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College of Science
Department of Physics

Hydrothermal Synthesis of ZnS-NPs for Modifying the SPF of Sunblock Lotion

Research Project

Submitted to the department of Physics in partial fulfillment of the requirements for the degree of B.A or BSc. In

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Abstract

This paper describes a dependable hydrothermal approach for producing zinc sulfide Nano powder (ZnO-NPs) aiming to enhancement the SPF factor of the commercial sunblock lotion. Thus, Zinc chloride $ZnCl_2$ and thiourea $CS(NH_2)_2$ was used as starting material for generating ZnS-NPs. UV-Vis spectroscopy were used to analyze the ZnS-NPs' and optical properties, The energy band gap was determined to be roughly 3.85 eV, which was typically lower than the energy band gap of ZnS in bulk. To improve UV light absorption and raise the SPF of commercial sunscreen lotion, different quantities of ZnS-NPs were applied. Sun protection factor (SPF) values were calculated from absorption data in the 290-320 nm range and the Mansur equation. It is evident that increasing the amount of zinc oxide nanoparticles also boosts SPF and UV absorption. In spite of using about 2g of ZnS-NPs, the SPF value improved to 70 percent (increased from 20 to 34). The high degree of crystallinity, combined with the Nano metric structure of hydrothermal manufactured ZnO-NPs, are the essential components for boosting dynamic scattering of incoming light for the purpose of increasing the SPF factor.

Chapter One (general introduction)

1.1- Introduction

Over the past two decades nanoparticles have gained great attention due to their small size that ranges between 1 to 100 nanometers in size .These particles manifest significantly different physical and chemical properties to their larger material counterparts and mostly used for improvement human wellbeing mainly in term of health care (Lu, F. and Astruc, D., 2018).

Zinc sulfide (ZnS) is an II-VI compound semiconductors , and nanoparticles made of Zinc sulfide (ZnS NPs) are well-known as excellent photo catalyst because of their unique optical properties such as band gap energy, retention time, the high light absorption, electron-hole recombination time, and high negative reduction-oxidation potential of excited electrons (O'Hare et.al, 2007) . ZnS nanoparticles have the abilities for applications in region such as non-straight optical Devices, antibacterial agent and rapid optical switches and they have been considered widely. Currently ZnS nanoparticle is commonly used in biomedical as well as optoelectronic applications. There are variety of methods available to synthesize ZnS particles such as electrochemical deposition and sonochemical while hydrothermal technique is most used method for preparation of nanoparticles which is solution reaction-based approach that occurs in a wide temperature range from room temperature to very high temperatures. In nature, ZnS is a white- to yellow-colored powder or crystal (Scott, and Barnes, 1972). It exists in two crystallographic forms having cubic (sphalerite or zincblende) or hexagonal (wurtzite) crystal structure as show in Fig. (1.1). The hexagonal form is a thermodynamically metastable phase, which is usually stable at very high temperature, while the cubic form is more thermodynamically stable phase at low temperature. ZnS has a direct transition type band structure. The cubic form has a band gap of 3.54 – 3.6 eV, whereas the band gap of hexagonal form is the highest being 3.74 –3.87 eV (Shao, et.al, 2003). ZnS exhibits high transparency over the wide spectrum region between 380 nm and 25 µm .The electrical resistivity is in the order of 10^4 Ω.cm with n-type electrical conductivity. It can be doped as both n-type and p-type semiconductor, which is unusual for the II–VI semiconductors (Hoa, et.al, 2009).

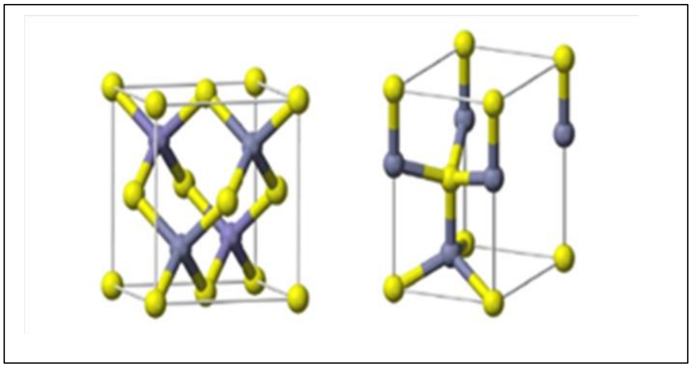

Fig. (1): The schematic diagrams of the zinc blende (left) and wurtzite (right) crystal structures of ZnS (Scott, and Barnes, 1972).

Since the early 1900s, sunscreens have been developed as protective agent against harmful ultraviolet (UV) radiation and have been proven to reduce rates of non-melanoma and melanoma . The efficacy of a sunscreen is usually expressed by the sun protection factor (SPF), which is defined as the UV energy required to produce a minimal erythema dose (MED) on protected skin, divided by the UV energy required to produce a MED on unprotected skin (Sudhahar, and Balasubramanian, 2013).

Manufacturers often uses nano sized minerals in sunscreens to enhance clarity and SPF that are both usable and effective. Thus far, zinc oxide or titanium dioxide nanoparticles are most common used type of nanoparticles in sunscreens . Many studies have produced no evidence that zinc oxide or titanium dioxide nanoparticles can cross the skin in significant amounts (Saiyao et.al, 2021).

However more research is needed to fully understand the extent to which nanoparticles may harm cells and organs if they're introduced into our bodies. There is limited data available regarding ZnS nanoparticles application in sunscreens.

1.2 aim of this study:

This research examines how (ZnS-NPs), which are generated through a hydrothermal synthesis, affect the Sun Protection Factor (SPF) of sunscreen lotion. The SPF values for different weight percentages of ZnS-NPs blended with a brand-name sunscreen lotion were determined using UV spectroscopy and the Mansur equation in the wavelength region of 290 to 320 nm. The SPF values were increased by increasing the quantity of ZnS-NPs.

Chapter Two

Experimental Techniques and Characterization Tools

2.1-Introduction

This chapter is divided into two sections. The first consists of a description of the experimental techniques used in this study to fabricate ZnO-NPs using the hydrothermal method. In this method, ($ZnCl_2$) and Thiourea CS(NH2)2 with deionized (DI) water are used as a stratifying material, and the effect of temperature on the growth of hydrothermal at (180 ^oC) has been studied. Lastly, using UV-VIS spectroscopy, the optical properties of the prepared powder have been evaluated. Different weights of the collected ZnS Nanopowder have been mixed with commercial sunblock lotion aiming to improve the SPF-factor. The complete experimental procedure is depicted in Figure (2).

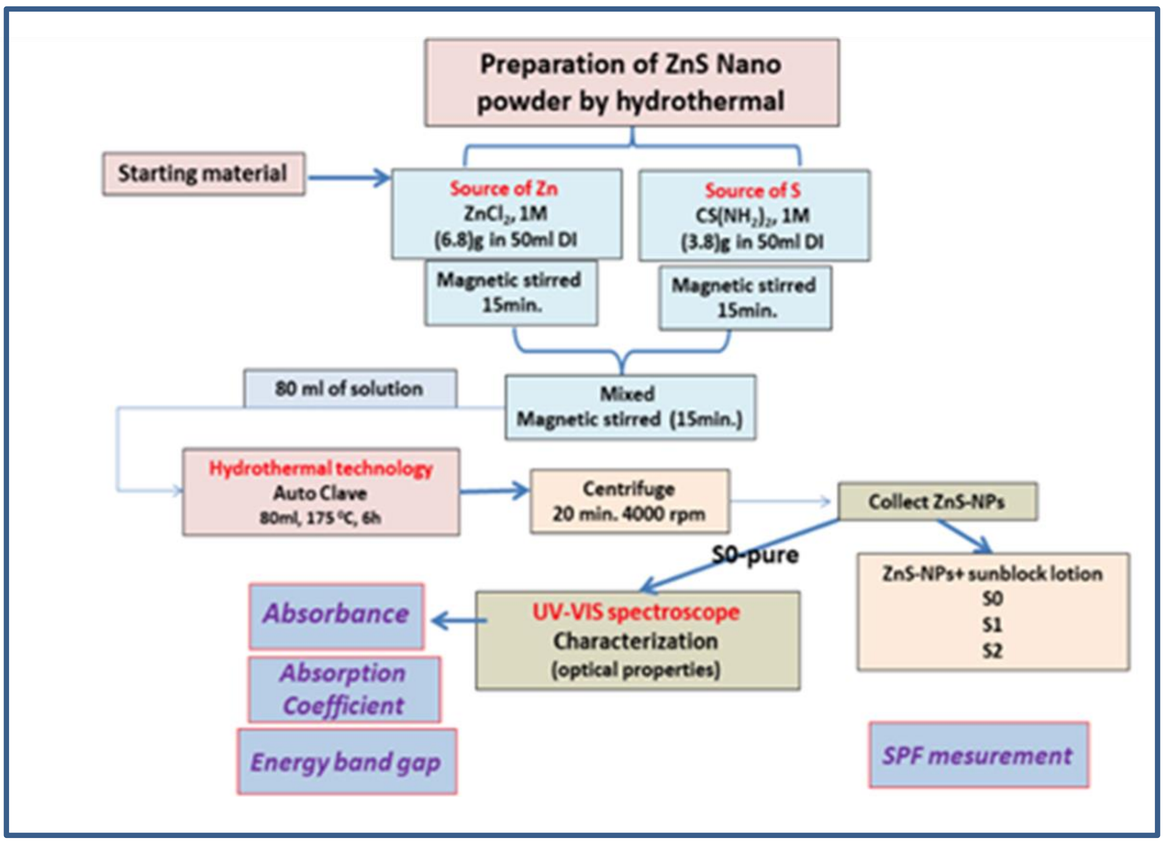

Fig (2) Experimental procedures flowchart.

Part One
ZnS-NPs Preparation

2.2- Hydrothermal Technique

Hydrothermal method is one of the most common and effective synthetic routes to fabricate the nano-material with a variety of morphologies. Hydrothermal synthesis is a heterogeneous chemical reaction in the presence of aqueous solvents (water) above 100˚C at pressures greater than 1 atmosphere in a closed system in order to dissolve and recrystallize materials which are relatively insoluble under normal conditions (Li et al., 2015).

2.3- Instruments for Hydrothermal Processes

A vessel/container (lined reaction chamber) with stand highly corrosive solvent at high temperature and pressure is the main part of a hydrothermal set up, which is known as autoclave reactor (Wang, 2003). Their actions take place in steel autoclaves, and inside is the Teflon vessels in the range 100-220˚C. Teflon is an inert material, so it does not get into the reaction with the starting materials. Teflon vessels are filled with the starting materials (transition metal oxide, organic component, secondary metal salt, and phosphoric acid) with the reaction solution (water was used for hydrothermal and organic solution used for solvothermal process). To provide enough pressure, minimum 50% of the reaction cup is filled with the solvent. Then, Teflon vessels are placed in steel autoclaves and putted in the oven. The reactions are kept for some hours or some days at a constant temperature above 100˚C (Shock, et al., 1992). The system is sealed well in order to avoid any solvent leakage during heating process. The sealed autoclave is kept into the electrically heated oven for providing desired temperature. On application of the desired hydrothermal synthesis temperature, an autogenously pressure is generated within the autoclave. At the end of the required reaction time, the reaction cups are cooled slowly to room temperature. Crystals that have best quality and size are formed in this cooling period. After that, the products are washed several times with pure water in order to remove the solvent traces from the products (Li et al., 2015).

In this work, a 100 ml Teflon reactor (Model: TeficBiotech) was used, as shown in Fig. (3). The reactor consists of inner Teflon or (PTFE) lined reaction chamber shelled with high quality Stainless Steel (SS) body. Also, upper and lower reactor Stainless Steel (SS) disk to cover the upper and bottom of Teflon chamber which closed with stainless steel cup engraved from inside supplier with treaded cup for well sealing.

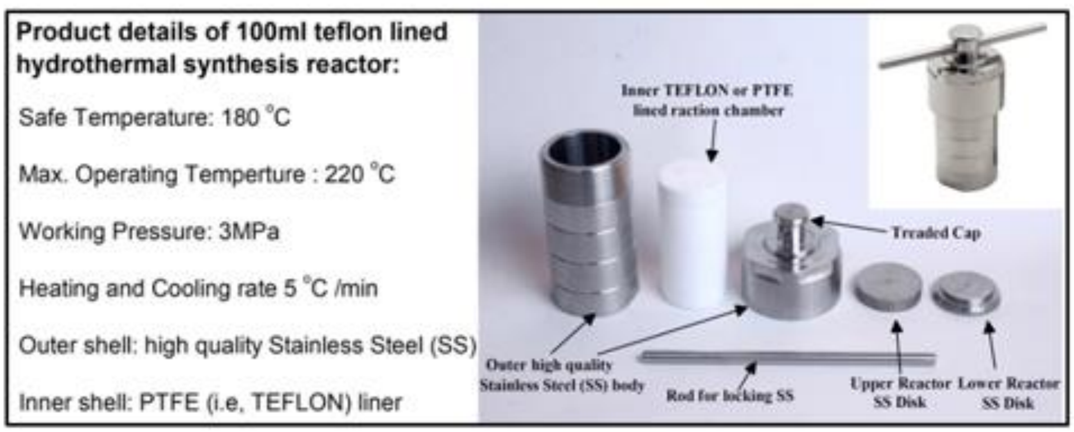

Fig.(3) Teflon lined autoclave 100 mL shows (Steel autoclave and Teflon vessel) with Product details

In hydrothermal synthesis, the grain size, particle morphology, microstructure, and phase composition can be controlled by tuning parameters such as temperature, process duration, and pH of the solution (Zhou et al., 2008). Furthermore, the reaction media plays an important role since the properties of the solvent can be adjusted by modifying the type and volume ratio of the solvent, where the solvothermal process named due to the type changing of the solvent (Deng et al., 2002).

2.4- Solutions Preparation

To create a solution and extract the nano-powder from it we used two materials the first one was $CS(NH_2)_2$ we used (3.8)g of it and add it into (50)ml water and stirred it for 15 minutes on the magnetic stirrer without heat , then we used the second one which is $ZnCl_2$ we added (6.8)g into (50)ml water and stirred it for 15 minutes on the magnetic stirrer without heat , then we mixed both solutions and stirred it for 20 minutes on the magnetic stirrer without heat , after that we put it inside the Teflon and put it inside the oven for 6 hours .

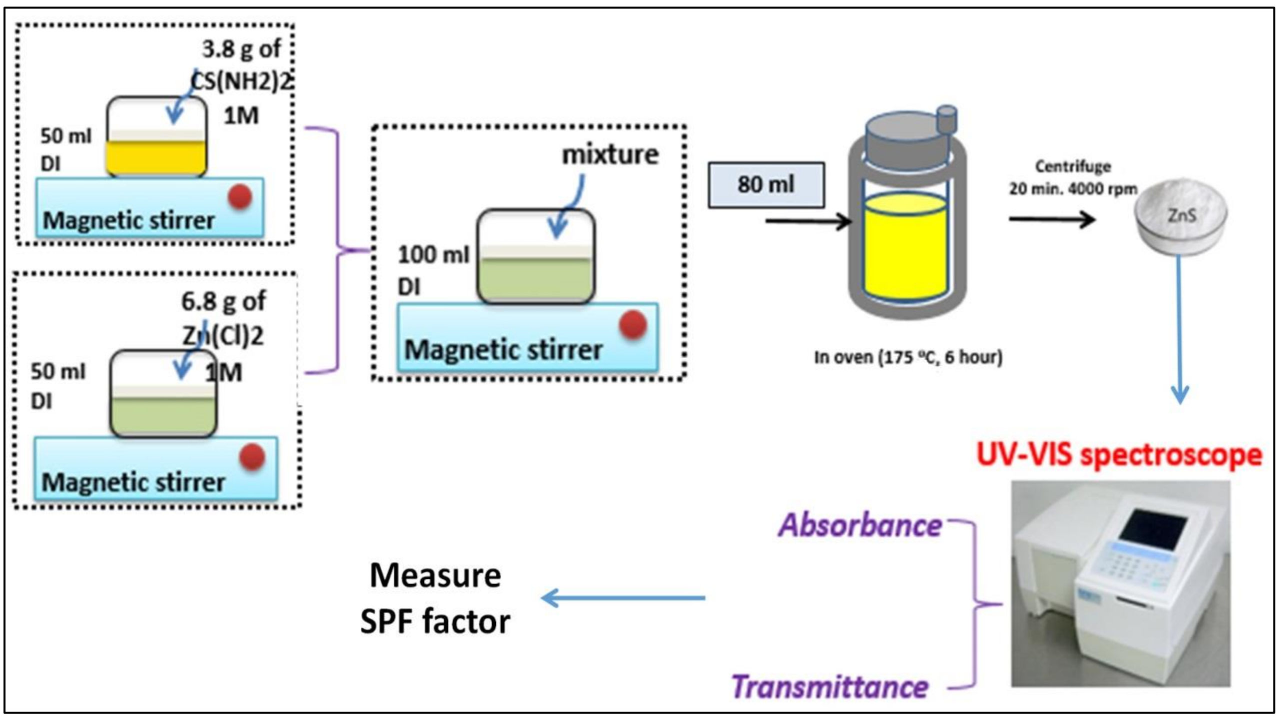

Fig. (4) Procedure for synthesis of ZnS Nano powder by hydrothermal

Part Two
Measurements and Analytical Techniques

2.5 - Optical analysis

The optical property study forms a considerable part while evaluating a thin film performance. The photon absorption, transmission characteristics, directs and indirect band-gap evaluation is some of the important parameters that are determined to characterize a thin film.

The optical transmittance (T%) and absorbance (A%) spectra of the samples were carried out at room temperature by (Shimadzu UV-VIS mini 1240) spectrophotometer in the wavelength range (200-1100 nm). The spectral distributions of transmittance for the ZnS-NPs were determined. The following steps can be used to calculate the optical measurements:

-The absorption coefficient(α)can be computed from the absorbance spectrum using the formula (Schroder, 2006):

$$\alpha = 4\pi k/\lambda, \quad \ldots\ldots\ldots\ldots\ldots\ldots.. \quad (2.12)$$

- The photon energy (hv) as a function of wavelength is calculated by (Islam, 1997):

$$hv = hc/\lambda \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots. \quad (2.13)$$

Where (λ) is the wavelength of the incident light.

The general band gap formula is given as (Schroder, 2006):

$$a(hv) = B\,(hv - Eg)\gamma \; \ldots\ldots\ldots\ldots\ldots\ldots..(2.14)$$

Where(B) is an energy-independent proportionality constant, and γ = 1/2, 3/2, 2, 3 for direct allowed, direct forbidden, indirect allowed, and indirect forbidden transitions respectively.(Eg) is the band gap energy.

-The band gap energy can be obtained by extrapolating the linear portion of $[a(hv)]^2$ vs. (hv) curve to zero absorption, where this is the usual method for the determination of the value of the energy band gap from absorption spectra (Schroder, 2006), and (Marinkovic, 2013).

2.6. Cosmetic applications of ZnS-Nanopowder

In order to apply nanoparticles of zinc oxide in cosmetics as a commercial product, physical sun cream was chosen (Sunblock lotion with SPF 20). They produced three separate samples. The initial sample was a sunscreen cream without ZnS-Nanopower it is the first sample (S0). (S1) was the second sample which had (1g) of ZnS-NPs. As well as the third sample (S2) had 2g of ZnS-Nanopower, the samples were analyzed with using a UV-VIS Spectrophotometer. The Mansur equation has been used to determine the SPF rating of sunscreen (Dutra et.al, 2003).

The Mansur equation is defined as:

$$SPF = CF \sum_{290}^{320} EE(\lambda) \times I(\lambda) \times Abs(\lambda) \qquad (1)$$

When the correction factor (CF) is set to 10, erythema effect spectrum is (EE), (A) is absorbance, and solar intensity spectrum is (1).

Chapter three
Result and discussion

3.1- Introduction

The optical characterization of prepared Nano-podwer gives information about the physical properties such as the band gap energy and band structure, etc... To study the optical properties of the films, the optical absorption spectra of the ZnS-Nano-powder were prepared at temperatures (180 ^{o}C) by hydrothermal method. In addition to the adding different amount of ZnS-NPs to the sunblock lotion aiming to enhancement its SPF factor.

3.2 - The absorbance spectra

The optical absorbance spectra of ZnS-NPs prepared were measured at room in the wavelength range of (200 - 1100) nm, as shown in Fig. (5). from this figure it was observed that the absorption is very low at invisible near infrared region, however the absorption is extreme high at ultraviolet region.

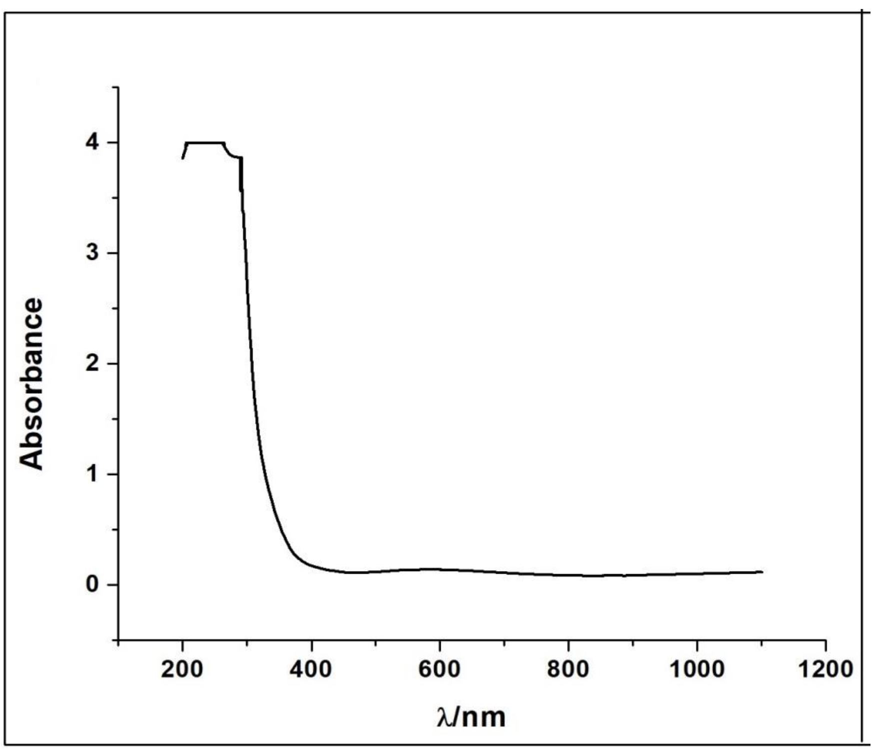

Fig. (5): absorbance spectra versus wavelength for ZnS-NPs.

3.5 - The optical band gap energy

The data point near the absorption edge can be used to determine the band gap (E_g) of the samples using equation ($\alpha h\nu = A (h\nu - Eg)^n$).

Fig. (6) shows the variation of [αhv] against (hv) for ZnS-NPs prepared by hydrothermal technique. The plot near the absorption edge indicates that ZnS-NPs is a direct band gap nature. The band gap is determined by extrapolating the straight line portion of the graph to the energy axis at α=0. Our results lie in the range of (3.85 eV), which is a good agreement with other researchers as compared in the table 3.1.

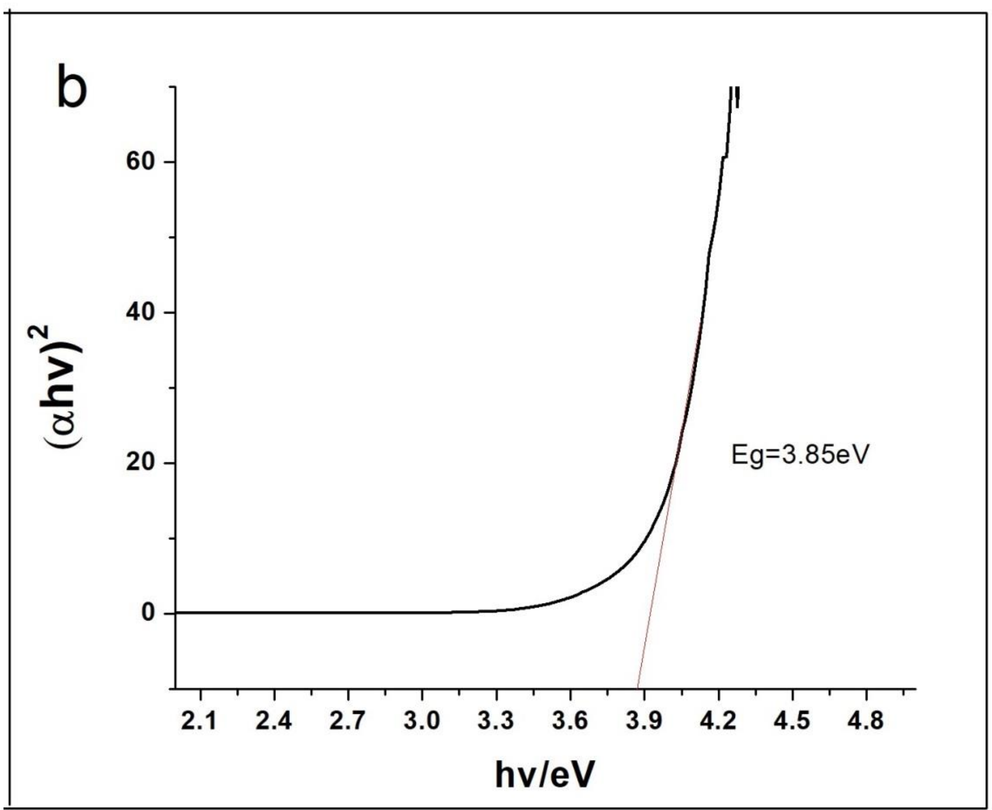

Fig. (6): Variation of $\alpha(h\nu)^2$ with photon energy for ZnS-NPs.

Table (3.1): values of determined optical energy band gap forZnS-NPs prepared by hydrothermal method

researcher	Energy band gap (ev)
(Sabaghi, et.al 2018)	3.81
(Aneesh, 2010)	3.443
Hoa, et al. 2009	3.77
This work	3.85

3.3 Synthesized ZnS-NPs to Develop SPF

Due to their greater production and lessened brightness, nanoparticles are recommended in cosmetics. However, it is uncertain how particle size affects UV absorption. As a result, the Sun Protection Factor (SPF) values and UV-VIS spectroscopy are utilized to evaluate nano'sperformance (Sudhahar et.al, 2013). To determine the samples' activity to absorbance in the UVA and UVB zones, UV-Vis Spectroscopy has been used. Figure 7 shows the absorbance spectra that measurements were taken in the range (200-800) nm, for sunscreen lotions untreated (S_0), mixed with different weight percentages of 1g (S_1), and with 2g (S_2) of ZnS-NPs. As shown in the table (1), the Sun Protection Factor (SPF) values for each of the samples are calculated by using the Mansur equation (1) to absorption data with wavelengths between 290 and 320 nm.

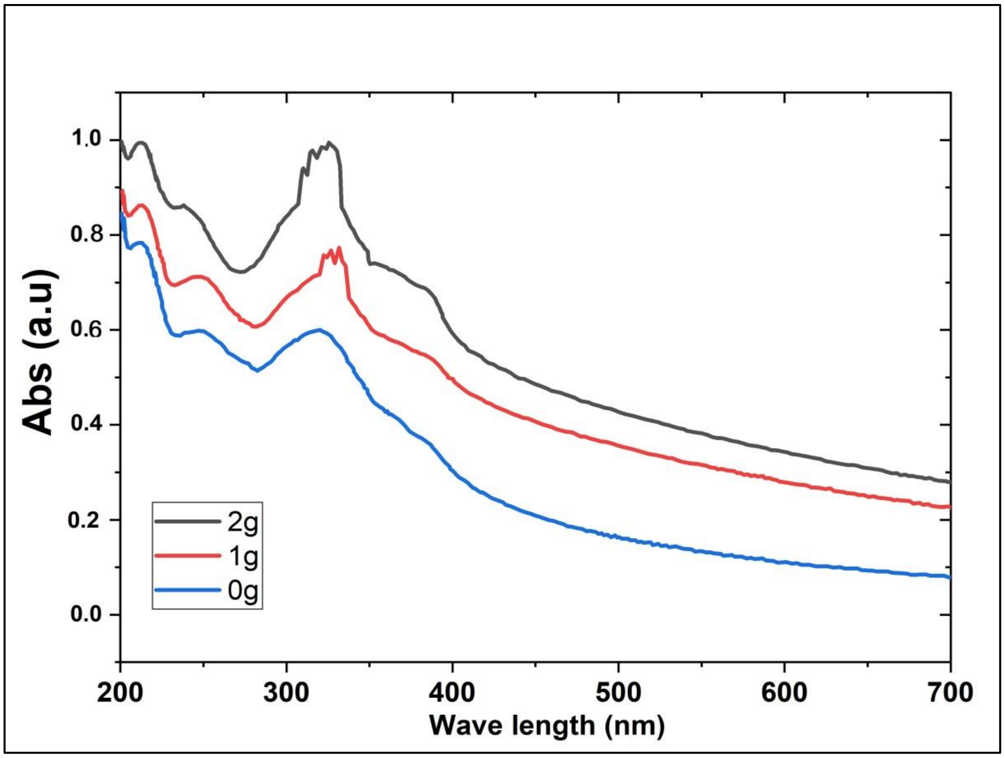

Fig.(7): UV-VIS Spectra of the samples (lotion mixed with different weight of ZnS-NPs)

Table 2: displays the Sun Protection Factor of basic lotion with different ZnS-NP weights.

Name of sample	ZnS-NPs (weight)	SPF rate
S_0	0	20
S_1	1g	28
S_2	2g	34

According to the results, the absorption and SPF value of the sunscreen lotion rise as ZnS-NP density increases, the value of SPF improved by 70 % when comparing with the standard samples. The nanometric size, high crystallinity, and presence of synthesized ZnS-NPs were validated by UV-VIS to account for these findings. These parameters promote the dynamic scatter of incoming light and enhance the sample's absorption of UV radiation. As ZnS-NP density increases, light will be scattered more widely. Finally, compared to identical nanoparticles made using other methods, synthesize nanoparticles are typically more reactive. Since they can be produced in large quantities and less taxing on the skin than other NPs made by a chemical method, hydrothermal synthesized nanoparticles' prospective method of developing a new brand UV composite filter (lotion combined with nanoparticles) is a step toward better UV-filters for human health and environment.

Chapter Four

Conclusions and Suggestions

4.1- Conclusion:

- ZnS-NPs have been susscfuly prepared by hydrothermal technology.
- The optical properties improve that the increase in the energy band gap of the prepared ZnS-NPs to (3.85eV) compared to (3.4eV) for bulk.
- Adding two gram of the ZnS-NPs is enough to enhancement the SPF factor of commercial sunblock lotion (with SPF=20) to 34 which is enhancement by 70%.

However, the result of this investigation shows that sunlight exposure to the skin has a great impact on our health, especially on our skin that it can damage our skin , skin burning , early aging of the skin , and all of this purposes can lead to akin cancer . For this situations people in all ages should limit the amount of time they spend in the sun . Best solution for avoiding UV radiation of sunlights is by applying sunscreens especially this types with high value of SPF that can radiates more incoming UV from sunlight’s , this reduces the risk of skin cancer.

4.2- Suggestions for future work

1- Using different metal oxide instate of ZnS to enhance the SPF factor of commercial sunblock lotion.

2- Synthesis ZnS-Nano powder by different method such as green method.

References

Lu, F. and Astruc, D., 2018. Nanomaterials for removal of toxic elements from water. *Coordination Chemistry Reviews*, *356*, pp.147-164.

O'Hare, I.P., Govender, K., O'Brien, P. and Smyth-Boyle, D., 2001. Chemical bath deposition of zinc sulfide from acidic solutions. *MRS Online Proceedings Library (OPL)*, *668*.

Scott, S.D. and Barnes, H.L., 1972. Sphalerite-wurtzite equilibria and stoichiometry. *Geochimica et Cosmochimica Acta*, *36*(11), pp.1275-1295.

Shao, L.X., Chang, K.H. and Hwang, H.L., 2003. Zinc sulfide thin films deposited by RF reactive sputtering for photovoltaic applications. *Applied Surface Science*, *212*, pp.305-310.

Krunks, M., Dedova, T. and Açik, I.O., 2006. Spray pyrolysis deposition of zinc oxide nanostructured layers. *Thin Solid Films*, *515*(3), pp.1157-1160.

Hoa, T.T.Q., Canh, T.D. and Long, N.N., 2009, September. Preparation of ZnS nanoparticles by hydrothermal method. In *Journal of Physics: Conference Series* (Vol. 187, No. 1, p. 012081). IOP Publishing.

Sudhahar, V., Balasubramanian V, 2013. Sun production factor (SPF) determination of marketed sunscreen formulation by in-vitro method using UV-VIS spectrophotometer. *Archives of Applied Science Research*. 5(6): p. 119-122.

Dutra, E.A., Oliveira, D.A.G.D.C., Kedor-Hackmann, E.R.M. and Santoro, M.I.R.M., 2004. Determination of sun protection factor (SPF) of sunscreens by ultraviolet spectrophotometry. *Revista Brasileira de Ciências Farmacêuticas*, *40*, pp.381-385.

Sudhahar, V. and Balasubramanian, V., 2013. Sun production factor (SPF) determination of marketed sunscreen formulation by In-Vitro method using UV-VIS spectrophotometer. *Archives of Applied Science Research*, *5*(6), pp.119-122.

Li, J., Wu, Q. and Wu, J., 2016. Synthesis of nanoparticles via solvothermal and hydrothermal methods. In *Handbook of nanoparticles* (pp. 295-328). Springer, Cham.

WANG, Z.L., 2003. New developments in transmission electron microscopy for nanotechnology. *Advanced Materials*, *15*(18), pp.1497-1514.

SHOCK, E.L., OELKERS, E.H., JOHNSON, J.W., SVERJENSKY, D.A. AND HELGESON, H.C., 1992. Calculation of the thermodynamic properties of aqueous species at high pressures and temperatures. Effective electrostatic radii, dissociation constants and standard partial molal properties to 1000 C and 5 kbar. *Journal of the Chemical Society*, *Faraday Transactions*, *88*(6), pp.803-826.

DENG, Z.X., WANG, C., SUN, X.M. AND LI, Y.D., 2002. Structure-directing coordination template effect of ethylenediamine in formations of ZnS and ZnSe nanocrystallites via solvothermal route. *Inorganic Chemistry*, *41*(4), pp.869-873.

ZHOU, F., ZHAO, X., YUAN, C. AND LI, L., 2008. Vanadium pentoxide nanowires: hydrothermal synthesis, formation mechanism, and phase control parameters. *Crystal Growth and Design*, *8*(2), pp.723-727.

Islam, M., 1997. *The development and characterization of novel Pd/Sn ohmic contacts to n-type GaAs* (Doctoral dissertation, Dublin City University).

Schroder, D.K., 2006. Semiconductor material and device characterization, Arizona State University Tempe, Aza John Wiley & Sons. *Inc*, *Publication*, p.192.

Marinkovic, M., 2013. *Contact resistance effects in thin film solar cells and thin film transistors* (Doctoral dissertation, Jacobs University Bremen).

Sabaghi, V., Davar, F. and Fereshteh, Z., 2018. ZnS nanoparticles prepared via simple reflux and hydrothermal method: Optical and photocatalytic properties. *Ceramics International*, *44*(7), pp.7545-7556.

Aneesh, M.P., 2010. Growth and characterization of nanostructured wide band gap semiconductors for optoelectronic applications. *Cochin University of Science & Technology*.

Hoa, T.T.Q., Canh, T.D. and Long, N.N., 2009, September. Preparation of ZnS nanoparticles by hydrothermal method. In *Journal of Physics: Conference Series* (Vol. 187, No. 1, p. 012081). IOP Publishing.