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The Absorption of Nanomaterial Thin Films at Liquid /Liquid Interface

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Abstract Nanomaterial refers to materials whose exist at the nanometer scale. The behaviour and the properties of nanomaterials as films at the interfaces between two immiscible liquids have extensively been studied in recent years and is of considerable importance in electronic and optoelectronic fields involving the applications for the generation of solar energy. The development of this technique has made its technology a fertile area for scientific research. The growth and ordering of Nano films at the interfacial region have made this new strategy more attractive. Generally, a thin film of nanomaterial's is small thicknesses created by wet chemical method. By this, a simple method gold and cadmium sulphide thin films of nanocrystals have been prepared. In this work, we report the results of our study on a thin film of gold nanocrystals at room temperature and CdS nanocrystals thin film at 40°C adhered at the interfacial region between two immiscible liquids. By using an easily useful experimental technique such as UV-vis Double Beam spectrophotometer films were investigated.

Keywords: liquid /liquid interface, nanomaterial's thin film.

امتصاص الأغشية الرقيقة لمواد النانوية بين سائلين غير ممتزجين

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الملخص المواد النانوية تشير إلى المواد التي توجد في مقياس النانومتر. مؤخراً تمت دراسة سلوك وخصائص المواد متناهية الصغر كأفلام بين سائلين غير قابلين للامتزاج واصبحت ذو أهمية كبيرة في المجالات الإلكترونية والإلكترونية الضوئية التي تستخدم لتوليد الطاقة الشمسية نمو وترتيب أفلام النانو في المنطقة البينية بين السائلين الغير ممتزجين جعل هذه الاستراتيجية أكثر جاذبية.اجمالاً فلام اغشية النانو الرقيقة تم إنشاؤها بواسطة الطريقة الكيميائية الرطبة. من خلال هذه الطريقة البسيطة، تم إعداد لأغشية رقيقة من الذهب والكبريتيد والكادميوم. في هذا العمل قمنا بعرض نتائج دراستنا على افلام الذهب بين السائلين الغير ممزوجين الذهب عند درجة حرارة الغرفة وافلام وكبريتيد الكادميوم عند درجة حرارة 40 درجة مئوية وباستخدام مطياف UV تم تحليل العينات.

الكلمات المفتاحية: افلام المواد النانوية، السطح البيني بين سائل/ سائل.

1. Introduction

The thin film at the interfacial region is the most exciting technologies that participate in the development of modern science and provide a clear idea for physical properties. The thin films are usually referred to layer or many layers of atoms whose thickness ranging from nanometer to several micrometres resulting from the thickening of atoms or molecules that have attractive properties differ from bulk such as physical and engineering properties. It can be found in technological applications in field effect [1-8] solar cells, optoelectronic devices such as touch screens, and high-performance thin film transistors devices [9-14]. For this reason, there is drawn considerable interest in facile synthetic routes for thin films with controllable size and size distribution. In addition, thin films are typically formed by deposited materials on a substrate by the used of various methods included Chemical Vapor Deposition, Thermal Evaporation, Physical Vapor Deposition Coating System, and chemical bath deposition method [15-19]. Two liquid phases for creating nanomaterials at the interface between water/oil is new strategies that possess attractive properties because of Surface tension, and viscosity effects as well as interfacial emulsification [20].

The potential use of the organic –aqueous interface to assemble nanocrystals has been studied [20]. Because of the quality of the medium, assembly using two immiscible liquids is less prone to defects than assembly using other techniques. Semiconducting materials are crucial for the advancement of many modern technologies. Recently, attention has been devoted to the optical and electrical properties of semiconductor thin film to improve the performance of the devices such as solar cells and related photonic, magnetic devices, light-emitting diodes, and photoconductors [21-26]. Scientists are concentrating on improving the controlled synthesis of semiconductor nanoparticles. For example,polycrystalline thin films of cadmium chalcogenide nanocrystals have been formed at the liquid/liquid interface via reacting cadmium cupferronate inorganic phase with dimethylselenourea in the aqueous phase[27]. Bawendi and co-workers [28] have synthesised metal selenide nanocrystals by reacting of dimethyladmium and trioctylphosphine selenide

As well As, Russel and his group [29] have characterized the assembly of phosphine oxide functionalized metal selenide nanoparticles of two different diameters by competitive adsorption at the toluene-water interface by employing fluorescence spectroscopy.

1.1.Stability of emulsion

Emulsions are obtained when one liquid (water) is dispersed into another immiscible liquid (oil). The stability of emulsions points to the ability to resist all the verities of their properties over time. Lots of processes need long living emulsions. However, emulsions are thermodynamically unstable, due to separate water and oil from each other. The water/oil phase separation occurs under various ways including:precipitation,coalescence, flocculation and Ostwald ripening [30-32]. Precipitation occurs when two phases with different densities are separated by gravity [31]. The coalescence occurs when two droplets far away from each other touch each other; the thin liquid films around the droplets are broken, resulting in the fusion of two contacting droplets [32].

Flocculation occurs when small droplets bind together to form large droplets [30]. This happens when the repulsion between two droplets is weak. Ostwald ripening results from the disappearance of the small droplets. This is due to the variation in solubility between the small and the large droplets [33]. As time passes, the molecules of the smaller droplets diffuse across the continuous medium and deposit onto the bigger droplets causing phase separation.

1.2. Application of thin Films

Over the last four decades, thin films have a large variety of industrial applications due to their very small size and large surface-to-volume ratio and they display novel uniqueness compared to the large particles of bulk material [34]. One of the important applications, optical and electrically active as well as magnetic thin films which can be used in the manufacture of solar cells and the manufacture of fiber optics which utilized in the transmission of information and communications, Manufacture of optical filters and coatings anti-reflectivity to minimize the loss of light reflection from the surfaces of these cells. As was used in the optical reagents, as well as their use in laser diodes.

Furthermore, films of semiconductor have many applications for optoelectronics, being utilized in photosensitive and photovoltaic devices [35-36] and optical windows for solar cells [37], as well as many other properties such as its increasing conductivity when irradiated with light, giving rise to use as a photo-resistor. It has been used in the manufacture of data storage devices in electronic computers It is known that these storage media have a large amount of information in their volumes small for manufactured devices. it also used in the manufacture of compact laser discs.

The main application of the use of nanocrystalline for biomedical applications, such as drug delivery and cancer treatment.

1.3. Deposition of Nano Thin Films at the Liquid-Liquid Interface.

The liquid–liquid the interface as not been used sufficiently for the synthesis of thin films of materials, but it is recently that there have been efforts to understand the composition and dynamics of the liquid–liquid interface [38]. We demonstrate in this work how nanocrystals film of gold as well as CdS semiconducting are generated at the interface between two immiscible liquids. Interfaces are an important means to create nanocrystals, providing a fertile environment for organized assembly of nanocrystals. The water /oil interface has unusual thermodynamic properties such as viscosity and density. The interface between two liquids is a heterogeneous region provides alternative path for the self-assembly nanocrystals which has a thickness on the order of a few nanometers (Fig1). One of the problems of this method is dynamic of interfacial charge-transfer reactions [39]. The exchange ions and solvent molecules determine the structure of two immiscible liquids has been recently investigated by advanced techniques [40].

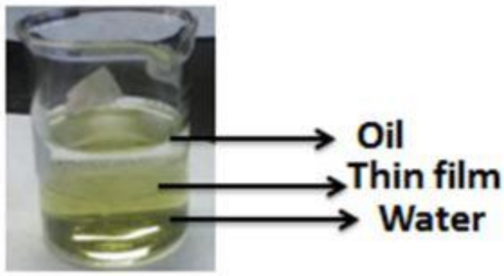

Fig 1: Exhibits thin film between oil / water.

1.4.Stages of Growth for Nanofilms

1. An approaching small atom on to the surface of a substrate and absorbed on the surface this step depending on the sticking coefficient.
2. Surface diffusion generally surface energy can be decreased if the atom has enough energy and time to diffuse to a low energy site and increases with temperature.
3. Chemical bonds occur between atoms and atoms substrate (see Fig.2).

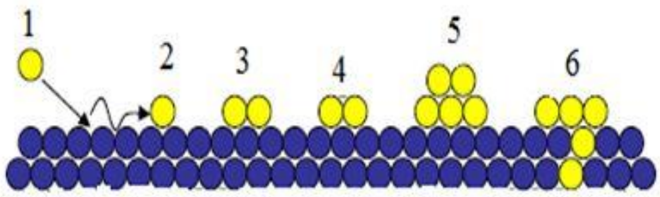

Fig 2: Steps of Nanocrystalline growth [41].

4. Nucleation which is heterogeneous for the stable thin film on the substrate surface reduces the surface energy by decreeing the surface area it depends on the critical nuclei size and temperature as well as the deposition rate the critical nuclei size increases with temperature and decreases with increasing deposition rate.
5. Crystal structure formation and defects.
6. Diffusion and grain growth by aggregation with other particles.

2. Experimental Section

We shall show the method of creation thin films with two examples and exhibits the using of UV-vis for analysis films. To create gold nanoparticles film citrate was used as capping agent. Citrate capped Au nanoparticles were synthesized according to a method reported previously [42]. Briefly, A 0.2 ml of $HAuCl_4$ solution was diluted with 19 ml of water and brought to boil for 15 min (solution I). A 1.2 ml of 0.5% sodium citrate aqueous solution ($Na_3C_6H_5O_7$) was rapidly added under stirring for 3hr to the solution (I). The heating was switch off as soon as the mixture of solutions changed to wine-red and keep stirring until the solution cooled to room temperature. The thin film was obtained at volume of 1.5 ml of the Au solution prepared above was diluted by 10 ml of distilled water and allow to contact with 10 ml of toluene solution containing 0.5 ml octylamine,5 ml ethanol was injected into the water layer to start the reaction and can pull hydrophilic citrate-stabilized Au-nanoparticles into the water/toluene. After 24 hours, a very thin film of Au had formed at the interface of liquids and was transferred to glass substrates. For preparing CdS films, 30 ml of hexane containing 0.13 mmol of cadmium chloride (CdCl2) as Cd^{+2} source prepared above was allowed to stand in contact with 30 ml of an aqueous layer containing drops of ethy-
amine acted as capping agent and 0.028 mmol sodium sulfide (Na_2S) as a source of S^{-2} the beaker was set into an oven, held at 40 ºC, and left undisturbed for 4 hours. After 4 hours, the interface of the two liquids changed to yellow colour, which indicated to the formation of a nanocrystalline thin film.

2.1. Absorption of Nano Films at the interface

The UV-vis spectroscopy is an advanced technique used to quantify the light that is absorbed and scattered by a sample in the form nanomaterial Fig.3.

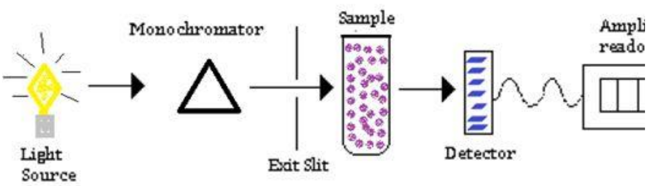

Fig.3: Components of a UV/Visible spectrophotometer [43].

a sample as the thin film is placed in appropriate place between a light source and a detector, the beam of light is passed through the sample, and the intensities of transmitted beams of light are observed over the wavelength range.

The absorption of a photon by the nano-films occur if its energy is greater than the bandgap because of the quantum confinement, decreasing the particle size results in the blue shift of the absorption.[44] A relatively sharp absorption indicated to the excitonic peak, the lowest excited state exhibiting a large oscillator strength. While the position of the peaks depends on: the bandgap, the size of the particle, its shape and width is strongly affected by the distribution in size, Therefore multy dispersed samples typically exhibit only a shoulder in the absorption spectrum at the position of the excitonic transition, which is responsible for the absorption of visible radiation. Less obvious absorption features in the smaller wavelength range correspond to excited states of higher energy [45] It can be emphasized that the larger the number of the spectral and the more distinctly they are resolved in the absorption spectrum, the smaller is the size dispersion of the sample.

A typical of the absorption spectra of our study on citrate-capped colloidal of gold nanoparticles and their assembled as films at the interfacial region between water /toluene in the presence of octylamine shows in Fig.4.

Generally, in collides of gold nanoparticles (blue curve) displays bands the absorption peak at 510 nm due to the Plasmon in the visible region of the electromagnetic spectrum [46]. Due to the small size of Au nanoparticles the interactions of light in resonance with the surface free electrons of gold nanoparticles, create oscillation [47] at the surface of nanoparticles as a result of this optical phenomena, known surface Plasmon resonance leads to absorption at a specific wavelength.

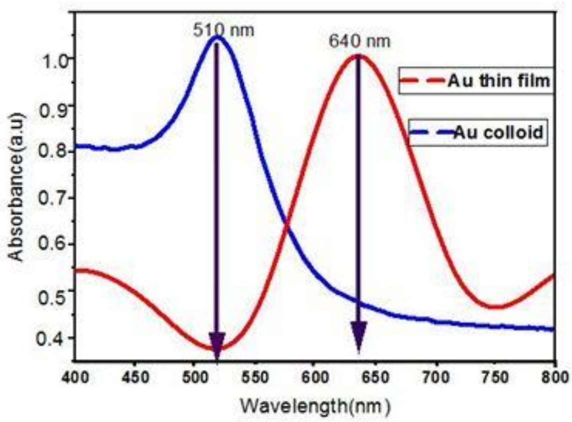

Fig.4: The UV-visible spectra of citrate capped Au nanoparticles a before and after assembly.

The wavelength of the absorption peak depends on size and shape of particles, in the case of thin film (red curve), there is a stronger couple of electrons resulting in redshift of the plasmon resonance wavelength to 640 nm. In effect, the film will conduct electricity better than isolated colloid.

When semiconductor nanocrystals interact with light the absorption band observed in the absorption spectra because of the transition of an electron from the valence band to conduction band which appeared at a specific wavelength:

In Fig.5, typical of the electronic spectra recorded for semiconductor nanoparticles of film at the water /n-hexane at 40°C.It exhibited the absorption approximately 600 nm because of the direct transition of electrons from the valence band to conduction band because of quantum size.

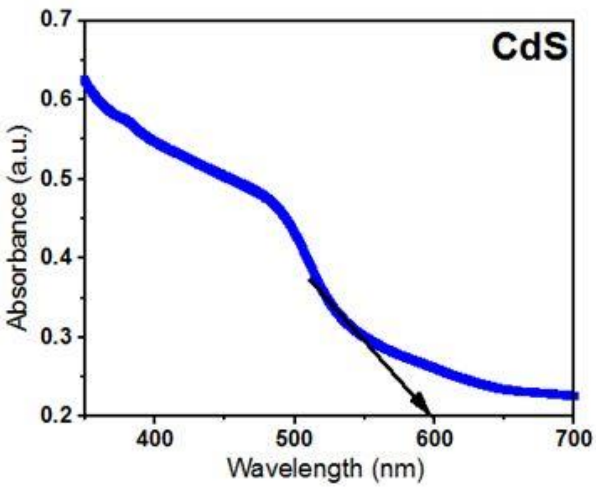

Fig.5: Absorption spectra of CdS film at water/n-hexane interface obtained at 40°C.

3. Conclusion

Nano thin films ranging from few nanometers to micrometres have been used for various applications including optoelectronics, photonic, and magnetic devices. The growth of nano-crystalline materials at the interface of two immiscible liquids is a growing area. Considerable development has been made to use different pair of immiscible liquids and the effect of temperature on the absorption spectra was investigated for different materials such as (Au, CdS). There is a great potential to produce nano-thin films cheaply by this technique at the commercial level.

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4. References

[1]- Akimov,Y.A., Koh,W. S., Sian,S. Y., Ren,S. (2010).Nanoparticles enhanced thin filmsolar cells metallic or dielectric nanoparticles . Applied Physics Letters. **96**: 073111.

[2]- Akimov, Y.u. A.and Koh, W. S.(2008). Resonant and nonresonant plasmonic nanoparticle enhancement for thin-film silicon solar cells. Nanotechnology. **21**:235201.

[3]- Han, L., Qin, D., Jiang, X.,Liu, Y., Wang, L., Chen, J. Cao .Y. (2006).Synthesis oh high qualityzinic blende CdSe nanocrystals and their application in hybrid solar cells. *Nanotechnology*.**17**: 4736–4742.

[4]- Bailey, R .E., Smith, A .M., Nie, S.(2004).Quantum dots in biology and medicine *Physica E*: Low-dimensional Systems and Nanostructures.**25**:1–12.

[5]- [5].Niitsoo, S. K., Sarkar, C., Pejoux, S., Rühle, D., Cahen,G., Hodes(2006) Chemical Bath Deposited CdS/CdSe- Sensitized Porous TiO2 Solar Cells. Photochemistry and Photobiology a-Chemistry.**181**: 306-313.

[6]- Nozik, A. (2002). Quantum dot solar cells. *Physica E*: Low-dimensional Systems and Nanostructures.**14**:115–120.

[7]- Robel,I.,Subramanian,V.,Kuno,M.,Kamat,P.V.(2006). Quantum Dot Solar Cells. Harvesting Light Energy with CdSe Nanocrystals Molecularly Linked to Mesoscopic TiO_2 Films. American Chemical Society.**128**: 2385–2393.

[8]- Chu, K .C., Su, W .S., Chen, Y. F. (2006). Liquid crystals driven by CdSe semiconductor. Journal of Applied Physics.**100**: 024516.

[9]- Muchuweni,E.,Sathiaraj,T.S.,Nyakotyo,H.(201 7). Synthesis and characterization of zinc oxide thin films for optoelectronic applications.Heliyon on Science direct.**3**: 00285.

[10]- Muchuweni,E., Sathiaraj,T.S., Nyakotyo,H(20 16) Effect of gallium doping on the structural, optical and electrical properties of zinc oxide thin films prepared by spray pyrolysis Ceramics International. 42 :10066-10070.

[11]- Oduor,A.O. and Gould, R..D.(1998). A comparison of the DC conduction properties in evaporated cadmium selenide thin films using gold and aluminum electrodes. Thin Solid Films. 317: 409-412.

[12]- Mohanchandra,K.P. and Uchil, J.(1997). Thermoelectric power of CdS and CdSe films deposited on vibrating substrates. Thin Solid Films.305: 124-129.

[13]- Lee, M.J. and Lee, S.C. (1999).Extraction of the trap density and mobility in poly-CdSe thin films. Solid-State Electronics. 43: 833-838.

[14]- Samanta,D.Samanta,B.Chaudhuri,A.K.S.,Pal .U.(1996) Electrical characterization of stable air-oxidized CdSe films prepared by thermal evaporation. Semiconductor Science and Technology.11: 548-553.

[15]- Bräuer,G.(2014). Films and Coatings: Technology and Recent Development. Comprehensive Materials Processing.**4**:57-73

[16]- Yang, J., Kecheng, Li., Jun ,F., Roy, G. G.(2015).Direct-liquid-evaporation chemical vapor deposition of smooth, highly conformal cobalt and cobalt nitride thin films. Materials Chemistry C.**3**:12098-12106.

[17]- Shelke ,H.D., Lokhande ,A.C., Kim ,J.H., Lok hande ,C.D.(2017). Photoelectrochemical (PEC) studies on Cu_2SnS_3 (CTS) thin films deposited by chemical bath deposition method. Colloid Interface Sci. **506**:144-153.

[18]- O'Brien,P., Saeed.J.(1996).Deposition and characterization of cadmium sulfide thin films by chemical bath deposition. J.Cryst.Growth.**158**:497-504.

[19]- Hiroshi,U.,Hideo,Y.,Yoshikazu,O.,Manabu,K.(2003).Thin CdS films prepared by metalorganic chemical vapor deposition. Solar Energy Materials & Solar Cells.**75**:219-226.

[20]- O'Brien, P. and Nomura, R.(1995). Single-molecule precursor chemistry for the deposition of chalcogenide(S or Se)-containing compound semiconductors by MOCVD and related methods. J. Mater. Chem.**5**: 1761-73.

[21]- Murai ,H.,Abe, T., .Matsuda,J., Sato,H., Chiba,S.,Kashiwaba,Y.(2005). Improvement in the light emission characteristics of CdS:Cu/CdS diodes. Applied Surface Science.**244**:351-354.

[22]- Ullrich,B.,Bagnall,D.M.,Sakai,H.,Segawa,Y.(1 999). Photoluminescence properties of thin CdS films on glass formed by laser

ablation.Solid state communications.**109**:757-760.

[23]- Vanalakar, S.A.,Mali, S.S., Suryavanshi, M.P., Patil, P.S.(2010) Quantum size effect in chemo synthesized nanostructured CdS thin films. Journal of *Nanomaterials* and Biostructures **5**:805–810.

[24]- Hur, S.G., Kim, E.T.,Lee, J.H.,Kim, G.H., Yoona, S.G(2008). Characterization of photoconductive CdS thin films prepared on glass substrates for photoconductive-sensor applications. Journal of Vacuum Science *and* Technology B.**26**: 1334–1337.

[25]- Dolocan,V.(1983).Electrical, photoelectrical and optical properties of cadmium selenide thin films. Rev. Roum. Phys.**28**: 647-654.

[26]- Prakash,G., Neupane,W., Tanju,Ma., Yildirim,Y.,Tang,L., Zhang,Y.Lu.(2019). 2D organic semiconductors, the future of green nanotechnology. Nano Materials Science.**1**: 246-259.

[27]- Kalyanikutty, K.P.,Gautam,U.K. and Rao,C.N.R.(2007).Ultra-Thin Crystalline Films of CdSe and CuSe Formed at the Organic-Aqueous Interface. Journal of Nanoscience and Nanotechnology. **7**: 1916-1922.

[28]- Murray, C.B., Norris, D.J. and Bawendi, M.G. (1993).Synthesis and characterization of nearly monodisperse CdE (E = sulfur, selenium, tellurium) semiconductor nanocrystallites. Journal of the American Society. **115**: 8706-8715.

[29]- Lin, Y., Skaff, H.,Emrick, T.,Dinsmore, A. D.,Russel, T. P.(2003).Nanoparticle Assembly and Transport at Liquid-Liquid Interfaces. Journal of Science .**299**: 226–229.

[30]- [30].Dickinson, E., Golding, M., Povey, M. J. W.(1997) Creaming and Flocculation of Oil-in-Water Emulsions Containing Sodium Caseinate. *Journal of Colloid Interface Sci.* **185**: 515-529.

[31]- Frising, T., Noïk, C., Dalmazzone, C.(2006) The Liquid/Liquid Sedimentation Process: From Droplet Coalescence to Technologically Enhanced Water/Oil Emulsion Gravity Separators. A Review. *Journal* of *Dispersion Science* and *Technology*. **27**:1035-1057.

[32]- Simovic,S.,Prestidge,C.A.(2004). Nanoparticles of VaryingHydrophobicityat the Emulsion DropletWater Interface: Adsorption and Coalescence Stability. Langmuir. **20**: 8357-8365.

[33]- Taylor,P.(1998).Ostwald ripening in emulsions. Adv. Colloid Interface Sci.75: 107-163.

[34]- Takeshima, T.,Tada, Y.,Sakaguchi, N., Watari, F., Fugetsu, B.(2015) DNA/Ag nanoparticles as antibacterial agents against gram-negative bacteria. Journal of Nanomaterials. **5**: 284–297.

[35]- Reynolds, D.C., Leies,G.L., Antes, L., Marburger,R.E.(1954) Photovoltaic effect in cadmium sulfide. Journal of Physical. Rev. **96**:533.

[36]- Yuan,X.Y.,Xie,T.,XuL,G.C.,Zhang.D.,Zhuang, Y.L.(2004) A simple synthesis route to CdS nanomaterials with different morphologies by sonochemical reduction. Journal of aterials Letters.**58**: 794-797.

[37]- Stanley, A.G.(1975). Cadmium sulfide solar cells. Applied Solid State Sciences . **5**: 251-366.

[38]- Rao,C.N.R and Kalyani,K.P.(2008).The Liquid–Liquid Interface as a Medium To Generate Nanocrystalline Films of Inorganic Materials. Accounts of chemical research.**41**:489-499.

[39]- Benjamin, I.(1996). Chemical Reactions and Solvation at Liquid Interfaces: A Microscopic Perspective. Chem. Rev. **96**:1449–1475.

[40]- Luo, G.,Malkova, S.,Yoon, J., Schultz, D. G., Lin, B.,Meron, M., Benjamin, I., Vanysek, P., Schlossman, M. L.(2006). Ion-Distributions Near a Liquid-Liquid Interface. Journal of *Science*.**311**:216–218.

[41]- K.Burak Ucer,Ph.D (2010) Thin Film Growth and Evolution Department of physics,Wake forest university.winston-salem, Carolina.,USA

[42]- Hauser, E.A. and Lynn, J.E.(1940) Separation and fractionation of colloidal systems. *Journal* of *Industrial* and *Engineering Chemistry* (Washington, D. C.).**32**: 659-62.

[43]- Dean,J.R., Jones, A. M., Holmes, D., Reed,R., Weyers,J., Jones.A.(2002) *Practical Skills in Chemistry*, Pearson Education Limited, UK, 165.

[44]- Gaponenko, S.V. (1998) Optical properties of semiconductor nanocrystals. Cambridge University Press, Cambridge (UK).

[45]- Gianluca, G., Jaco, J. G., Ward van der, S., Indy , F., Baldur, B., Nicholas, K., Sachin K.,Laurens ,D. Siebbeles,A., and Arjan, J. H.(2019). Spectroscopic Evidence for the Contribution of Holes to the Bleach of Cd-Chalcogenide Quantum Dots. *Nano* Letters.**19**:3002-3010

[46]- Palaniappan, S., Dalila, M., Robert,W., Franck,D.,Rabah,B., Sabine.S.(2019). Plasmon Induced Electrocatalysiswith Multi-Component Nanostructures. Journal of Materials.**12**:43.

[47]- Lee,J.H.,Hyeon,Y.C.,Hye,K.C., Lee,Y., Jeong,W.C.(2018). Application of Gold Nanoparticle to Plasmonic Biosensors International Journal of Molecular Sciences.**19**:2021.