Summary

This thesis focused on two main purposes: (1) preparation of gold, silver, zinc sulfide, silver/zinc sulfide core-shell nanoparticles (2) investigation of the effects of incorporating the prepared samples with the solar cells

This Thesis contains Four Main Chapters as Follows:

Chapter I

This chapter contains two main sections: an exhaustive introduction to nanomaterials and a literature review. It has started with a brief history of nanomaterials. Then, it presented the introduction of nanomaterials. Some important definition of nanomaterials has been mentioned. In addition, the classification of nanomaterials according to origin, dimensionality, morphology, and composition was reviewed. Also, the two main factors that affect the properties of nanoparticles, such as quantum confinement effect and surface effect, were explained. Preparation methods of nanomaterials based on the built structure and starting state of materials were presented. Properties, importance, and some applications of nanomaterials were highlighted. Outline several previous studies related to preparing gold, silver, zinc sulfide, silver/zinc sulfide core-shell nanoparticles, and their application in the solar cell were reviewed. Aim and plan of the work are written at the end of this chapter.

Chapter II:

This chapter contains some of the underlying theoretical principles required to understand the mathematical basis of the instruments used in the characterization of our prepared nanoparticle samples. It has initiated with a short introduction to electromagnetic radiation. Then, introduce the

mathematical basis of UV-Vis spectroscopy, transmission electron microscopy, dynamic light scattering, x-ray diffraction, Fourier transform infrared spectroscopy. Moreover, solar cell generations, parameters, factors affecting their efficiency were described in detail.

Chapter III:

In this chapter, the chemicals and experimental methods used to prepare the gold, silver, zinc sulfide, and silver/zinc sulfide core-shell nanoparticles were mentioned.

Gold nanoparticles were prepared in two different methods: First method, a fixed concentration of gold chloride hydrate ($HAuCl_4.3H_2O$) and cetyltrimethylammonium bromide (CTAB) with a change in the ratio of sodium borohydride ($NaBH_4$). Second method: fixed concentration of gold chloride hydrate ($HAuCl_4.3H_2O$) and sodium borohydride ($NaBH_4$) with a change in the ratio of cetyltrimethylammonium bromide (CTAB).

Silver nanoparticles were prepared using a fixed concentration of cetyltrimethylammonium bromide (CTAB) (in chloroform), sodium borohydride ($NaBH_4$), and polyvinylpyrrolidone (PVP) with different ratios of silver nitrate ($AgNO_3$).

Zinc sulfide nanoparticles were prepared in two different ways (i) constant sodium sulfide (Na_2S) molar ratio and temperature with different zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) molar ratios. (ii) fixed sodium sulfide (Na_2S) and zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) molar ratio with different temperatures [50°-100°].

 Two steps were used to prepare silver/zinc sulfide core-shell nanoparticles: first, preparation of silver nanoparticles using ascorbic acid ($C_6H_8O_6$),

polyvinylpyrrolidone (PVP), sodium hydroxide (NaOH), and silver nitrate ($AgNO_3$). Second step: using a fixed amount of zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$), ammonium nitrate (NH_4NO_3), polyvinylpyrrolidone (PVP), sodium sulfide (Na_2S), and ascorbic acid ($C_6H_8O_6$) at a different quantity of as-prepared silver nanoparticles (first step).

In addition to the above, components of the characterization technique such as UV-Visible spectroscopy, transmission electron microscopy, dynamic light scattering, x-ray diffraction, Fourier transform spectroscopy, solar cell deposition, and current-voltage equipment was also reviewed.

Chapter IV:

During this chapter, the result obtained from our present prepared samples were presented and explained, where the ultraviolet-visible spectra of gold nanoparticles were measured and discussed. The distinctive band of the surface plasmonic resonance (SPR) appeared at wavelengths 527nm, 526nm, 526nm, and 526nm for [AuNPs(S1)-AuNPs(S4)] samples, respectively. The SPR band appeared at 528 nm for all samples [AuNPs (S5)- AuNPs(S8)]. We concluded from these results that the particle sizes of AuNPs do not affect by the change of concentrations for both sodium borohydride (NaBH4) and ammonium bromide (CTAB). However, it has an apparent effect on the full width at half maximum (FWHM) of SPR bands. Surface plasmonic resonance (SPR) bands of silver nanoparticles (AgNPs) samples was appeared at (414nm, 413nm, 415nm, 417nm, and 425nm) for the samples [AgNPs(S9)- AgNPs(S13)], respectively. These results indicated that the SPR band's position was shifted to a higher wavelength by increasing the silver nitrate concentration, which means the particle size increased. Also, FWHM was increased by increasing the silver nitrate

concentration. Maybe attributed to the increase of the particle sizes by the increasing of silver ions, which leads to a decrease the number of silver nanoparticles, but it increases the particle sizes. Absorption bands of zinc sulfide has appeared at (305 nm, 289 nm, 287 nm, 284 nm, and 283 nm) for the samples [ZnSNPs(S14)- ZnSNPs(S18)], and at (308 nm, 307 nm, 304 nm, 303 nm, and 300 nm) for the samples [ZnSNPs(S19)- ZnSNPs(S24)], respectively. The optical band gaps were calculated via Tauc's plot at (4.66 eV, 4.78 eV, 4.92 eV, and 4.93 eV for the samples [ZnSNPs(S14)- ZnSNPs(S18)], and at (4.77 eV, 4.74 eV, 4.75 eV, 4.74 eV, 4.73 eV, and 4.66 eV) for samples [ZnSNPs(S19)- ZnSNPs(S24)], respectively. Based on the quantum size effect, as the wavelength decrease, the particle size also decreases, and the band gap increased. The plasmon band position of the as-prepared silver nanoparticles AgNPs(S25) that used in core-shell preparation has appeared at 408 nm. Absorption bands of the silver/zinc sulfide core-shell nanoparticles were observed at 450 nm, 469 nm, and 498 nm for the samples [Ag/ZnS(S26)-Ag/ZnS(S28)], respectively. The broadening that occurred in the bands implying to the formation of the core-shell.

TEM images of gold nanoparticles visualize the nanoparticles spherical form with a narrow size polydispersity, except for some triangle and hexagon form that has appeared in AuNPs(S7). The particle sizes were calculated for the TEM image using ImageJ software, then the average sizes were obtained by Gaussian distribution at 7 nm, 7 nm, and 10 nm for the samples AuNPs(S3), AuNPs(S4), and AuNPs(S7), respectively. TEM images of the sample AgNPs(S10) showed that the particles were formed as a dark point with a spherical shape with an average size of 2 nm, whereas most of the

silver nanoparticles of AgNPs(S11) were spherical with a random distribution with average size 4 nm. Zinc sulfide images have confirmed the preparation of ZnSNPs with a nearly spherical shape; also, it shows that TEM images have two regions, one is low distribution, and the other is high. The average particle sizes were estimated at 5 nm, 3 nm, 3 nm, and 3 nm for ZnSNPs(S14) and ZnSNPs(S18), ZnSNPs(S19), and ZnSNPs(S22), respectively. Silver/zinc sulfide core-shell nanoparticle images reveal a different image contrast implying that a zinc sulfide shell successfully coated the surface of the silver nanoparticles. The average particle sizes were estimated at 27 nm, 81 nm, and 177 nm for Ag/ZnS(S26), Ag/ZnS(S27), and Ag/ZnS(S28), respectively.

Dynamic light scattering has also been used to estimate the average particle size of the samples. The average particle sizes were obtained at 33.03 nm, 23.46 nm, and 30.26 nm for gold nanoparticles AuNPs(S3), AuNPs(S4), and AuNPs(S7), respectively, at 87 nm and 77.68 nm for silver nanoparticles AgNPs(S10) and AgNPs(S11), at 11.74 nm, 132.9 nm, and 315.9 nm for zinc sulfide nanoparticles ZnSNPs(S14), ZnSNPs(S19), and ZnSNPs(S22), respectively, and at 39.04 nm, 127.8 nm, and 48.39 nm for silver/zinc sulfide core-shell nanoparticles Ag/ZnS(S26), Ag/ZnS(S27), and Ag/ZnS(S28), respectively. The large variation in particle size obtained by dynamic light scattering and transmission electron microscopy is logical because dynamic light scattering measures the average particle size of huge quantity comparable with the transmission electron microscopy. Besides that, TEM measure only the inorganic core of the particle, since the organic shell is less electron-dense in comparison to the inorganic core and thus transparent in TEM.

The crystalline nature of gold, silver, and zinc sulfide nanoparticles were studied using x-ray diffraction. The particle sizes were calculated using Scherrer's equation from the mean peak at 2θ around ($38.45°$) is 21.48 nm, 33.57 nm, and 30.74 nm for the samples [AuNPs(S1)-AuNPs(S3)], and it was at 9.94 nm, 8.25 nm, and 8.59 nm for the samples [AuNPs(S5)-AuNPs(S7)], respectively. The mean peak of silver nanoparticles was seen at 2θ around ($37.7°$), and the crystal sizes calculated at 8.08 nm, 7.89 nm, 8.12 nm, 12.42 nm, and 8.23 nm for the samples [AgNPs(S9)-AgNPs(S13)], respectively. The particles size of zinc sulfide were measured at 2θ ($28°$) is 2.83 nm, 2.18 nm, 2.19 nm, 2.15 nm, and 2.14 nm for the samples [ZnSNPs(S14)-ZnSNPs(S18)], and the particle size is 2.83 nm, 4.04 nm, 3.97 nm, 3.92 nm, 3.76 nm, and 4.17 nm for the samples [ZnSNPs(S19)-ZnSNPs(S24)], respectively.

Fourier transform infrared results studies the chemical coordination between our nanoparticles prepared samples and the functional groups of capping materials. Gold nanoparticles obtained a band at about 1481 cm^{-1} indicating the coordination of gold nanoparticles with $C - N^+$ group in the CTAB molecule. In addition, the absorption bands appeared in the silver nanoparticles spectra at around 1346 cm^{-1} resulted from the involvement of nitrogen atom in pyrrolidine in silver nanoparticles formation. Also, the band position shift that occurs in silver nanoparticles occurred at 530 cm^{-1}, and 452 cm^{-1} indicates to the coordination between silver atom and oxygen or nitrogen atom. Furthermore, the zinc sulfide nanoparticles spectra reveal a band at about 1004 cm^{-1} and 925 cm^{-1} due to the asymmetric and symmetric $Zn - S$ vibration. Moreover, silver/zinc sulfide core-shell nanoparticles show a variation in the band position from the capping materials due to the

surrounding of silver nanoparticles by zinc sulfide nanoparticles, which proved the formation of the core-shell.

The current-voltage characteristics of the polycrystalline silicon solar cell deposited by gold, silver, zinc sulfide, silver/zinc sulfide core-shell nanoparticles under illumination were investigated. The effect of the nanoparticles on the parameter of the solar cell, such as open-circuit voltage (V_{OC}), short circuit current (I_{SC}), maximum circuit voltage (I_m), and the maximum circuit current (I_m) were measured, fill factor (FF), and power conversion efficiency (η) were calculated. Compared with the power conversion efficiency achieved for polycrystalline silicon solar cell (η =14.29 %), cell deposited by gold nanoparticles exhibit efficiency at (η = 13.65 % and 13.14%) for AuNPs(7 nm) and AuNPs(10 nm) , zinc sulfide at (η = 12.57 % and 11.74%) for ZnSNPs(2.15 nm) and ZnSNPs(3.97 nm), silver/zinc sulfide core-shell nanoparticles at (η = 13.02 %) for Ag/ZnS(177 nm). From these findings, we can conclude that the nanoparticles sample does not affect the efficiencies of the solar cells, which may be attributed to the low surface coverage of the silicon solar cells by the nanoparticles leading to reduce light scattering. Moreover, the samples may require annealing at high temperatures before measurements to evaporate the water from the surface of the samples. What assured our hypothesis, photocurrent measurements show a remarkable enhancement that has examined after a long time of I-V measurements, which caused the sample to dry. The photocurrent values were estimated at 58.5, 72, 75.7, 78.4, 76.3, 76.5, and 79.4 for the samples blank (silicon solar cell), Si/AuNPs(S7), Si/AgNPs(S11), Si/ZnSNPs(S17), Si/ZnSNPs(S21), Si/[Ag/ZnS(S26)], and Si/[Ag/ZnS(S28)], respectively.