

AZERBAIJAN NATIONAL ACADEMY OF SCIENCES
INSTITUTE OF CHEMICAL PROBLEMS

Written by

MAHMOUD ELROUBY MOHAMMED MAHMOUD

**ELECTROCHEMICAL SYNTHESIS OF CADMIUM SULFIDE THIN AND
NANO FILMS FROM THIOSULFATE SOLUTIONS ON DIFFERENT
ELECTRODES (Ni, Pt AND MWCNT) AND STUDY OF SOME THEIR
PROPERTIES**

2308.01- Electrochemistry

SUMMARY

of

A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy in Chemistry

Baku - 2014

The work was performed at the Institute of Chemical Problems named akad.M.F. Nagiyev of Azerbaijan National Academy of Sciences

Scientific supervisor:

D. Sc. Chem.

A.Sh. Aliyev

Official opponents:

Prof. D. Sc. Chem.

V. N. Fateev

Prof. D. Sc. Chem.

I. I. Mustafayev

The leader organization: Baku State University (Physical and Colloid chemistry department)

Defense of the Dissertation will be held on "27" March 2014 at 10⁰⁰ o'clock in the Dissertation Council D.01.021, Institute of Chemical Problems named acad. M.F. Nagiyev, National Academy of Sciences of Azerbaijan, Baku, H. Javid Ave, 29.

The Dissertation is available in the library of the Institute of Chemical Problems named acad. M.F. Nagiyev, National Academy of Sciences of Azerbaijan.

The summary was sent at "21" February 2014

Dissertation council,
Scientific secretary
Ph.D. of technical sciences,

S.A. Aliyeva

The relevance of the work. In the twenty-first century, information technologies, industry of devices (electronics), and the rapid development of alternative energy sources and optoelectronics industry are main problems facing the development of science. One of the main directions for the development of knowledge-based industries is to spend less expensive material than the highest quality materials and producing of highly efficient product materials. Nanoscience and nanotechnology in this regard in the last 20 years, have a number of available advantageous, and they are studied on the basis of their properties in the development of the industry that has entered a new stage. Thus, the small size of nanoparticles gave them different physical properties differ from the bulk materials and opportunity for using in various fields of engineering and technologies. In this respect, the interesting field of electrochemical applications of carbon nanotube (including double layer capacitors, fuel cells, solar cells and electrochemical deposition process), is growing by the day.

Alternative energy such as solar is one of energy sources which has some important and useful features. Solar energy is one of renewable energy sources that are not depleted ecologically. Solar energy can be converted into other type of energy by using variety of methods. The Conversion of solar energy into electrical or chemical energy, in the visible light region via semiconductor materials that have high efficiency is one of the actual problems. To solve this problem, by synthesis of semiconductor materials that have high photo- effective properties. The synthesis of semiconductor materials can be achieved by different methods. For example, chemical deposition, pyrolytic decomposition, vacuum thermal evaporation and electrochemical methods. The electrochemical method has a great potential effect for synthesis of nano and thin layers of semiconductors compared with the other methods. First of all, it should be noted that, the electrochemical method has very good properties, by changing the electrolyte composition and electrolysis conditions and parametres, the synthesis of semiconductors can be easily controlled in the desired and suitable form. For that, the electrochemical method provides advantages compared with the other methods.

Cadmium sulfide semi-conductor thin and nano films electrochemically synthstized hashigher photo-efficiency in the visible region of the solar spectrum, therefore, it still has not lost its relevance. In addition, cadmium sulfide can be used as a buffer layer in photovoltaic devices, or it can be used widely as window layers in solar cells with an absorber layer of CdTe, Cu₂S, or CuInSe₂, and it plays an indispensable role. It should be noted that, the synthesis of nano and thin layers of cadmium sulfide is used in solar cells and batteries in different countries of the world.

The aim of the dissertation. Synthesis of cadmium sulfide thin films and nano - wires by electrochemical method on different electrodes platinum, nickel, and multi walled carbon nanotube (MWCNT) from thiosulfate acidic solutions and

studying some thermo-electrical, electrochemical and photo-electrochemical properties of the produced films is the main aim of the work.

These goals had been achieved, by resolving the following problems in the dissertation;

1. Studing and identification of kinetics and the mechanism of the electrochemical reduction of thiosulfate anion in acidic solution on Pt and MWCNT electrodes.
2. Studing and identification of the electrochemical deposition of cadmium ions in acidic solution on Pt and MWCNT electrodes.
3. Synthesis of cadmium sulfide nano and thin layers by electrochemical method and studying of kinetics and the mechanism of the electrodeposition on various electrodes from solutions containing Cd^{2+} and thiosulfate.
4. According to the stepwise characterization and detecting the composition of the nano and thin films of n-type hexagonal crystalline CdS, the optimal electrodeposition conditions have been detected.
5. Studying the thermoelectrical, electro- and photo - electrochemical properties of the obtained thin films and nano - structure CdS have been performed.

Scientific novelty. For the first time, from the acidic thiosulphate solutions, CdS nanoparticles and nanowires on Ni and multi walled carbon nano tubes electrodes were obtained by electrochemical way. CdS/Ni and CdS/MWCNT hetero-systems have been investigated through the photo-electrochemical studies. The photo-activity of these systems have been relatively enhanced in the visible light region. For the first time, the kinetics and the mechanism of the Cd electrodeposition and thiosulfate electroreduction processes on MWCNT paste electrode, have been identified and studied.

The main provisions of the defense:

- Development of the electrochemical synthesis of high-quality pure n-type hexagonal crystalline semiconductor CdS thin films in the form of nanoparticles and nano-wires from acidic thiosulfate electrolyte solution on Ni, Pt and MWCNT electrodes.

- Cd and $\text{S}_2\text{O}_3^{2-}$ separately and together were electrochemically reduced, the kinetics of the electroreduction process were also studied on Pt and MWCNT electrodes. The electrochemical process was studied for the possible detection of their mechanisms.

- The properties of the electrodeposition process of semiconductor thin films and nano-coatings CdS were detected by studying the effects of electrolysis conditions and electrolyte composition that are useful for practical purposes.

- Studying of some thermo-electrical, electrochemical and photo-electrochemical properties of thin and nano films structure of CdS.

The practical significance of the dissertation work.

The scientific results obtained by the electrochemical synthesis of n-type hexagonal crystalline CdS thin and nano films can be used for the conversion of solar energy and chemical energy into electricity and also used for the creation of heterosystems used for various purposes. The main provisions of the dissertation may be offered as a subject for electrochemistry of semiconductors and nanotechnology courses.

The reliability of the results: The experimental part of the dissertation is devoted to obtain latest model of the structure of high photo-sensitivity, and repeatedly CdS by the mean of electrochemical devices. Kinetic regularities and some electro-, photo-electrochemical properties have been determined by different methods. The results were analyzed in comparison with data from the literature.

Approbation of the work: Materials of the dissertation have been reported and discussed in the following conferences and symposia. First International Conference on Chemistry and Chemical Engineering (Baku, 2013), with the participation of foreign countries. Young scientists, graduate students and students of VII All-Russian conference "Mendeleev - 2013" (St. Petersburg, 2013). International Symposium of Material science and Engineering Technology "ISMET 2013" (China, Guangchu). Academic MF Nagiyev scientific conference devoted to the 105th anniversary (Baku, 2013).

Published materials: The results of the dissertation work are; 13 scientific articles (including 9 papers and 4 conference material) have been published. 7 articles were published in scientific international journals in various countries around the world.

Structure and scope of the dissertation: The dissertation consists of introduction, 4 chapters, main conclusions, 157 cited references, 177 pages, 75 figures and 4 tables.

A brief summary of the work

The work consists of an introduction and four chapters. The introduction part consists of; the relevance of the work, identify the goals and objectives of the research, the scientific novelty of the work, the practical value and scientific significance of the results.

The first chapter provides literature surveys on the electrodeposition of cadmium sulfide on metal substrates from different media and different electrochemical methods, as well as electrochemical application of carbon nano tubes as a substrate.

The second chapter describes the materials and methods for the study of electrochemical processes in relation to the co-deposition of cadmium and sulfur, methods of preparation of solutions and electrodes. The methods of elemental analysis of the cathodic deposits, determination of physical and electrochemical properties of semiconductor films have been described.

Solutions for the electrodeposition of the Cd-S alloys were prepared as follow:

A certain amount of CdSO_4 was dissolved in deionized water containing a necessary amount of H_2SO_4 to give a clear solution at the required pH, then adding required amounts of $\text{Na}_2\text{S}_2\text{O}_3$ and thiourea were dissolved in a small amount of deionized water.

The electrolyte was used in photoelectrochemical studies was a solution of 0.5 M Na_2SO_4 .

Multi walled carbon nanotube paste electrode can be prepared by mixing multiwall carbon nanotubes with paraffin oil in a mortar and pestle. The paste was then packed into a polyethylene tube of a diameter 3 mm. Electrical contact was made by pushing a copper wire down the tube into the back of the mixture.

The investigation of the conductivity type of the electrodeposited cadmium sulfide was performed by physical and electrochemical methods in this work.

The electrodeposits of CdS was investigated and characterized by XRD, EDX, SEM analysis, the nickel substrate was used due to its availability.

For studying kinetics and mechanism of Cd-S alloy electrodeposition, can be done by potentiodynamic cyclic and potentiostatic polarization curves. The polarization curves were recorded by using of **IVIUMSTAT** electrochemical interface— computerized potentiostat.

All of electrochemical processes were carried out in a quartz glass three-electrode electrochemical cell equipped with a jacket of four slots. Silver / silver chloride electrode was used as a reference electrode. Auxiliary electrode is a platinum foil, its surface is approximately 100 times greater than the surface of the working electrode.

The **ModuLight**-module was used as a light source. The add-on module operates in combination with the IviumStat. The ModuLight, by default, contains 7 LEDs with wavelengths ranging from 460-740 nm.

The chemical composition percent of Cd and S in the electrodeposited Cd-S was determined by using of JEOL JSX 3222 Element Analyzer with energy-dispersive X-ray fluorescence spectroscopy (EDXRF), system (JEOL, Japan).

The surface morphology of the modified electrodes with the electrodeposited CdS was carried out using a JEOL JSM-5500 LV Scanning Electron Microscope, SEM, (JOEL, Japan). At an acceleration voltage of 15 k eV and a working distance of about 4-5 mm.

The conductivity type of the electrodeposited CdS layers was determined by using temperature-conductivity relation and Mott-Schottky method and also photoelectrochemical measurements.

☒ Third and fourth chapters contain the following;

1. THE ELECTROCHEMICAL REDUCTION OF THIOSULFATE AND CADMIUM ON Pt- AND MWCNT ELECTRODES

To obtain a successful electrodeposition of CdS, first it should to study the mechanism of the electrochemical reduction behavior of both thiosulfate and

cadmium ions alone. So, it is necessary to recognize and detect the optimal conditions of their electroreduction alone to obtain their optimal co-electrodeposition via the cyclic voltammetric technique.

The voltammetric response of thiosulfate is found to be sensitive to pH, concentration, temperature as well as of the scan rate potential.

Fig. 1 shows the cyclic voltammogram of the 0.01 M $\text{Na}_2\text{S}_2\text{O}_3$ solution containing sulfuric acid at pH = 3, room temperature (295 K) and scan rate of 0.02 V s^{-1} on Pt and MWCNT electrodes.

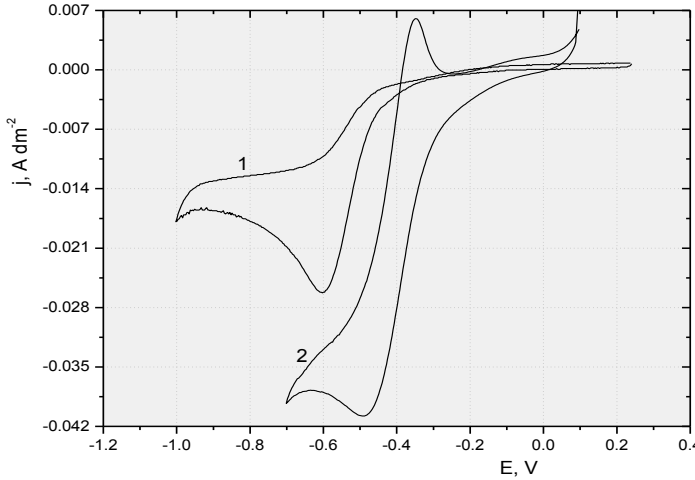
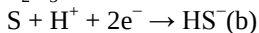
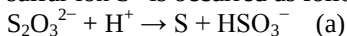


Fig.1. Cyclic voltammogram of 0.01-M $\text{Na}_2\text{S}_2\text{O}_3$ at 0.02 Vs^{-1} on (1) Pt-electrode, (2) MWCNT electrode at pH = 3 and $T = 295\text{K}$.

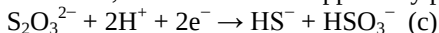
The cathodic peak (lower peak) is observed at -0.6 and -0.49 V on Pt and MWCNT electrodes respectively. It has an irreversible behavior on Pt electrode but has some reversibility on MWCNT electrode. Moreover, the reduction peak of thiosulfate was observed at around -0.8 V on titanium electrode in other work. This difference in behavior and potential of reduction peak value may be attributed to the difference in hydrogen over potential between Ti, Pt and MWCNT electrodes.

Based on the obtain data, the linear response obtained for the correlation between the cathodic peak current density and the square root of the potential scan rate (J_p^c vs. $v^{1/2}$), the diffusion coefficient (D) of thiosulfate was calculated, by the aid of Randles-Sevcik equation to be $1.76 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. The diffusion coefficient value depends on the viscosity and temperature of the electrolyte and not on the electrode material type.

From the obvious data, the mechanism of the electroreduction of thiosulfate at the previous mentioned conditions can be deduced. At the lower pH values (acidic media), the elemental sulfur and hydrogen sulfite (HSO_3^-) ion were released from the investigated $\text{S}_2\text{O}_3^{2-}$ ion. Consecutive reduction of the colloidal sulfur to sulfur ion S^{2-} is occurred as follow;



Therefore, the total reaction apparently proceeds electrochemically as follow:



At more acidic solutions and at longtime electroreduction electrolysis or/and at very low scan rates, the resulted liberated HSO_3^- ions from the dissociated thiosulfate in acidic media can be reduced to sulfur then to S^{2-} ions and water.

The resultant ions of S^{2-} from the electrochemical reduction of thiosulfate can be adsorbed on the surface of the electrode. This will facilitate the production of the semiconductor (CdS) in the following process.

From the data of the dependence of the cyclic voltammetric behavior on temperature it can be noted that, by comparison the value of the activation energy of the electrochemical reduction of thiosulfate ion on platinum electrode and the activation energy on carbon nanotube electrode, in case of platinum electrode the activation energy starting from 24.7 kJ/mole at cathodic potential of -0.468 V to 20.8 kJ/mole at -0.63 V, while the activation energy in case of MWCNT starting from 20.86 kJ/mole at -0.350 V to 20.705 kJ/mole at -0.600 V. This confirms that, in case of platinum the reaction need activation energy more than in case of carbon nano tube electrode to accomplish the reaction (electrochemical reduction of thiosulfate) at these conditions. This is due to that, the carbon nano tube has a catalytic nature more than the platinum at this regard.

The voltammetric response of the investigated cadmium ions is found to be sensitive to pH, concentration, temperature as well as of the scan rate of potential.

Fig. 2 shows the cyclic voltammogram of the 0.01 M Cd^{2+} ions solution containing sulfuric acid at pH = 2.5, room temperature (295K) and scan rate of 0.05 Vs^{-1} on Pt and MWCNT electrodes. It can be observed that, the location of the cathodic peak potential for the electroreduction of cadmium ions was observed around -0.85 and -0.92 V on Pt and MWCNT electrodes respectively. This peak corresponds to the electroreduction of cadmium ion into cadmium metal ($\text{Cd}^{2+} + 2\text{e}^- = \text{Cd}$). Also, the location of the anodic peak potential is observed at -0.52 and -0.43 V on Pt and MWCNT electrodes respectively, which corresponds to the electro-oxidation of the electrodeposited Cd metal ($\text{Cd} - 2\text{e}^- = \text{Cd}^{2+}$). So the peak potential separation is equal to $\Delta E_p > 0.33$ V. This means that the process is a quasi-reversible process at these conditions. Furthermore a pre-adsorbed cathodic weak peak is observed at -0.65 V on MWCNT electrode. This pre-peak is attributed to the adsorption of cadmium ions on the surface of multi walled carbon nano tube paste electrode

(MWCNT). MWCNT is considered and used as a good adsorbent of heavy metal ions from its solutions. It is also noted that, at the cathodic branches (lower peaks), one current crossover was found. This gives an indication to the presence of the typical nucleation process at these conditions.

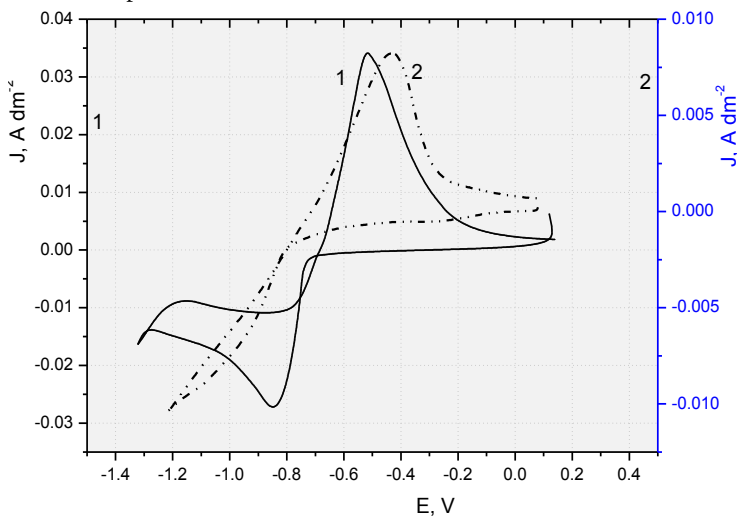


Fig. 2. Cyclic Voltammogram of 0.01-M Cd^{2+} at 0.05 V s^{-1} , $\text{pH} = 2.5$ on (1) Pt and (2) MWCNT electrodes at 295K.

By following the Randles–Sevcik equation and based on the obtained linear response for the correlation between the cathodic peak current density and the square root of the potential scan rate (j_p^c vs. $v^{1/2}$), it can be concluded that, the electron transfer process of the electrochemical reduction of cadmium ion on the particular Pt and MWCNT electrodes is controlled via diffusion phenomena at these conditions. The diffusion coefficient (D) of cadmium ions was calculated to be $3.06 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. This value is larger than the value of thiosulfate at the same conditions.

Effect of the temperature on the electrochemical reduction of Cd^{2+} ions of concentration 0.01 M on the platinum and MWCNT electrodes in the range between 22 and 70 °C, at $\text{pH} = 2.5$ was performed in this work.

Fig.3 shows the scanning electron microscopy photos of the surface morphology of cadmium electrodeposited on multi walled carbon nanotube paste electrode, the conditions are mentioned above, potentiostatically deposited. Homogeneous crystallization was formed at these conditions. The figure shows that, after the electrodeposition process the average diameter of the electrodeposited cadmium are in the range of nanometer (20-70 nm). The

electrodeposited cadmium, as seen in the figure, covers all the distances and the creases (gaps) in between the MWCNTs.

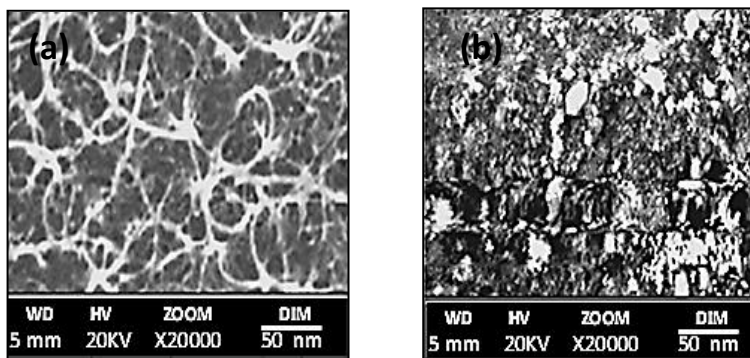


Fig. 3. SEM of (a) MWCNT and (b) electrodeposited cadmium as the conditions are mentioned in Fig. 2.

2. THE ELECTROCHEMICAL DEPOSITION OF CADMIUM SULFIDE ON Pt- AND MWCNT ELECTRODES

After knowing the electrochemical behavior of cadmium and thiosulfate at platinum and carbon nanotube paste electrode (MWCNT), the optimal conditions for electrodeposition of CdS can be easily detected. Nickel sheet was chosen as a substrate for further analysis (SEM, XRD and EDX) of the electrodeposited CdS in this work.

The electrodeposited CdS from thiosulfate acidic solution on platinum and MWCNT electrodes was characterized and examined electrochemically using Mott-Schottky method, physically using temperature ohmic resistance test and photo-electrochemically in sodium thiosulfate solution of concentration 0.5 M.

The cathodic electrodeposition of CdS from aqueous solutions of cadmium sulfate and sodium thiosulfate $\text{S}_2\text{O}_3^{2-}$ in acidic media at 313K, has been achieved using a combination of cyclic voltammetric and potentiostatic techniques in this work. The aim of the present work is to detect the optimal conditions of the electrodeposition method of n-type hexagonal crystalline structure of thin film, nanoparticles and nanowires of CdS on Pt, Ni and MWCNT electrodes of high photosensitive property.

Fig. 4 shows the cyclic voltammograms of $0.01 \text{ M Cd}^{2+} + 0.1 \text{ M S}_2\text{O}_3^{2-}$ without and with 0.1 M thiourea (TU) at 313K on Pt electrode.

The presence of thiourea as an additive can cause grain refining and brightening effect extremely smooth the deposits were obtained. The surface

roughness as well as the mean grain size of the deposits also approached minimum values above this thiourea concentration.

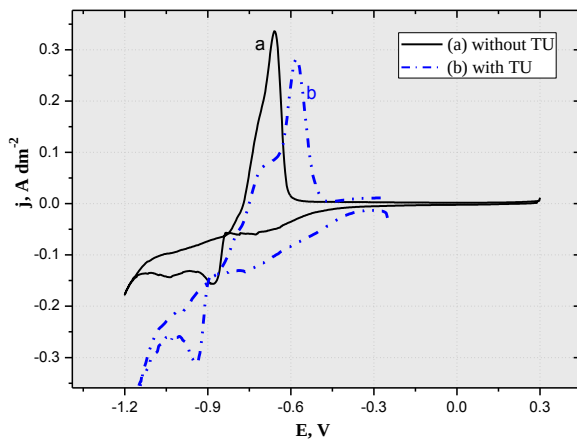


Fig.4. Cyclic Voltammogram of 0.01-M Cd^{2+} + 0.1 M $\text{S}_2\text{O}_3^{2-}$ without TU (a) and with TU (b) at 0.02 V s^{-1} , pH = 2.5 on Pt- electrode at 313K.

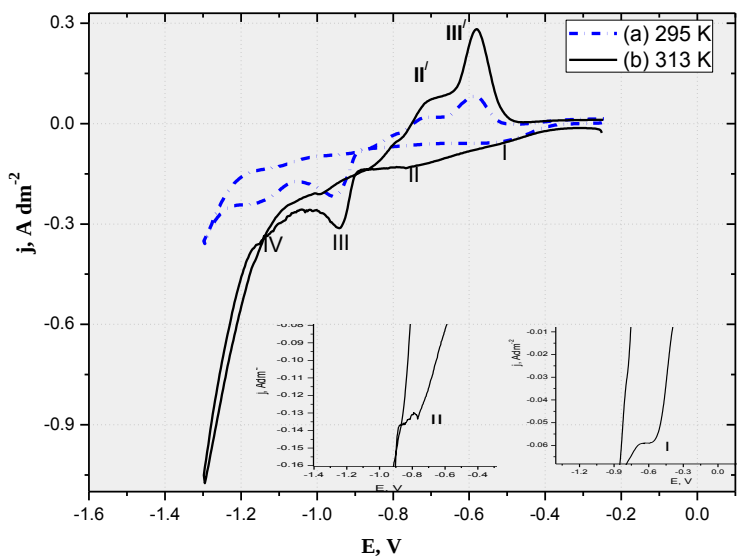


Fig.5. C.V. of 0.01M Cd^{2+} + 0.1M $\text{S}_2\text{O}_3^{2-}$ + 0.1 M $(\text{NH}_2)_2\text{CS}$ at 0.02 V s^{-1} , at pH = 2.5 on Pt- electrode at (a) at 295K and (b) 313K.

It is found in this work that, the optimum condition for the electrodeposition of CdS from thiosulfate acidic aqueous solution on Pt electrode (confirmed by XRD analysis below) as described in Fig. 5(b). Figure 5 shows the cyclic voltammograms of the Pt electrode in 0.01 M Cd^{2+} + 0.1 M $\text{S}_2\text{O}_3^{2-}$ + 0.1 M thiourea (TU) at room temperature 22 °C (a) and at 40 °C (b).

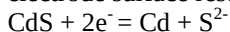
As seen from the shown data, the increase of temperature leads to an increase of the height of the cathodic peak current density (rate of the electrodeposition was accelerated) of the electrodeposition process. But at temperatures higher than 40 °C, it is noted that the electrodeposited cadmium sulfide leaves out the electrode surface. This may be attributed to, higher temperatures lead the electrodeposited CdS becomes amorphous material and the adhesion to the electrode decreases at these conditions.

It is observed that from Fig. 5.2(b), the first cathodic peak (I) at cathodic potential of about ~ -0.55 V attributed to the electroreduction of the colloidal sulfur which produced from the dissociation of thiosulfate at these conditions (acidic). It is also noted that in Fig. 5 (b), the second cathodic peak potential (II) is appeared at a cathodic potential of about ~ -0.75 V attributed to the electrodeposition of CdS (confirmed by XRD). At this potential the electroreduced adsorbed sulfur ions react with the cadmium ions electrochemically on the electrode surface giving CdS. The resulted CdS is adsorbed on the electrode surface of platinum. The resulted liberated HSO_3^- ions from the dissociated thiosulfate in acidic media can be reduced to sulfur then to S^{2-} ions and water.

The formed sulfur ions can be adsorbed on the electrode surface and react with cadmium to form CdS;

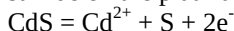
$\text{S}^{2-}(\text{adsorbed}) + \text{Cd}^{2+} = \text{CdS}(\text{adsorbed at the electrode surface}) \dots \text{second peak, II.}$

Also it can be noted in Fig. 5(b), the third cathodic peak potential, III, appears at a potential of ~ -0.93 V at which the free unreacted Cd^{2+} ions are discharged into Cd(0). The fourth cathodic peak, IV, in Fig. 5(b) appears at potential of ~ -1.15 V attributed to the electroreduction decomposition of the electrodeposited CdS on the electrode surface resulting Cd(0) and S^{2-} ;



The wave potential (II') relates to oxidation of S^{2-} to S. At more positive potentials, sulfur (S) can be oxidized to HSO_3^- in acidic media.

The wave potential (III') relates to the oxidation of the electrodeposited cadmium sulfide on the platinum electrode surface;



The separation of the anodic and cathodic waves ΔE_p , depending on the rate of the applied potential scan rate, this indicates that, the process dealing with a quasi-reversible processes.

After knowing the suitable deposition potential for cadmium sulfide from cyclic voltammetric measurements and the optimum conditions, chronoamperometric method can be used for the electrodeposition of CdS. Potential step chronoamperometry is an important and useful experimental technique achieved by stepping the potential ($E_d = -0.8$ V, in between peak II and peak III as in Fig.5b) from one point on a voltammetric wave to another and monitoring the current response.

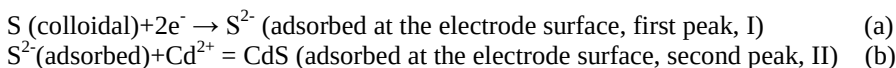
During the chronoamperometric deposition process of cadmium sulfide and by passing the time, the current is decreased but not sharply, moves to more positive direction, this due to the formation of well adsorbed cadmium sulfide layers on the platinum electrode surface, this blocks the electrode surface, hence its electrochemical activity decreases. Furthermore the formed layers of cadmium sulfide (semiconductor material) are less conductive than the platinum itself.

The heterostructure composite of MWCNTs and a semiconductor becomes very important if MWCNTs are employed in optoelectronic devices. CdS has been synthesized electrochemically on multi walled carbon nanotubes paste electrode (MWCNT) from aqueous solutions consists of Cd^{2+} and $\text{S}_2\text{O}_3^{2-}$ at 313K, using potentiostatic technique in this work. Cyclic voltammetric response of thiosulfate and Cd^{2+} together has been investigated. The optimum conditions of CdS electrodeposition were determined on MWCNT electrode.

Fig. 6 shows the cyclic voltammograms of the MWCNT electrode in a solution consists of 0.01 M Cd^{2+} + 0.1 M $\text{S}_2\text{O}_3^{2-}$ + 0.1 M $(\text{NH}_2)_2\text{CS}$ at pH = 2.5, temperature of 313K and potential scan rate of 0.02 Vs^{-1} . It is observed from the figure that, the cathodic peak potential of Cd^{2+} and $\text{S}_2\text{O}_3^{2-}$ in mixture is shifted to more negative potential compared with the cathodic potential peaks of cadmium ions and thiosulfate alone. This shift may be attributed to the formation of cadmium sulfide.

The first cathodic peak (I) (Figure 6) is appeared at a potential of about ~ -0.55 V attributed to the electroreduction of the colloidal sulfur which dissociated from thiosulfate at these conditions converting into sulfide ions that adsorbed on the electrode surface of carbon nano tubes. Moreover the colloidal sulfur can be resulted from hydrogen sulfite (the second product of the dissociation of thiosulfate in acidic media);

The second cathodic peak potential (II) is a slight peak and appeared at a potential of about ~ -0.85 V. This peak is attributed to the electrodeposition of cadmium sulfide and was confirmed by XRD analysis;

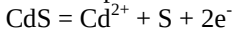


At the third cathodic peak potential III, was observed at potential of ~ -0.93 V, a crossover takes place indicating to presence of a nucleation process. At this peak

the free un-reacted Cd^{2+} ions are discharged into cadmium metal $\text{Cd}(0)$ and adsorbed into the electrode surface of carbon nano tubes which have high adsorbability.

The wave potential (I') relates to oxidation of S^{2-} to S. At more positive potentials, Sulfur (S) can be oxidized to HSO_3^- in acidic media.

The oxidation wave potential (II') relates to the oxidation and dissociation of the electrodeposited cadmium sulfide on the MWCNT paste electrode surface;



The oxidation wave potential (III') relates to oxidation of the electrodeposited adsorbed free unreacted cadmium metal to cadmium metal ion Cd^{2+} .

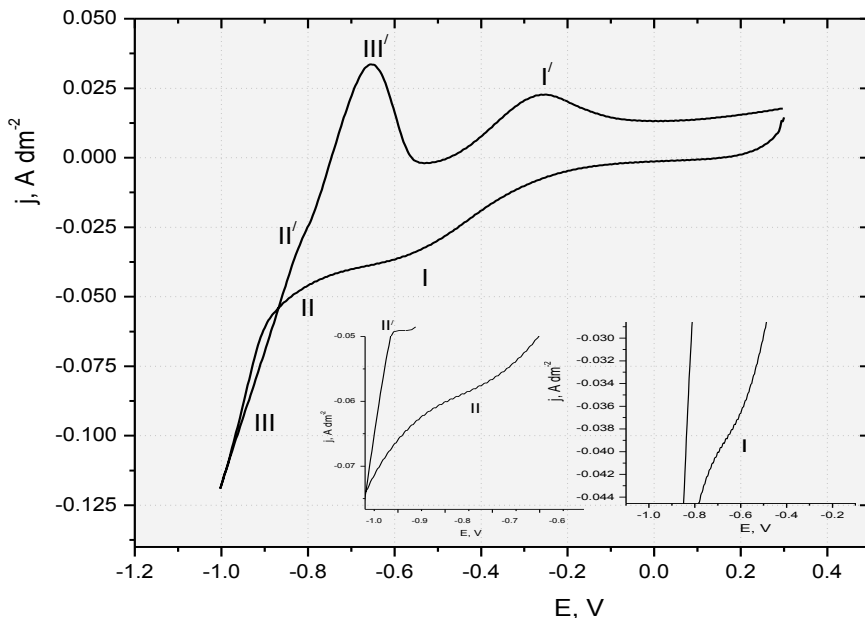


Fig. 6. Cyclic Voltammogram of 0.01-M Cd^{2+} + 0.1 $\text{S}_2\text{O}_3^{2-}$ M + 0.1 M $(\text{NH}_2)_2\text{CS}$ at 0.02 V s^{-1} , at pH = 2.5 on MWCNT- electrode at 313K.

Chronoamperometric method was used for the electrodeposition of CdS on MWCNT in this work. The condition of chronoamperometric method for the electrodeposition of CdS on multi walled carbon nanotube paste electrode is; 0.01 M Cd^{2+} + 0.1 M $\text{S}_2\text{O}_3^{2-}$ + 0.1 M thiourea, $(\text{NH}_2)_2\text{CS}$ and sulfuric acid at pH = 2.5. The applied constant potential is $E = -0.8 \text{ V}$, the temperature of the electrodeposition bath is 313 K and the time of the electrodeposition duration is 7200 second under stirring conditions.

Because of Ni is more available and cheaper than the platinum and carbon nanotubes, so it can be introduced as a substrate for the analysis such as SEM, XRD....etc.

Before the analysis step it should be done, at first a cyclic voltammetric experiment at the Nickel substrate as an electrode to investigate its behavior in the electrodeposition process of cadmium sulfide, CdS.

Fig. 7 shows the cyclic voltammetry of Ni electrode in a solution consists of 0.01 M Cd^{2+} + 0.1 M $\text{S}_2\text{O}_3^{2-}$ at pH = 2.5 and at a temperature of 40 °C. This behavior seems to look like the behavior on Pt electrode at the same conditions. For that reason, nickel can be used as a substrate for the electrodeposition of cadmium sulfide, CdS and further analysis.

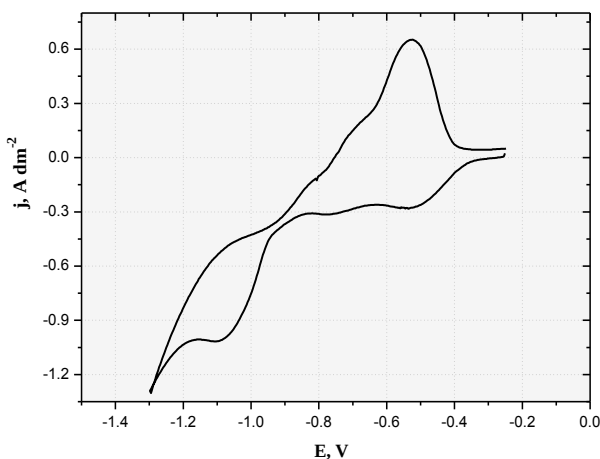


Fig. 7. Cyclic Voltammogram of 0.01-M Cd^{2+} + 0.1 $\text{S}_2\text{O}_3^{2-}$ + 0.1M $(\text{NH}_2)_2\text{CS}$ at 0.02 V s^{-1} , at pH = 2.5 on Ni- electrode at 313K.

The XRD patterns of the electrodeposited cadmium sulfide film deposited via chronoamperometric method at fixed potential of - 0.80 V (the potential at which pure cadmium sulfide film only is electrodeposited) for two hours from solution contains of 0.1 M $\text{S}_2\text{O}_3^{2-}$ + 0.01 M Cd^{2+} + 0.1 M $(\text{NH}_2)_2\text{CS}$ on Ni substrate at pH = 2.5 and temperature of 313K was performed. The XRD data reveals that, at these conditions polycrystalline hexagonal CdS thin film is obtained. The XRD data is listed in Table 1.

From XRD data, it is also illustrated that when the deposition potential is fixed at a potential of - 0.80 V (second cathodic peak II, Fig. 5b), pure CdS is only deposited

on the electrode surface. But when the deposition potential is fixed at a potential of -1.2 V (fourth cathodic peak IV) cadmium sulfide and cadmium metal Cd(0) are electrodeposited as confirmed from the XRD data. Also, it was found that, when the deposition potential is fixed at potential less than -0.6 V, the electrodeposited CdS and sulfur are obtained, this also was confirmed by EDX analysis.

Table 1. Experimental XRD data related to CdS films.

2 θ	d(°Å)	I	hkl	2 θ	d(°Å)	I	hkl
24.81	3.59	63	100	54.58	1.68	5	004
26.51	3.36	94	002	58.28	1.58	3	202
28.18	3.16	105	101	60.84	1.52	3	104
36.62	2.45	30	102	66.77	1.40	14	203
43.68	2.07	50	110	69.26	1.36	5	210
47.84	1.90	51	103	70.86	1.33	7	211
50.88	1.79	10	200	72.40	1.30	4	114
51.83	1.76	30	112	75.48	1.26	8	105
52.80	1.73	16	201				

EDX elemental analysis is used for studying the chemical composition and percent of Cd and S in the electrodeposited CdS. The effect of electrodeposition time and electrodeposition potential on the percent ratio of cadmium and sulfur in the electrodeposited CdS films were studied.

Fig. 8 shows the relation between the electrodeposition time and the cadmium mass percent at fixed deposition potential of -0.8 V, conditions as in Fig. 7. From Figure 8 it can be noted that, at 15 minutes the mass present of cadmium in the electrodeposited CdS (45.7 %) is less than the mass present of sulfur (54.3%). This means that at this time the rate of the electrodeposition of sulfur is higher than the rate of deposition of cadmium at the mentioned conditions, i.e. sulfur is firstly deposited. When the electrodeposition time is exceeded to be 30 minutes the percent of cadmium is sharply increased from 45.7 to 57.84 %. This means that the rate of the electrodeposition of cadmium became more than the rate of the electrodeposition of S at this time. This confirms that, the colloidal sulfur is firstly reduced to the electrode surface converting into sulfur ions S^{-2} , these ions cover the electrode surface and attract cadmium ions of the opposite charges in addition, the negative charge of the polarized electrode surface. After that, the percent of electrodeposited cadmium in the electrodeposited CdS is increased slightly from 57.84 % to 61.28 % at the time range from 30 to 90 minutes. The percent of cadmium again increased sharply from 61.28 % to 74 % at 120 minutes to reach

the theoretical percent value of cadmium in CdS (77.8%). This agrees with the results of XRD analysis. Where, when the electrodeposition of CdS was performed at potential of -0.8 V and electrodeposition time of 2 hours, the XRD analysis results show a pure CdS.

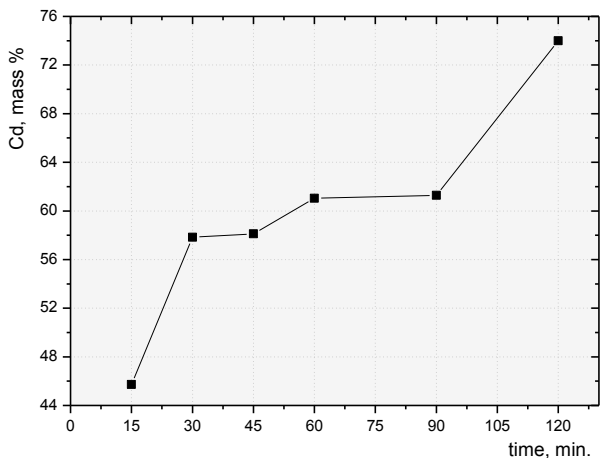


Fig.8. Relation between the electrodeposition time and the Cd mass % in the electrodeposited CdS at $E_d = -0.8$ V, conditions as in Fig.7.

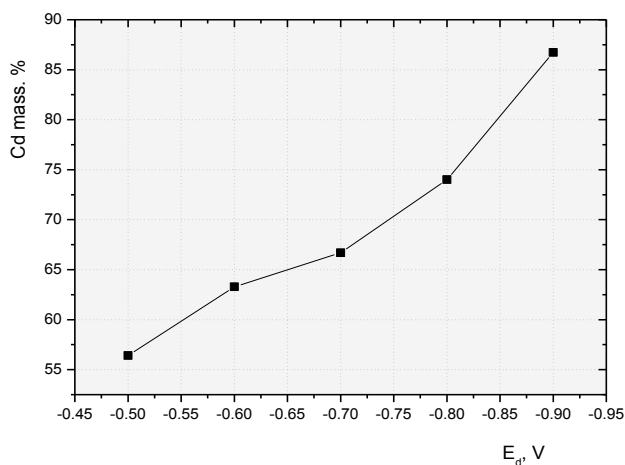


Fig. 9. Relation between the E_d and the cadmium mass % at deposition time of two hours, conditions as in Fig. 7.

Fig. 9 shows the relation between the electrodeposition potential ranged from -0.5 to -0.9 V and the cadmium mass percent at fixed deposition time (two hours), conditions as in Fig. 7. From Figure 9 it can be noted that, at the electrodeposition potential of -0.5 V the mass present of cadmium in the electrodeposited CdS (65.42 %) is more than the mass present of sulfur (43.58 %). This due to, this potential is sufficient to reduce the sulfur but not completely sufficient for reducing all cadmium ions on the electrode surface. When the deposition potential is increased to be -0.6 V the cadmium percent in the electrodeposited film of CdS increased to be 63.28 %, but this value still lower than that of the theoretical value of cadmium content in the CdS. And so on, the cadmium percent increases by increasing the applied electrodeposition potential.

At the electrodeposition potential of -0.8 V the cadmium mass percent in CdS reached to be 74 %, this value is close to the theoretical value. The mass percent of cadmium in CdS reached to be 86.73 % when the applied electrodeposition potential was -0.9 V.

So, from the previous results, it can be deduced that, the suitable electrodeposition potential is -0.8 V. This means that, pure CdS can be obtained at electrodeposition potential of -0.8 V and at electrodeposition time of two hours, these conditions described in Fig. 7. Also it was confirmed by XRD analysis as explained previously.

Typical SEM images of the CdS electrodeposited onto Ni substrate and MWCNT paste electrode under different operating conditions were performed.

The SEM images were taken for the electrodeposited chronoamperometrically CdS from a solution consists of 0.01 M Cd^{2+} + 0.1 M $\text{S}_2\text{O}_3^{2-}$ at $\text{pH} = 2.5$, temperature = 313K on Ni substrate at fixed certain potential at different electrodeposition certain times (Fig.10). Form the obtained results it can be noted that, the shape and the morphology of the images of the electrodeposition of CdS depend on the time and the deposition potential values at these conditions.

By increasing the electrodeposition time, the electrodeposited CdS arranged in a crystalline hexagonal shape and the alloying process is enhanced at this condition. Image (1), at which the electrodeposition potential is two hours, shows a layer of thin film of the electrodeposited material (gray color) surmounted white-colored crystalline materials. The corresponding EDX analysis for image (1) shows a better percent between sulfur and cadmium of the electrodeposited CdS.

The best one as shown in image (1) at potential -0.8 V at these conditions was observed. But when the potential is increased to be -0.9 V (image (2)) the cadmium sulfide is deposited with a high percentage of cadmium metal as confirmed with XRD and EDX analysis, also cadmium is appeared clearly in this image as a black particles.

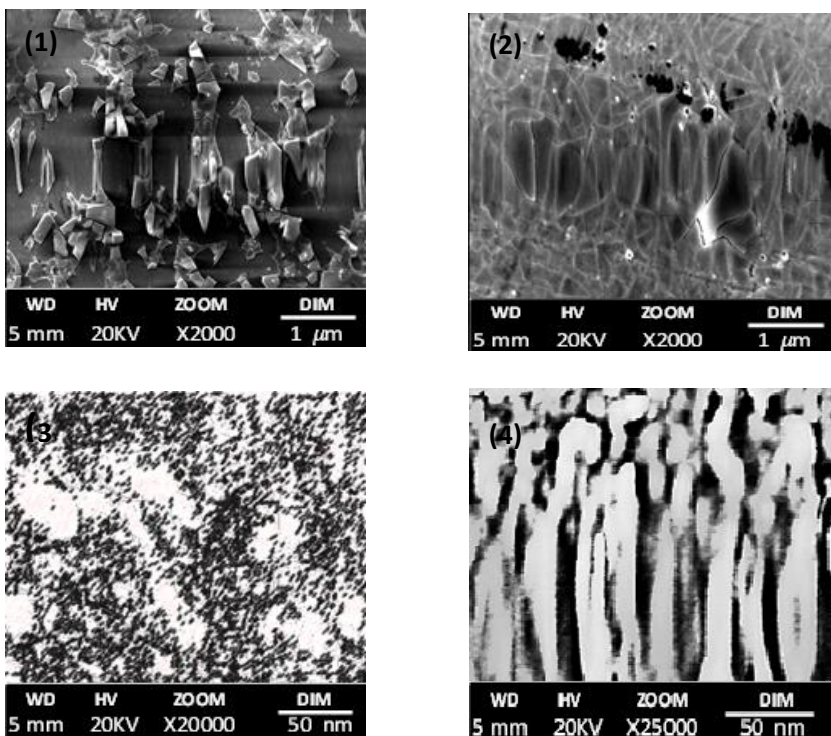


Fig.10. SEM images of the electrodeposited CdS on Ni (1, 2); (1) at E = -0.9 V, (2) at E = -0.8 V and MWCNT (3, 4), substrate (1) without AAO template (2) with AAO template (conditions as described in Fig.7).

The SEM images of the electrodeposited chrono-amperometrically CdS from a solution consists of $0.01 \text{ M Cd}^{2+} + 0.1 \text{ M S}_2\text{O}_3^{2-}$ at pH = 2.5, temperature = 313K on MWCNT paste electrode at electrodeposition time (two hours) at fixed electrodeposition potential of - 0.8 V (optimum condition), with and without the template (anodized aluminum oxide, AAO) were taken. It can be noted that, the electrodeposited particles of CdS are in the range of nanometer of average size 15-20 nm without using AAO template, depending on the substrate material (MWCNT) and formed with the shape of the substrate material. Image (4), after using the AAO as a template, shows the electrodeposited CdS in the form of nano wires in the range of about 200 nanometer in long and 15-18 nanometer in diameter.

3. SOME PHYSICAL PROPERTIES OF THE ELECTRODEPOSITED CADMIUM SULFIDE ON Pt-, Ni AND CARBON NANO TUBE PASTE ELECTRODES

The electrical resistivity measurements with temperature were made for thin film of the electrodeposited Cd-S alloy on nickel electrode, because of its availability more than Pt and MWCNT. Moreover, these measurements depend on the CdS semiconductor not on the substrate. Such measurements were done for films of electrodeposited CdS alloy containing (1) 74 wt% Cd, 26 wt% S (pure CdS) and (2) 54.3 wt% Cd, 45.7 wt% S (impure CdS). The resistivity of the investigated film at room temperature was in the range $(1-1.5) \times 10^{-2}$ ohm cm.

As can be seen from Fig. 11, the temperature dependence of the logarithm of conductivity has a linear plot. It can be noted that, the conductivity at relatively low temperatures increases slightly with increasing the temperature. After that, by increasing the temperature, the conductivity is relatively sharply increases. ΔE for samples 1 and 2 of semiconductor conductivity (intrinsic conduction) are 0.14 and 0.10 eV, respectively. B , (temperature coefficient) was calculated, it is used to give an indication for the sensitivity and characterizing the physical properties of the investigated substance. α was calculated as the temperature coefficient of the resistivity. α decrease from 0.0223 to 0.0171 with increasing the temperature from 350 to 400 K for sample 1 and from 0.0257 to 0.0197 for sample 2, as seen in table 2.

As can be seen from the table, the electrodeposited films of CdS have small values of α and ΔE . These are some of the parameters determining and show the practical application of these layers in the manufactory of the photosensitive devices.

Table2. Constants for the semiconductor CdS from conductivity-temp.measurements:

No.	Composition of the film, mas. %	ΔE , eV	B, K	$\alpha \times 10^2$	
				α^{350}, K^{-1}	α^{400}, K^{-1}
1	74 Cd + 26 S	0.10	2728	2.23	1.71
2	54.3 Cd + 45.7 S	0.14	3153	2.57	1.97

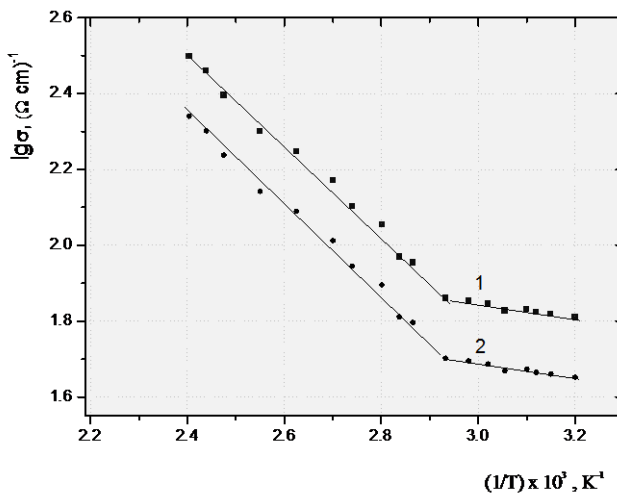


Fig.11. Dependence of the logarithm of electrical conductivity on the temperature invers of the electrodeposited CdS of composition of (1) 74 wt% Cd and 26 wt% S and (2) 54.3 wt% Cd and 45.7 wt S%.

3.2. Electrochemical Impedance measurements (Mott-Schottky plots) of the electrodeposited CdS

Mott-Schottky analysis is a powerful tool to probe the semi-conductive properties of the electrodeposited films on metals substrates, by which the thickness of spacecharge layer, donor or acceptor density and flat-band potential for the these films can be calculated and obtained.

Figure 12 exhibits the Mott-schottky plot for the electrodeposited CdS thin film prepared at the optimum conditions on Pt, Ni and MWCNT electrodes. The capacitance measurement was carried out at 1000 Hz within the potential range from + 0.4 to - 0.8 V in the cathodic direction. The nature of the plots indicates that, the electrodeposited semi-conductor CdS is of n-type behavior. Extrapolation of the plot to the potential axis gives a flat band potential V_{fb} of -1.1, 1.18 and 1.22 V (vs. Ag/AgCl) for CdS on Pt, Ni and MWCNT respectively. That value accurately reflects the thermodynamic ability of CdS n-type semiconductor to reduce water to hydrogen at these conditions. The values of the carrier density (N_D) were calculated and listed in table 3 below. These values indicate that the electrodeposited CdS deposited on Pt, Ni and MWCNT electrodes at these conditions is suitable for using as a photo anode in the solar cell systems. The thickness δ_{sc} values of the space-charge layer were calculated and listed in the table at the mentioned conditions.

Table3.Capacitance measurements data for the electrodeposited CdS on Pt, Ni and MWCNT substrates.

No.	Electrode type	δ_{SC} , °A	$N_D \times 10^{17}$, cm ³	V_{fb} , V
1.	CdS/Pt	0.23	1.42	-1.10
2.	CdS/Ni	0.15	1.04	-1.18
3.	CdS/MWCNT	0.43	2.30	-1.22

From table 3 it can be noted that, the density carriers N_D , The thickness δ_{SC} of the space-charger layer and the flat band potential for CdS electrodeposited on MWCNT electrodes deviate from the values of CdS on Ni and Pt. The deviation is most probably due to the action of surface states in the nano polycrystalline CdS that capturing and immobilizing the carriers. This also reflects the electrochemical properties of the electrodeposited CdS become more enhanced when deposited at the surface of MWCNT electrode.

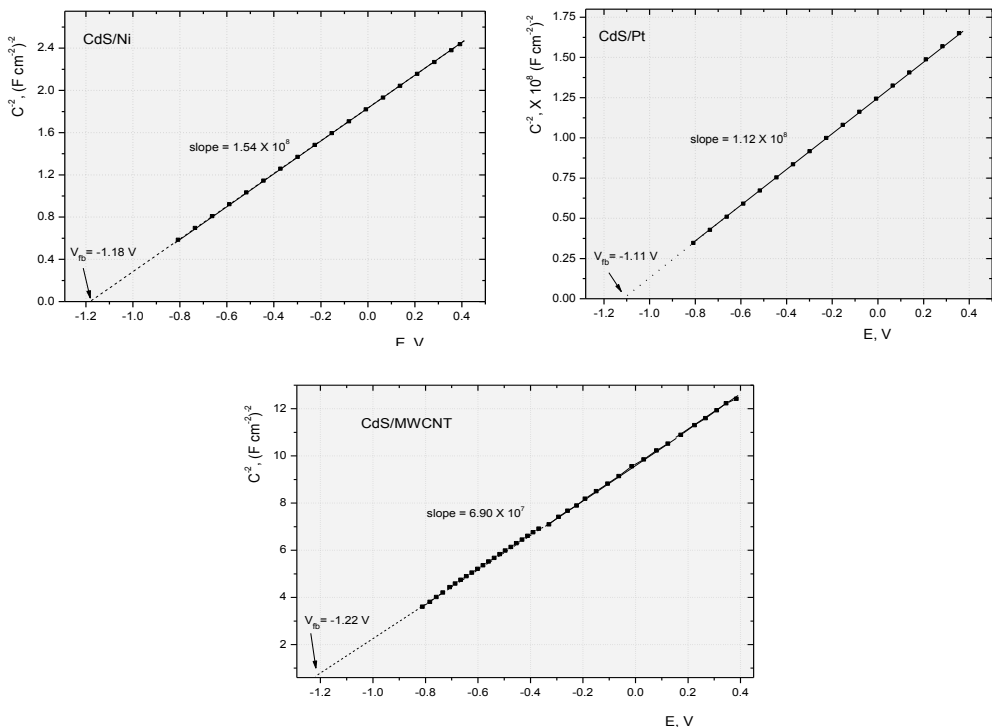


Fig. 12. Mott-Schottky plot of the electrodeposited CdS on Pt, Ni and MWCNT substrate, condition as described previously, immersed in 0.5 M Na_2SO_4 .

3.3. Photoelectrochemical properties of the electrodeposited CdS

The study of photoelectrochemical properties of n-type hexagonal polycrystalline electrodeposited CdS on Ni, Pt and MWCNT were performed in a solution of 0.5 M Na₂SO₄. CdS was electrodeposited and prepared on Ni, Pt and MWCNT at the optimum conditions.

From the obtained data it can be noted that, the photocurrent of n-CdS/MWCNT appears higher than n-CdS/Ni and n-CdS/Pt at the selected potential range(-0.3 to 1.2 V). Furthermore, the photocurrent increases from 0.0 to 0.8 V, and the anodic current at the system of CdS/MWCNT is slightly higher than CdS/Ni and on Pt. This may be due to the transformation of the generated carriers in the electrodeposited CdS into MWCNT accelerates the process.

The spectral dependence of the photocurrent on the anodes of n-CdS/Pt, n-CdS/Ni and n-CdS/MWCNT are shown in Fig. 13. As can be seen from the figure, the n-CdS/Pt electrode absorbs light of a wavelength ranging from 580 to 660 nm, the n-CdS/MWCNT electrode absorbs light of a wavelength ranging from 500 to 620 nm, and the n-CdS/Pt electrode absorbs light of a wavelength ranging from 460 to 630 nm. This means that the last electrode is relatively the most suitable for the solar cell system and for hydrogen production.

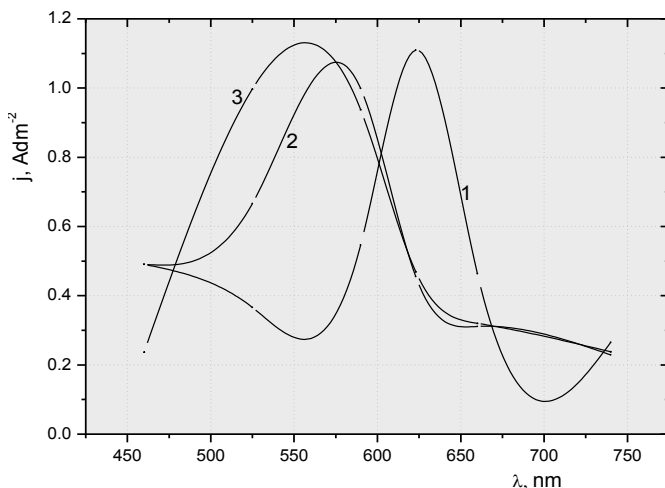


Fig. 13. Plot of photocurrent vs. λ for n-CdS/Pt electrodes (1), n-CdS/Ni (2) and (3) n-CdS/MWCNT under conditions of the interaction of light with a spectral composition range of $740 > \lambda > 450$ (visible light region).

The hetero-system of CdS/MWCNT, as of the other electrodes in this work, absorbs the light in a wider wavelength region than that of the other electrodes

listed in this work. It covers a broader spectral sensitivity, i.e. the spectral sensitivity of the hetero-system shifted to lower values of wavelengths than the other electrodes.

The values of energy gap (E_g) for each electrode system can be calculated from the value of the maximum photocurrent corresponding to the $\lambda_{\max}$, from the well-known Planck equation; $E = hc / \lambda$, where h is the Planck's constant (4.14×10^{-15} eV. s) and c is the velocity of light in vacuum (3×10^8 m.s⁻¹).

The E_g value for CdS/MWCNT electrode is more suitable for solar cell system than the other electrodes, where the efficiency could be further improved by using the MWCNT as a substrate for the electrodeposited CdS.

The photo response of CdS/Pt, CdS/Ni and CdS/MWCNT under a bias volt of (amplitude) 50 mV and at light illumination at $\lambda_{\max}$ for each system was performed. It can be noted that, as the incident light turned on and off, the device current changed between a high and low state for all electrode systems. It is also observed that, the number of signals (on- off) for the CdS/MWCNT is higher that of the other electrodes at the same conditions, this means that the CdS/MWCNT is more sensitive than the other electrodes. Based on the above data of the spectrophotometric analysis, it can be concluded that the application of the MWCNT as a substrate for the electrodeposition of CdS enhance the photo-sensitivity of the system.

THE MAIN CONCLUSIONS

1. The experimental results demonstrate that, the electroreduction of thiosulfate on the platinum and MWCNT electrodes were optimized and achieved easily and studied in a comparative way in our work. The electroreduction of thiosulfate on MWCNT paste electrode was found to be easier than in case of platinum electrode in this work. Thiosulfate dissociates in acidic media to give colloidal sulfur and sulfite ion that can be electroreduced into sulfur ions S^{-2} , the resulted sulfide ions adsorbed on the MWCNT surface more than the platinum electrode.
2. The diffusion coefficient value (D) of the thiosulfate ion was calculated from sweep voltammetric method (Randles–Sevcik equation) and amperometric method (Cottrell's equation) on platinum and MWCNT paste electrode, it was found to be (all methods and electrodes) $\sim 1.77 \times 10^{-7}$ cm² s⁻¹. This means that D value depends only on the nature of the electrolyte (conc., temp., density) and not on the electrode type. This value was used for further calculations for knowing the kinetic parameters of the electrode process.
3. The mechanistic analysis by cyclic voltammetry and potentiostatic I-t transients clearly show that, the electrodeposition of cadmium is a diffusion-controlled process on carbon nanotube (for the first time, electrodeposition of cadmium on MWCNT was performed) and platinum electrodes. The optimum conditions for

the electrodeposition of cadmium, suitable for our work, are: 0.01 M Cd^{2+} , pH=2.5 and $T = 313 \text{ K}$. SEM analysis shows that the electrodeposited cadmium is in the range of nanometer in diameter. And it has a homogeneous crystallization at these conditions.

4. For the first time, pure n-type hexagonal crystalline CdS thin and nano films were electrodeposited on Ni and MWCNT electrodes by means of cyclic voltammetric and chronoamperometric techniques. This can be accomplished by applying the optimal conditions at fixed electrodeposition potential of - 0.8 V vs, Ag/AgCl/KCl (sat.) for two hours in a bath contains 0.1 M $\text{S}_2\text{O}_3^{2-}$ + 0.01 M Cd^{2+} + 0.1 M $(\text{NH}_2)_2\text{CS}$ at pH = 2.5 and temperature = 313K under stirring conditions. The obtained CdS of different forms confirmed by SEM, XRD and EDX analysis
5. From the data of the electro-conductivity measurements versus temperature of the electrodeposited CdS reveal that, by increasing the temperature the electrical resistivity decreases slightly, going through a point at 340 K and then decreases more sharply, this behavior is characteristic for n-type semiconductor materials. It is also noted that, the electrical resistivity of the film which contains (1) 74 wt% Cd and 26 wt% S is lower than the film which contains 54.3 wt% Cd and 45.7 wt% S. This due to the sulfur content in the later one is higher than the first electrodeposited CdS film. In addition, this indicates to that, the pure crystalline film (1) has lower electrical resistivity than the impure and non-crystalline film (2). The electrodeposited alloy films of CdS have small values of α and ΔE .
6. The nature the Mott- Schottky plots behavior for the electrodeposited CdS on the investigated substrates indicates that, the electrodeposited semiconductor CdS is of n-type semiconductor. From these plots flat band potentials V_{fb} were determined for the electrodeposited n-CdS on Ni, Pt and MWCNT. The value of the carrier density (N_D) was also determined for the mentioned electrodes. The N_D values were found to be in order of 10^{17} cm^{-3} . it can be noted that, the density carriers N_D , The thickness δ_{sc} of the space-charger layer and the flat band potential for CdS electrodeposited on MWCNT electrodes deviate from that were obtained for CdS on Ni and Pt. This also reflects the electrochemical properties of the electrodeposited CdS became more enhanced when deposited at the surface of MWCNT electrode.
7. The electrodeposited photo-anodes of CdS on Pt, Ni and MWCNT show different anodic dark currents are much lower than the currents during irradiation. The photocurrent increases with the anode electrode polarization from 0.0 to 0.8 V, and the anode current at the system of CdS/MWCNT slightly higher than CdS/Ni and on Pt substrate. From the i-t curves and the values λ_{max} and E_g , one can conclude that, the electrodeposited CdS on MWCNT is much stable and suitable than the electrodeposited CdS on Ni and Pt substrates for solar cell system.

Important results of the work are presented in the following publications

1. Mammadov M.N., Aliyev A.Sh., Mahmoud Elrouby. Electrodeposition of cadmium sulfide.// Int. J. Thin Film Sci. Tec. 2012. vol.1. no. 2. P.43-53.
2. Mahmoud Elrouby. Electrochemical applications of carbon nanotube.// J. Nano. Adv. Mat. 2013. Vol.1. No. 1. P. 23-38.
3. А.Ш. Алиев, Махмуд Эль-Руби, М.Н. Мамедов. применение углеродных нанотрубок в электрохимии.// химических проблемы. 2012. No. 1. С. 11-20.
4. Махмуд Эль-Руби, А.Ш. Алиев, М.Н. Мамедов. Электроосаждение сульфида кадмия.// химических проблемы. 2012. No. 2. С. 194-206.
5. Elrouby M., Aliyev A.Sh. Effect of Temperature, pH, Concentration and Scan Rate on the Electroreduction Behavior of Thiosulfate Anion on Platinum Electrode in Aqueous Solution.// Caspian journal of applied sciences research. 2013. Vol. 2. no. 7, P. 18-25.
6. Aliyev A.Sh., El-rourby M., Abbasov M.T., Suleymanov A.S. Electrochemical Reduction Studies on the Behavior of Thiosulfate on Multi Walled Carbon Nano Tubes Paste Electrode.// Nanoscience and Nanotechnology: An International Journal. 2013. Vol. 3. no. 3. P.60-64.
7. Aliyev A.Sh., El-rourby M., Hasanli Z.H., et. al. Electrodeposition of Cadmium on Multi-Walled Carbon Nanotube. // Int. J. Nano Mater. Sci. 2013. Vol. 2. No. 1. P. 36-48.
8. Elrouby M., Aliyev A.Sh. Electrochemical Synthesis of CdS on Multi Walled Carbon Nanotube Paste Electrode.// Adv. Mater. Res. 2013. Vol. 787. P. 417-422.
9. Aliyev A.Sh., Elrouby M. Electrochemical Studies on the Cathodic Electrodeposition of n-type semiconductor CdS thin film from Thiosulfate Acidic Aqueous Solution.// Int. J. Thin Film Sci. Tec. 2013. Vol. 2. no. 3. P. 195-205.
10. Mahmoud Elrouby. Electrochemical synthesis of Cadmium Sulfide Nanowires on Carbon Nanotube.// 1st international chemistry and chemical engineering conference. Baku. 2013. P.81.
11. Mahmoud Elrouby, A.Sh. Aliyev. Electrodeposition of CdS Nano-wires.// VII всероссийская Конференция молодых учёных, аспирантов и студентов с международным участием по химии и наноматериалам «МЕНДЕЛЕЕВ-2013» секция 5. физическая химия. Russia. 2013. P.15-16.
12. Elrouby M., Aliyev A.Sh. Electrochemical Synthesis of CdS on Multi Walled Carbon Nanotube Paste Electrode.// 2nd International Symposium on Materials Science and Engineering Technology "ISMSET 2013". China. 2013. P.16.
13. Aliyev A.Sh., El-rourby M., Abbasov M.T., Hasanli Z.H., et. al. Potentiostatic Deposition of Cadmium on Multi-Walled Carbon Nanotubes Paste Electrode.// Akademik M.F. Nagiyev – 105 illiyinə Həsrolunmus Elmi Konferansın. Baku. 2013. P.78-80.

Электрохимический синтез тонких и нано пленок сульфида кадмия из тиосульфатных растворов на различных электродах (Ni, Pt и MWCNT) и исследование некоторых их свойств

Резюме

Диссертация посвящена разработке научно-технических основ получения сульфида кадмия n-типа проводимости в виде тонких пленок, наночастиц и нанопроволок путем электрохимического синтеза из кислых тиосульфатных растворов на электродах из Ni, Pt и MWCNT, а также изучению их некоторых электрофизических, электрохимических и фотоэлектрохимических свойств.

Для достижения этой цели использовали электрохимические и физико-химические методы исследования, был определен характер поляризационных кривых при осаждении кадмия, серы, а также сульфида кадмия. Снятием циклических потенциодинамических кривых определены кинетика и механизм совместного осаждения кадмия с серой, определены области потенциалов, при которых осаждались тонкие пленки стехиометрического состава, установлены оптимальный состав электролита и условия электролиза, при которых получались удовлетворительные покрытия. Исследовано влияние различных факторов на состав и свойства осаждаемых покрытий, таких как концентрация компонентов электролита, температура, скорость развертки потенциала, время электролиза, pH раствора.

Впервые были сняты циклические вольтамперные кривые осаждения кадмия, серы в отдельности, а также их совместного осаждения на MWCNT электроде, определены кинетика и механизм их электровосстановления на этом электроде.

После определения области потенциалов совместного осаждения кадмия с серой, потенциостатическим методом были получены пленки CdS в виде поликристаллических гексагональных тонких пленок и нанопроволок.

Структура, химический состав, размер наночастиц электроосажденного сульфида кадмия были определены методами РФА, EXA и SEM.

Был разработан оптимальный состав электролита и условия электролиза для осаждения гексагональных поликристаллических тонких пленок и нанопроволок сульфида кадмия, обладающих n-типом проводимости. Используя метод Мотта-Шоттки и другие методы определена зависимость электропроводности от температуры на CdS/(Ni, Pt, MWCNT) и некоторые полупроводниковые константы (V_{fb} , N_D , α , β , ΔE).

Фотоэлектрохимические свойства электроосажденных сульфида кадмия на Ni, Pt и MWCNT электродах были изучены в растворе 0.5M Na₂SO₄ в темноте и при освещении.

**Müxtəlif Elektrodalarda (Ni, Pt, MWCNT) Tiosulfat Məhlullarından
Kadmium-Sulfidin Nazik və Nano Təbəqələrinin Elektrokimyəvi Sintezi,
Onların Bəzi Xassələrinin Tədqiqi**

xülasə

Dissertasiya işi elektrokimyəvi yolla n-tip cadmium sulfidin nazik təbəqələrin, nanonaqillərinin turş tiosulfid məhlullarından müxtəlif elektrodalarda (Ni, Pt, və MWCNT) sintezinin elmi-texniki əsaslarının işlənilib hazırlanmasına həsr olunmuşdur. Alınmış cadmium sulfidin elektrofiziki, elektrokimyəvi və fotoelektrokimyəvi xassələri tədqiq edilmişdir. Bu məqsədlə işdə elektrokimyəvi və fiziki kimyəvi metodlardan istifadə etməklə stexiometrik tərkibə uyğun cadmium sulfidin sintezi üçün prosesin kinetika mexanizmi müəyyən edilmiş, elektrolitik birgə çökmə potensialı təyin edilmiş, elektrolitin tərkibi və elektrolizin optimal şəraiti müəyyənləşdirilmişdir.

İlk dəfə olaraq elektrodalarda tsiklik voltampermetrik üsulla kadmium və sulfid ionlarının ayrılıqda və onların birgə çökmə prosesinin kinetika və mexanizmi öyrənilmişdir. Birgə çökmə potensialı müəyyən edildikdən sonar həmin potensialda potensiostatik üsulla elektroliz prosesi aparılmışdır. Elektrosintez prosesində alınan Cd-S ərintisinin tərkibinə müxtəlif faktorların o cümlədən elektrolitdəki maddələrin qatılığının, temperaturun, pH-in, çökmə potensialının və çökdürmə müddətinin təsiri öyrənilmişdir.

Elektrosintez üsulu ilə müxtəlif elektrodalarda alınmış cadmium sulfidin quruluşu, element kimyəvi tərkibi və alınmış nanohissəciklərinin ölçüləri RFA, EKA və SEM analiz metodları vasitəsilə təyin edilmişdir. İstifadə olunmuş bu üsulların köməyi ilə stexiometrik tərkibə uyğun n-tip heksaqonal quruluşa malik polikristallik cadmium sulfidin, nazik təbəqələr və nanonaqillər şəklində alınması üçün optimal şərait müəyyənləşdirilmişdir.

Metto-Şotki və başqa metodlardan istifadə edərək CdS/(Ni, Pt, MWCNT) –in elektrik keçiriciliyinin temperaturdan asılılığı, N_D , V_{fb} təyin edilmiş, yarımkeçiricilik xassəsini göstərən bir sıra parametrlər hesablanmışdır (α , β , ΔE). Ni, Pt və MWCNT elektrodalarda optimal şəraitdə elektrolitik yolla çökdürülmüş n-tip CdS-in nazik və nanotəbəqələrinin elektrokimyəvi və fotoelektrokimyəvi xassələri 0,5 M Na₂SO₄ məhlulunda qaranlıqda və işıqda tədqiq edilmişdir.

**AZƏRBAYCAN MİLLİ ELMLƏR AKADEMİYASI
AKADEMİK M.F.NAĞİYEV ad.
KİMYA PROBLEMLƏRİ İNSTİTUTU**

Əlyazması hüququnda

MAHMOUD ELROUBY MOHAMMED MAHMOUD

**MÜXTƏLİF ELEKTRODLARDA (Ni, Pt, MWCNT)
TİOSULFAT MƏHLULLARINDAN KADMIUM-SULFİDİN
NAZİK VƏ NANO TƏBƏQƏLƏRİNİN ELEKTROKİMYƏVİ
SİNTEZİ, ONLARIN BƏZİ XASSƏLƏRİNİN TƏDQIQI**

2308.01- “Elektrokimya“

Kimya elmləri üzrə fəlsəfə doktoru elmi dərəcəsi
almaq üçün təqdim olunmuş dissertasiyasının

A V T O R E F E R A T I

Bakı -2014