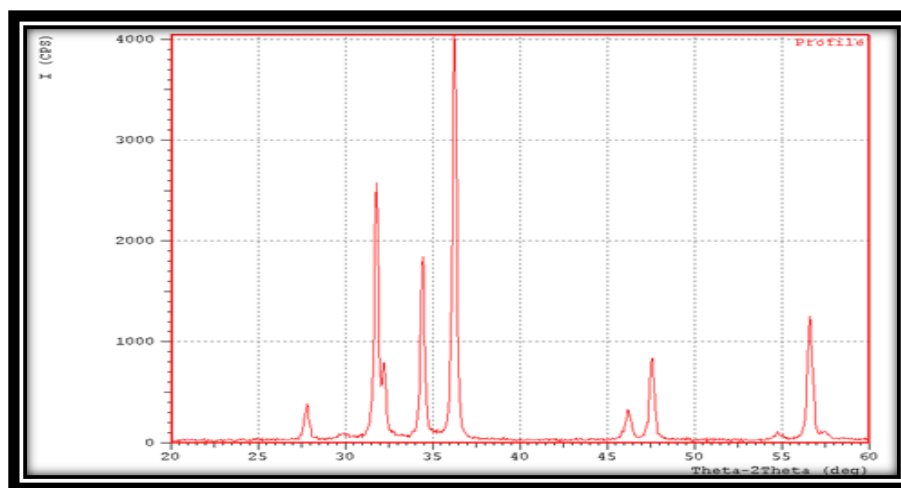


Fig. (2c) X-Ray Diffraction Patterns of Zinc Oxide, Doped with 5.88 AgNO₃

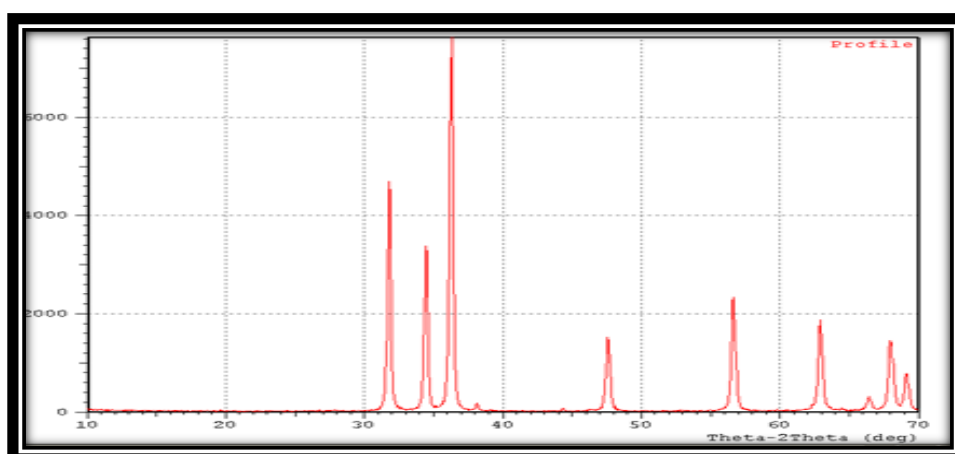


Fig. (2d) X-Ray Diffraction Patterns of Zinc Oxide, Doped with 11.7 AgNO₃

2. Scanning Electron Microscopic (SEM)

Electron photomicrographs of ZnO nanoparticles obtained from direct precipitation of 4.7 g Zn(NO₃)₂·6H₂O and 3.0 g CO(NH₂)₂ calcined at 500 °C for 3 hr. as shown in Figure.3(a,b,c,d),

reveal the SEM images of ZnO nanoparticles and ZnO after adding dope AgNO₃ with (0.05,0.1,0.2), It is observed that the particles are well defined and small spherical shaped with agglomerated particles as shown in Figure. 3(a)[9].

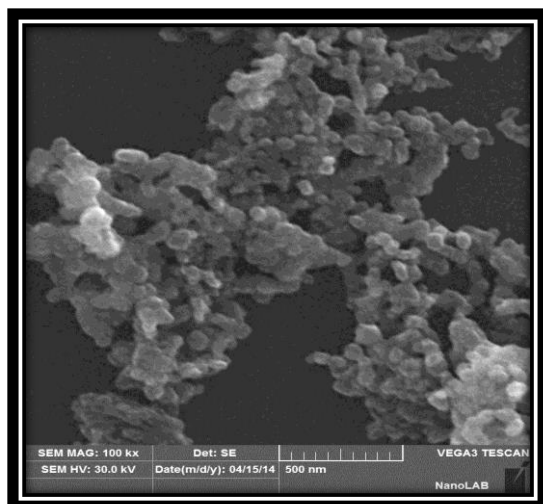
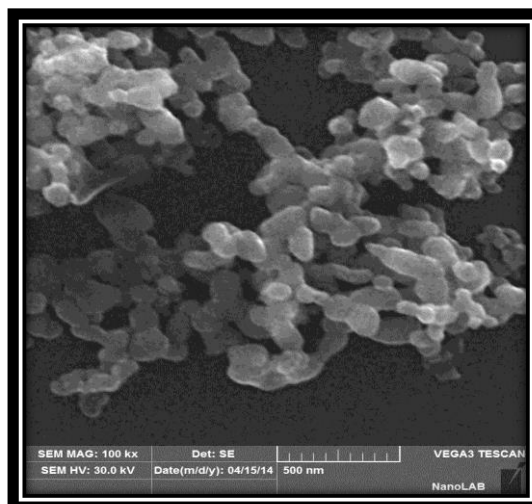


Fig.(3a) SEM Image of Pure ZnO100 KX.



3c) SEM Image of ZnO, 5.8M AgNO₃100KX

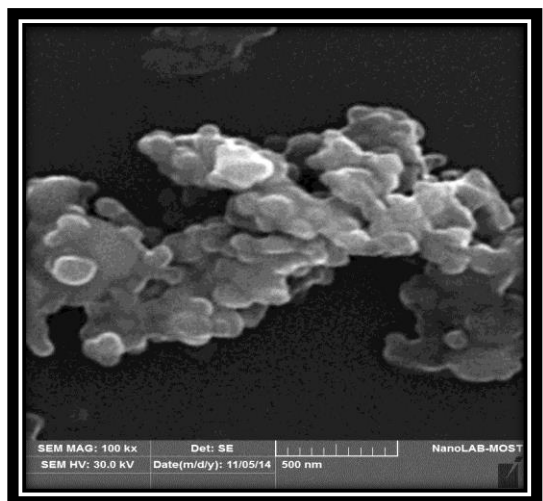
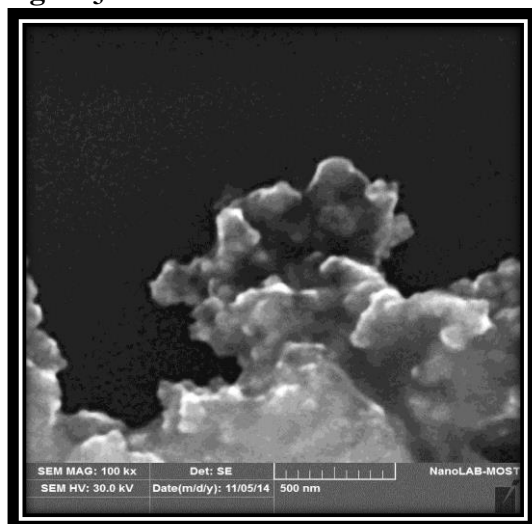


Fig.(3b) SEM Image of ZnO, 2.9M AgNO₃ 100KX



3d) SEM Image of ZnO,11.7M AgNO₃ 100KX.

3. Fourier Transforms Infrared Spectroscopy

Absorbance spectra in infrared region for the pure ZnO particles powder before and after adding dope AgNO₃ as shown Figures. 4a, 4b, 4c, and (4d) .in before they showed main absorption band to O-H stretching of hydroxyl group at 3437.15 cm⁻¹ , asymmetric and symmetric C=O stretching of Zinc nitrate at 1631.78 and 1516.05 cm⁻¹, O-H bending of hydroxyl group at 528cm⁻¹and ZnO stretching of ZnO at 459.06 cm⁻¹ .After dopping the spectra showed O-H stretching of hydroxyl group at 3444.87-3433.29 cm⁻¹,

asymmetric and symmetric C=O stretching of Zinc nitrate at 1662.21-1651.07 and 1516.05-1543.05 cm⁻¹ , O-H bending of hydroxyl group at 520-524cm⁻¹and ZnO stretching of ZnO at 462.91-451.34-478.35 cm⁻¹. These spectra indicate no much change to the surface of the ZnO particles due to adsorption and main function of the surface when adding AgNO₃ (0.1g=0.0058 M) it appear 424.34cm⁻¹ and with AgNO₃ (0.2g=0.01M) 420.48cm⁻¹ and with AgNO₃ (0.05g=0.002 M) 412.77cm⁻¹ [10] .

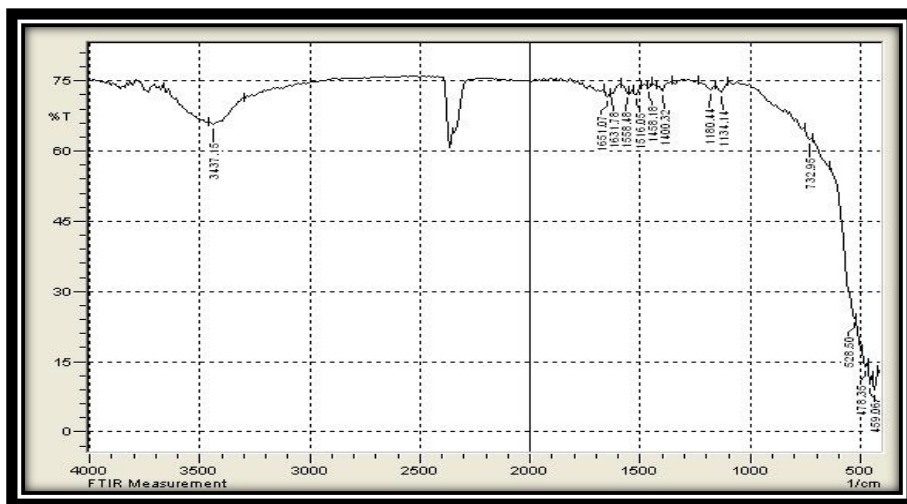


Fig. (4a) FTIR Spectrum of ZnO Nanoparticles

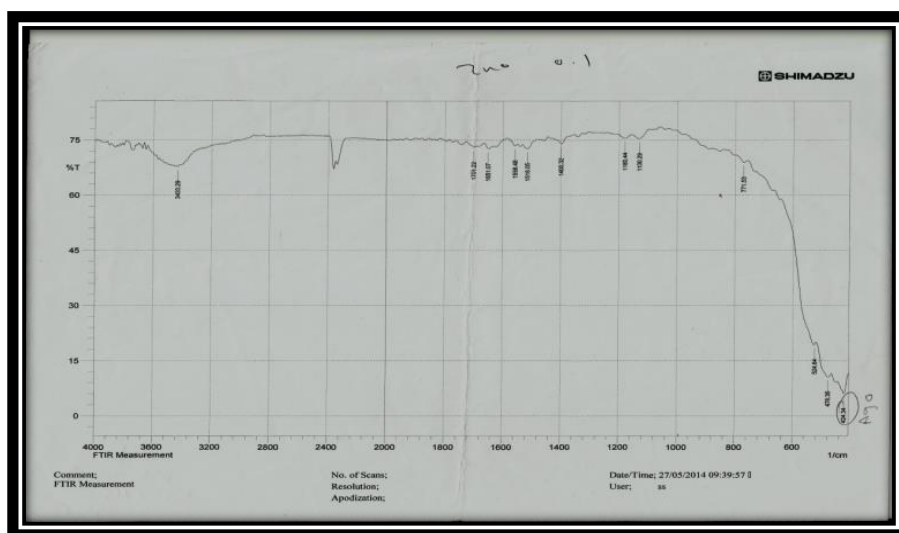


Fig.(4b) FTIR Spectrum of ZnO Doped with 0.1g AgNO₃

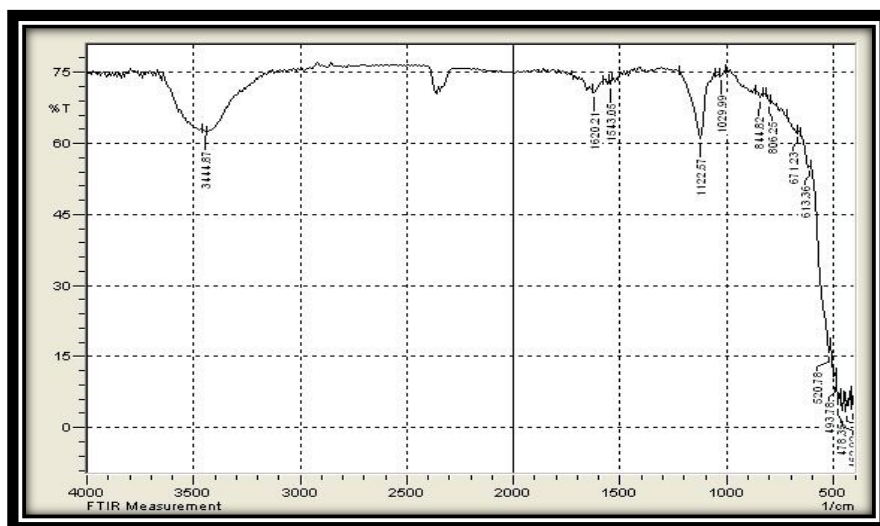


Fig. (4c) FTIR Spectrum of ZnO Doped with 0.05g AgNO₃

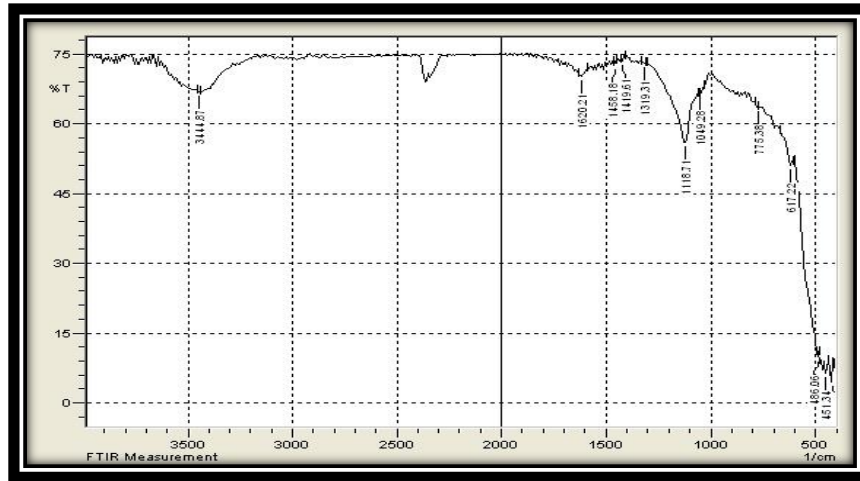
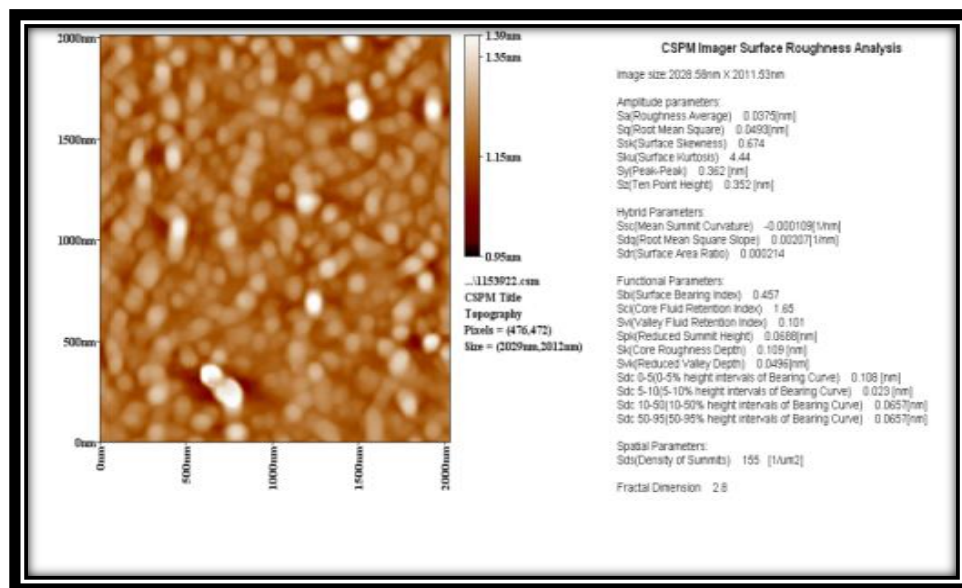


Fig. (4d) FTIR Spectrum of ZnO Doped with 0.2g AgNO₃

4. Atomic force microscopy (AFM)

Atomic Force Microscopic AFM is a powerful characterization tool for surfaces at the micro and nano level as a result of the superior resolution capabilities of the instrument. The AFM image, Figure 5(a,b,c,d), of ZnO and the different doping Ag malaria reseal clear differences in particle size surface roughness and 10 point high as shown in Table (1) .The topography(two and three dimensional) of all samples are seen to be identical and represent a spherical well oriented nanoparticles.

Granularity distribution charts for the four samples prepared are represented in Figures (5(a pure ZnO, b ZnO and 0.1AgNO₃ ,c 0.05 AgNO₃, d 0.2 AgNO₃)). They show that the diameter of the particles in the range (50-200), (60-180),(70-200) and the average particle size are 125.77, 89.49, 92.06, and 76.71 nm for the ZnO pure and after adding different concentration of AgNO₃ (0.1, 0.05, 0.2) respectively which reflex weed control on particle formation at the nano scale as shown in Table(2) [11-12] .



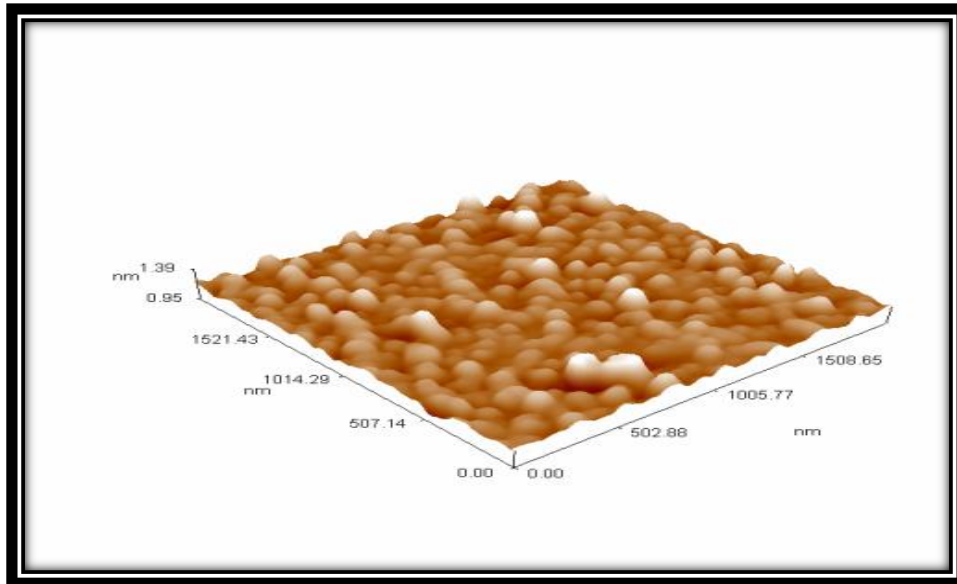


Fig. 5(a) AFM Image of ZnO Pure

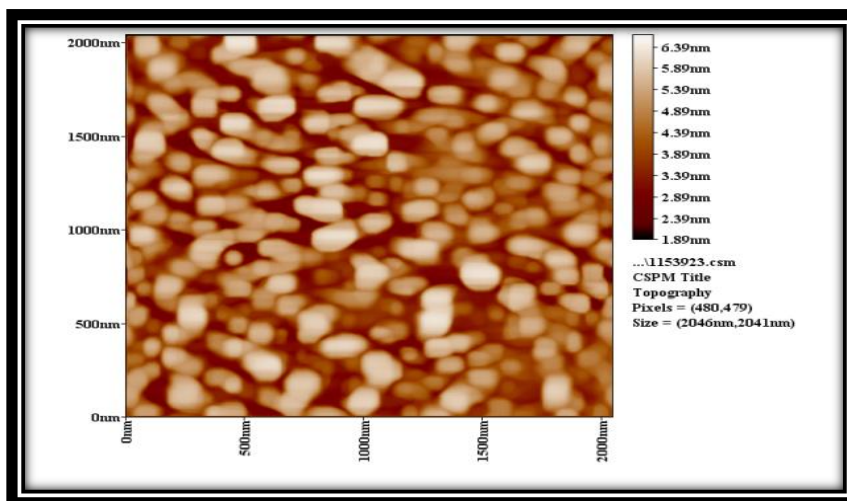
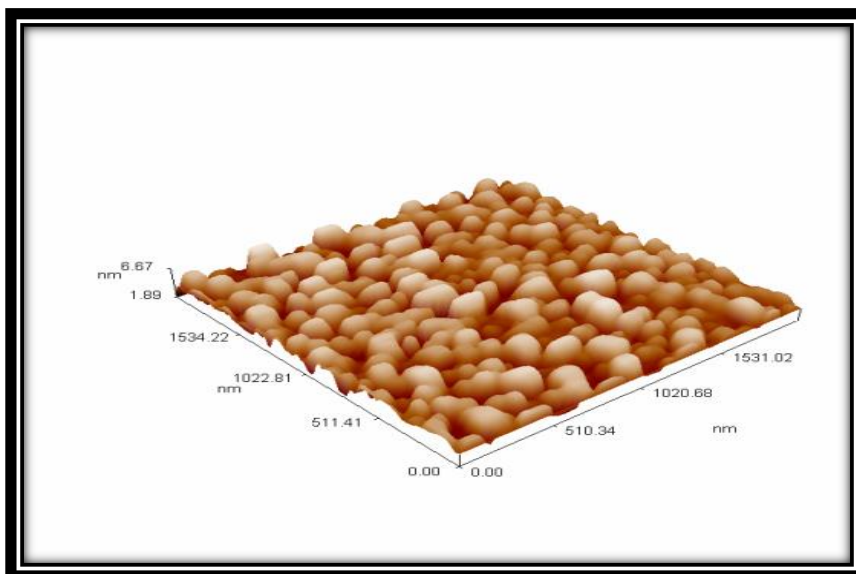


Fig. 5(b) AFM Image for ZnO with AgNO₃ (5.8M)

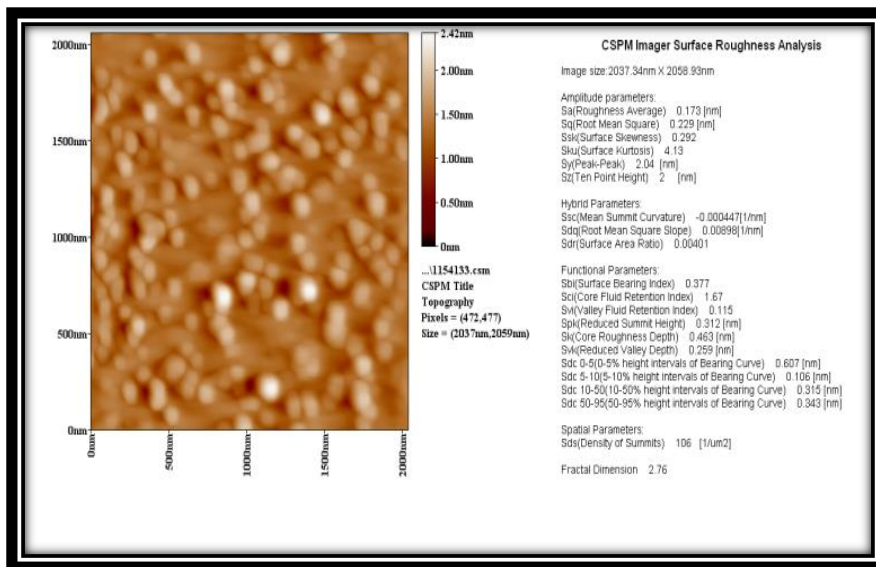
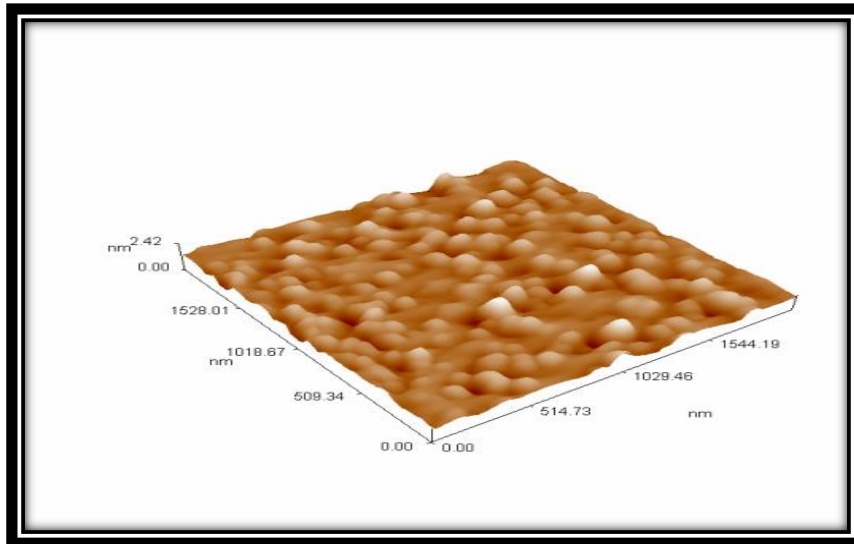
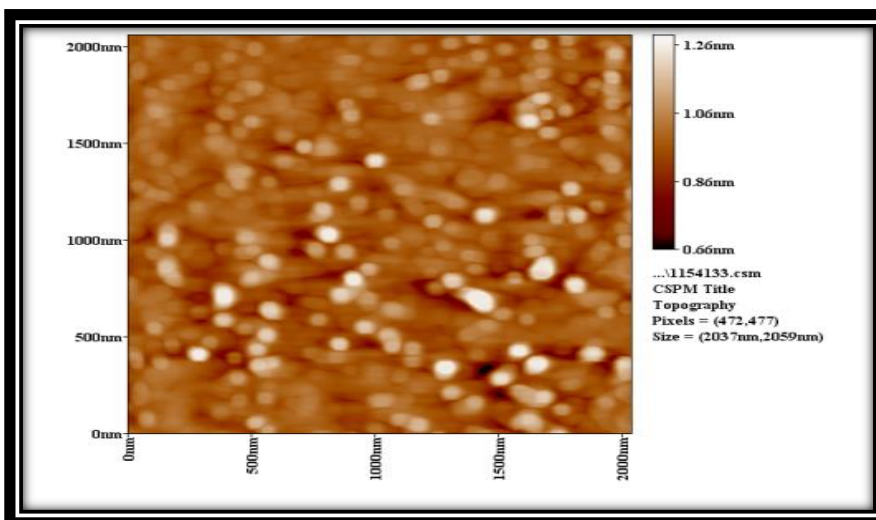


Fig. 5(c) AFM Image for ZnO with AgNO₃ (2.9M)



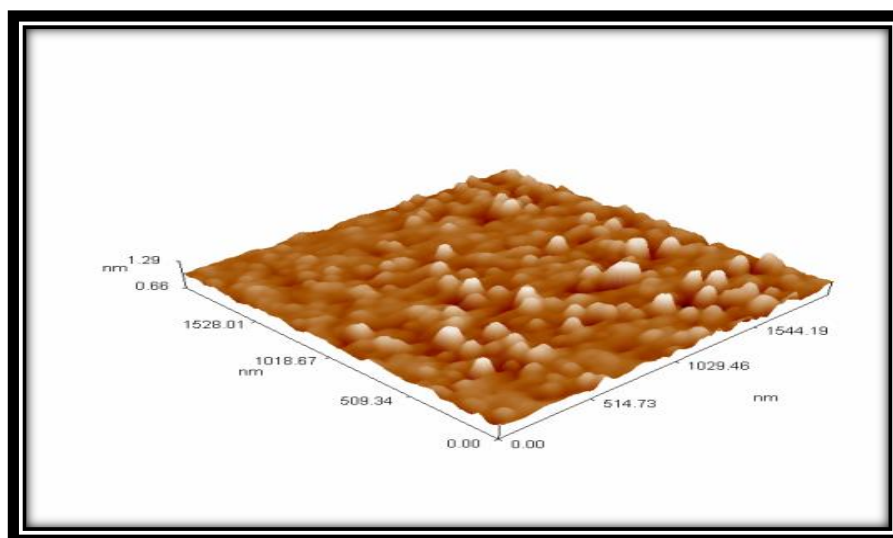


Fig. 5(d) AFM Image for ZnO with AgNO₃ (11.7M)

Table (2) The Average Particle Size and Roughness and 10 Point of the Four Samples

Sample	Average Particle size nm	Roughness	10point Height
Pure ZnO	125.77	0.0375	0.352
0.1	89.49	0.784	2.17
0.05	92.06	0.173	2
0.2	76.71	0.048	0.542

Conclusions:

In this work, the pure ZnO nanoparticles with adding different concentrations of AgNO₃ (0.002 M, 0.0058 M, 0.01 M) are successfully prepared by the direct precipitation method using zinc nitrate as zinc source and urea as precipitating agent in aqueous solution, silver nitrate is added in different concentration. In XRD analysis, the size range of the generated ZnO powder is approximately 25–28 nm and the nanoparticle size decreases when different concentrations of silver nitrate are added. The SEM analysis shows that the particles morphology is of a spherical structure. The FT-IR spectrum shows the existence of OH⁻, -CO₂, -NO⁻² and -CO groups in unclaimed sample. The band gap is lower for synthesized ZnO nanoparticles than their bulk counterparts. Thus, the synthesis of ZnO

nanoparticles by direct precipitation method is simple.

References:

- [1] Brida, D.; Fortunato, E.; Ferreira, I.; Aguas, H. and Martins, R. 2002. New insights on large area flexible position sensitive detectors, *J. Non-Cryst. Solids*. 5(3):1272–1276.
- [2] Wang, Z. L. 2004. Zinc oxide nanostructures: growth properties and Applications, *J. Phys. Condens. Matter*. 30(16): 829–858.
- [3] Sucheai, M.; Christoulakis, S.; Moschovis, K.; Katsarakis, N.; And Kiriakidis, G. 2006. ZnO transparent thin films for gas sensor applications ", *Thin Solid Films*. 515(2):551–554.
- [4] Ashour, A.; Kaid, M.; El-Syed, A. N. Z. and Ibrahim, A. A. 2006. Physical properties of ZnO thin films deposited by spray pyrolysis technique, *Appl. Surf. Sci.* 252 (22):7844–7848.
- [5] Chen, J. C. and Tang, C. T. 2007. Preparation and application of granular ZnO/Al₂O₃ catalyst for the removal of hazardous trichloroethylene, *J. Hazard Mater.* 142 (2) :88–96.
- [6] Yousaf, A. S. And Salamat, A. 2007-2008. Why Nanoscience and Nanotechnology? What is there for

- us? Journal of Faculty of Engineering & Technology .12(4): 11-20.
- [7] Bagheri, S.; Chandrappa, K. G. C. and Abd Hamid, Sh. B. 2013. Facile synthesis of nano sized ZnO by direct precipitation method, Derpharma chemical 5(3) :265-270.
- [8] Varshney, R. Bhadauria, S. 2010 .Electrolytic Synthesis and Characterizations of Silver Nanopowder, Adv. Mat. Lett. 1(3): 232-244
- [9] Hamedani, N. F. and Farzaneh, F. 2006 .Synthesis of ZnO Nanocrystals with Hexagonal (Wurtzite) Structure in Water Using Microwave Irradiation, J. Sci. I. R. Iran 17(3): 231- 234.
- [10] Dong Pham, T. and Lee, B. K. 2014. Feasibility of Silver Doped TiO₂/Glass Fiber Photocatalyst under Visible Irradiation as an Indoor Air Germicide, Int. J. Environ. Res. Public Health. 18(11): 3271- 3288.
- [11] Velmurugan, R. Sreedhar, B. and Swaminathan, M. 2011. Nanostructure AgBr loaded TiO₂An efficient sunlight active photocatalyst for degradation of Reactive Red 120, J Chem. Cent. 9(3): 5-46
- [12] Zavala, G. 2008. Atomic Force, a tool for characterization, synthesis and process.J. Colloid polym.sci.286 (6):85-95.

تحضير اكاسيد اشباه الموصلات النانوية اوكسيد الخارصين النقي و اضافته تراكيز مختلفة من نترات الفضة

هبة سامي عبدالوهاب

استاذ مساعد دكتور علي سلمان الطائي

قسم الكيمياء، كلية العلوم للنبات، جامعة بغداد، بغداد، العراق.

الخلاصة:

تم تحضير النموذج بطريقة الترسيب المباشرة لتخليق اوكسيد الخارصين باستخدام نترات الخارصين واليوربا في المحلول المائي و اضافة نترات الفضة بتراكيز مختلفة. وقد تم دراسة خواص النموذج بواسطة حيود الاشعة السينية ومجهر الماسح الضوئي ومجهر القوة الذرية وطيف الاشعة تحت الحمراء. اظهرت النتائج بان متوسط حجم الجسيمات النانوية لاوكسيد الخارصين النقي 28 نانومتر وبعد اضافة المنشط (نترات الفضة) بتراكيز مختلفة (0,05غم مذابة في 100مل=0,002مولاري) و(0.1غم مذابة في 100مل=0,0058مولاري) وصل الى 26نانومتر و باضافة (0,2غم مذابة في 100مل=0,01مولاري) وصل الى 25 نانومتر. اظهر طيف الاشعة تحت الحمراء المجاميع الفعالة (CO⁻، NO₂⁻، COO⁻، OH⁻) وموقع اوكسيد الفضة واوكسيد الخارصين. تم استخدام مجهر القوة الذرية ومجهر الماسح الالكتروني لتحليل النموذج المحضر.

الكلمات المفتاحية: الدقائق النانوية لأوكسيد الخارصين، مطعم (نترات الفضة)، حيود الاشعة السينية ، مجهر الماسح الضوئي، مجهر القوة الذرية.