CHEMIJA. 2015. Vol. 26. No. 3. P. 193–197

Preparation of CdS nanoparticles by microwave-assisted synthesis

L. Tamašauskaitė-Tamašiūnaitė*,

G. Grincienė,

B. Šimkūnaitė-Stanynienė,

L. Naruškevičius,

V. Pakštas,

A. Selskis,

E. Norkus

Center for Physical Sciences and Technology,
A. Goštauto St. 9,
Vilnius LT-01108, Lithuania

In the present study a rapid microwave heating method was used to prepare CdS nanoparticles. The morphology, structure and composition of the prepared CdS were examined by means of field-emission scanning electron microscopy and X-ray diffraction. The optical properties of the CdS thin films formed and deposited onto glass substrates were investigated by means of UV/Vis spectrophotometric measurements.

It has been found that the size and structure of CdS particles synthesized by rapid heating irradiation depend on the alkalinity of the reaction mixture and the microwave power. The synthesized CdS nanoparticles have a band gap of 2.5–2.7 eV.

Key words: cadmium sulfide, microwave synthesis

INTRODUCTION

Cadmium sulfide is an important II-IV semiconductor with a direct band gap of 2.42 eV at room temperature for various applications in optoelectronic, electronic devices and solar cells. The size, structure and morphology of CdS nanoparticles play a major role on the physical and optical properties of CdS thin films.

A variety of methods have been developed to prepare absorber CdS layers for thin solar cells such as vacuum evaporation [1], chemical vapor deposition [2], spray deposition [3–5], electrochemical synthesis [6, 7], electrodeposition [8–10], chemical bath deposition (CBD) [11–16], the successive ionic layer adsorption and reaction (SILAR) method [17–19], etc. Nowadays a rapid microwave heating method, in many ways, superior to traditional heating (reactions are completed in minutes compared to hours and days) is widely used to prepare metal nanoparticles. CdS nanocrystals with various structures have been prepared by microwave synthesis [20–23].

This study is focused on preparation of CdS nanoparticles by means of a rapid microwave heating method using cadmium nitrate and thiourea precursors. The influence of the reaction mixture medium and power on the size and structure of synthesized CdS was investigated. The morphology, structure and composition of prepared CdS nanocrystals were examined by means of X-ray diffraction. The optical properties of the CdS thin films formed and deposited onto glass substrates were investigated by means of UV/Vis spectrophotometric measurements.

EXPERIMENTAL

Chemicals

$Cd(NO_3)_2$, CH_4N_2S, EDTA, NaOH, 2-propanol, ethanol and ethylene glycol were purchased from Sigma-Aldrich Supply. All chemicals were of analytical grade and used without further purification. Ultra-pure water with the resistivity of 18.2 Mz cm^{-1} was used to prepare all the solutions.

Fabrication of CdS by microwave synthesis

The CdS nanoparticles were synthesized by means of microwave synthesis using cadmium nitrate and thiourea as precursors. The reaction mixture containing 0.1 mol l^{-1} $Cd(NO_3)_2$, 0.2 mol l^{-1} CH_4N_2S and 0.005 mol l^{-1} EDTA and different amounts of NaOH (being pH 7.98, 8.72, 8.94 and 9.22)

* Corresponding author. E-mail: loreta.tamasauskaite@ftmc.lt

was used for the synthesis of CdS. The precursor solution was prepared using required amounts of 0.1 mol l^{-1} $Cd(NO_3)_2$, 0.2 mol l^{-1} CH_4N_2S and 0.005 mol l^{-1} EDTA. The solution pH was adjusted by adding NaOH. The reaction mixture pH was measured with a Cyberscan pH 1100 pH-meter (Eutech Instruments, USA). The prepared reaction mixture was put into a Monowave 300 microwave reactor (Anton Paar). Synthesis of CdS nanoparticles was carried out at a temperature of 100 °C for 10 min at a holding power of 100–800 W. After preparation, the synthesized catalysts were washed with ultra-pure water, ethanol and then filtered and dried in a vacuum oven at 80 °C for 2 h.

Characterization of catalysts

Optical absorption studies of the CdS layers formed and deposited on the glass substrates were carried out in the wavelength range of 300–800 nm using a Lambda 35 UV–VIS spectrophotometer (Perkin Elmer). For optical absorption experiments, thin CdS layers were deposited on the glass sheet. The initial CdS nanocrystals powder was prepared from the reaction mixture containing 0.1 mol l^{-1} $Cd(NO_3)_2$, 0.2 mol l^{-1} CH_4N_2S, 0.005 mol l^{-1} EDTA and different amount of NaOH, i. e. at different pH values. Synthesis was carried out at a temperature of 100 °C for 10 min at different holding powers. Then, the 15 g of CdS powders obtained were mixed with 2 ml of ethanol and sonicated for 10 min. Then, 10 µl of the prepared CdS slurry was pippeted on the surface of a sheet of glass and dried at room temperature for 24 h.

X-ray diffraction patterns of CdS nanocrystal powders were recorded using a D8 diffractometer (Bruker AXS, Germany, 2003) with Cu Kα radiation using a Ni/graphite monochromator. A step-scan mode was used in the 2-theta range from 20° to 90° with a step length of 0.02° and a counting time of 5 s per step.

The morphology and composition of the CdS layers deposited on the glassy carbon by the spin coating technique were characterized using a SEM/FIB workstation Helios Nanolab 650 with an energy dispersive X-ray (EDX) spectrometer INCA Energy 350 X-Max 20. For experiments, the CdS nanocrystals were prepared from the reaction mixture containing 0.1 mol l^{-1} $Cd(NO_3)_2$, 0.2 mol l^{-1} CH_4N_2S, 0.005 mol l^{-1} EDTA; pH 8.5. Synthesis was carried out at 100 °C for 10 min at a holding power of 100 W. Then, the 15 mg of the CdS powders obtained were mixed with 2 ml of 2-propanol and ethylene glycol and sonicated for 10 min. Then, 10 µl of the prepared CdS slurries were deposited on the surface of glassy carbon using a spin-coater WS-650-23 (Laurell Technologies Corporation, USA) at rpm = 700 and accelaration 1 200 for 180 s.

RESULTS AND DISCUSSION

Figure 1 presents the XRD patterns of CdS nanoparticles synthesized using the reaction mixture of pH 7.98 (pattern 1) and 9.22 (pattern 2). According to the X-ray diffraction data, the obtained CdS nanoparticles have a hexagonal crystalline

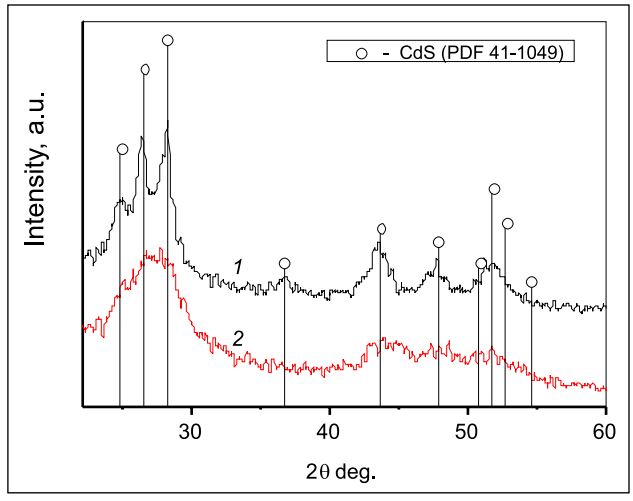

Fig. 1. XRD patterns of CdS powders prepared by microwave synthesis. The reaction mixture containing 0.1 mol l^{-1} $Cd(NO_3)_2$, 0.2 mol l^{-1} CH_4N_2S and 0.005 mol l^{-1} EDTA. The pH of the reaction mixture was 7.98 (pattern 1) and 9.22 (pattern 2). Synthesis was carried out at 100 °C for 10 min by holding power at 100 W

structure with a crystal lattice parameters of a = 0.414092 nm and c = 0.67198 nm (PDF 41-1049). The Scherrer equation was used to calculate the average size of CdS particles. The average size of CdS crystallites, obtained from the reaction mixture with pH 7.98 and 9.22, was 9.2 and 2.0 nm, respectively. Notably, the XRD peaks attributable to CdS became broader with increase in pH of the reaction mixture. As seen, the size of the obtained CdS nanocrystallites decreases with increase in pH value of the reaction mixture.

The properties of CdS nanoparticles, synthesized using different reaction mixture pH and power, were investigated by means of UV/Vis spectroscopy. The UV–Vis absorption spectra for the prepared CdS nanoparticles samples were recorded in the wavelength range of 300–800 nm at room temperature and are given in Fig. 2a. In order to confirm the nature of optical transition in all samples, the optical data were analyzed using a classical absorption equation known as the Tauc equation [24]:

$$\alpha = \alpha_o (h\nu - E_g)^n / h\nu, \quad (1)$$

where α_o is the constant, $h\nu$ is the incident photon energy, E_g is the separation between the bottom of the conduction band and top of the valence band and n is the constant. For allowed direct transition, $n = 1/2$, and for allowed indirect transition $n = 2$. The plots of $(ah\nu)^2$ versus $h\nu$ for all the CdS samples obtained at different reaction mixture pH are shown in Fig. 2b. As evident, the CdS nanoparticles, synthesized from the reaction mixture with different pH of 7.98, 8.72, 8.94 and 9.22, have band gap energy of 2.46, 2.60, 2.66 and 2.46 eV, respectively. Higher band gap energy has CdS prepared from the reaction mixture with pH of 8.72 and 8.94.

The influence of synthesis parameters, e. g. holding power, on properties of CdS nanoparticles was also investigated.

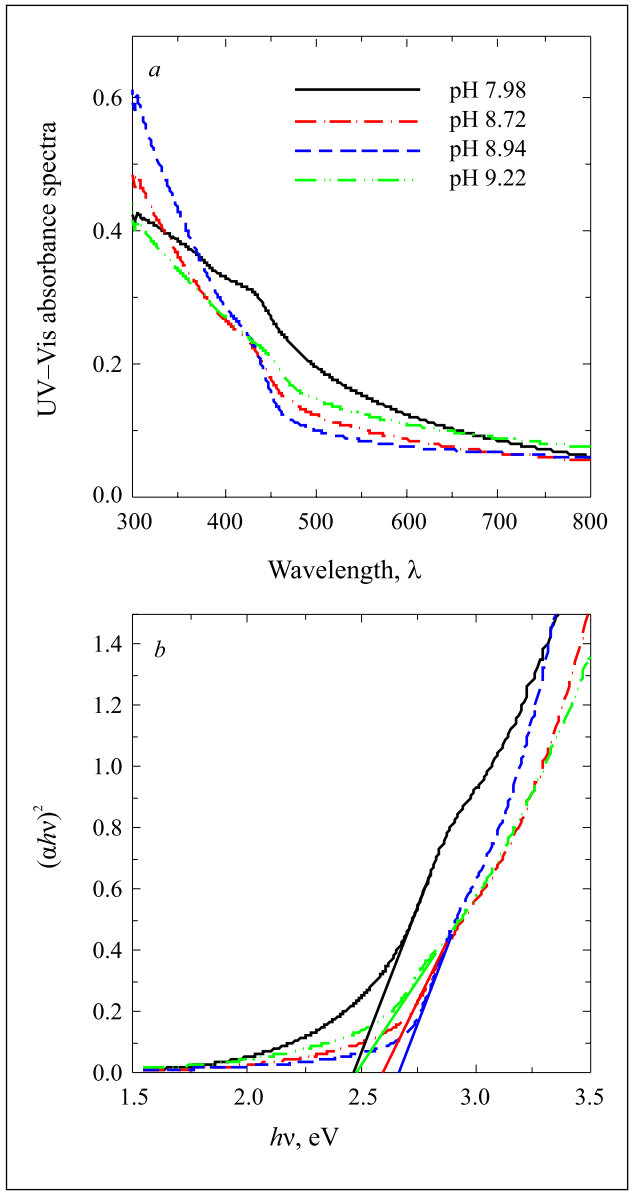

Fig. 2. (*a*) UV–Vis absorbance spectra of CdS deposited on the glass sheet. The CdS nanoparticles were prepared from the reaction mixture (mol l^{-1}): $Cd(NO_3)_2$ – 0.1, $CS(NH_2)_2$ – 0.2, EDTA – 0.005. The reaction mixture pH: 7.98 (*solid line*), 8.72 (*dash-dotted line*), 8.94 (*dashed line*) and 9.22 (*dash-dot-dotted line*). Parameters of microwave synthesis: t = 100 °C, P = 100 W, τ = 10 min. (*b*) Plot of $(\alpha h\nu)^2$ versus $h\nu$

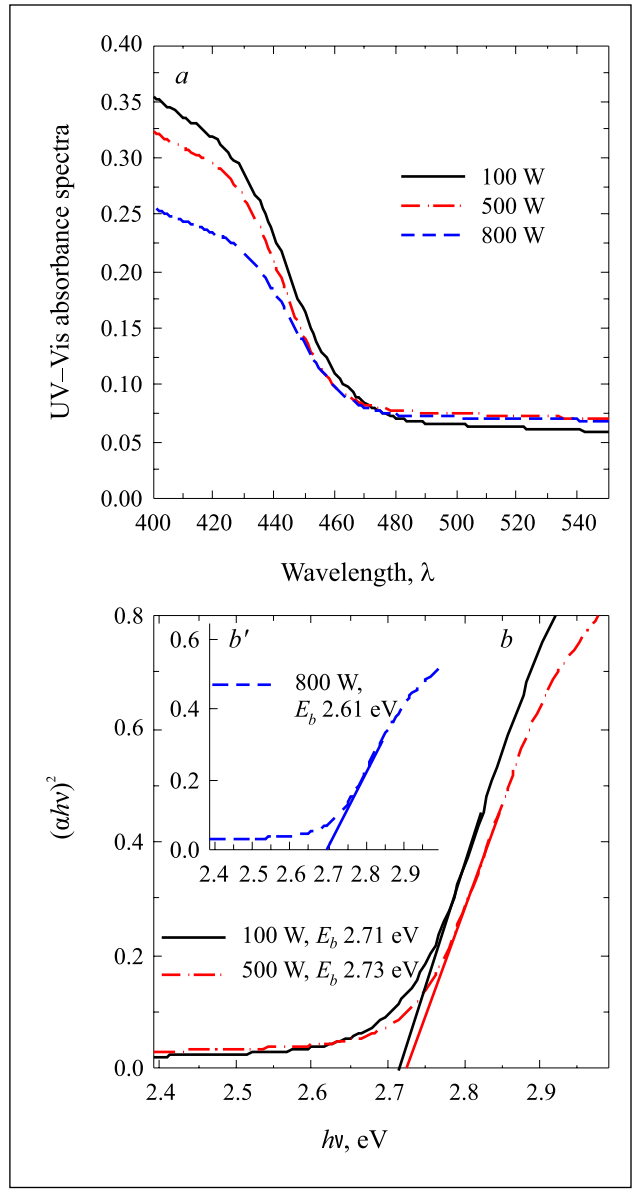

Fig. 3. (*a*) UV–Vis absorbance spectra of CdS deposited on the glass sheet. CdS was prepared from the reaction mixture (mol l^{-1}): $Cd(NO_3)_2$ – 0.1, CH_4N_2S – 0.2, EDTA – 0.005; pH 8.5. Parameters of microwave synthesis: t = 100 °C; P (W): 100 (*solid line*), 500 (*dashed line*) and 800 (*dash-dotted line*); τ = 10 min. (*b*) Plot of $(\alpha h\nu)^2$ versus $h\nu$

Figure 3 presents the optical properties of the CdS layers deposited on the surface of the glass sheet. The CdS nanocrystals were obtained from the reaction mixture containing 0.1 mol l–1 Cd(NO3)2, 0.2 mol l–1 CH4N2S and 0.005 mol l–1 EDTA; pH 8.5. Synthesis was carried out at a temperature of 100 °C for 10 min and at different holding powers of 100, 500 and 800 W. As seen from the data in Fig. 3, when the CdS nanoparticles were synthesized at holding power from 100 up to 500 W, the obtained CdS has a band gap energy of 2.7 eV, while the band gap energy decreases slightly from 2.7 to 2.6 eV with increase of the holding power from 500 to 800 W.

Figure 4 shows the FESEM views of CdS layers formed by spin-coating on the glassy carbon from the ethylene glycol (a) and 2-propanol (b) solutions. The initial CdS nanocrystals were prepared from the reaction mixture containing 0.1 mol l^{-1} $Cd(NO_3)_2$, 0.2 mol l^{-1} CH_4N_2S, 0.005 mol l^{-1} EDTA; pH 8.5. Synthesis was carried out at a temperature of 100 °C for 10 min at a holding power of 100 W. As seen, the CdS layers formed from the ethylene glycol solution cover completely the surface of glassy carbon, while the CdS layers deposited from the 2-propanol solution are cracked. It should be noted that generally the CdS layers have good adhesion with the surface of substrate.

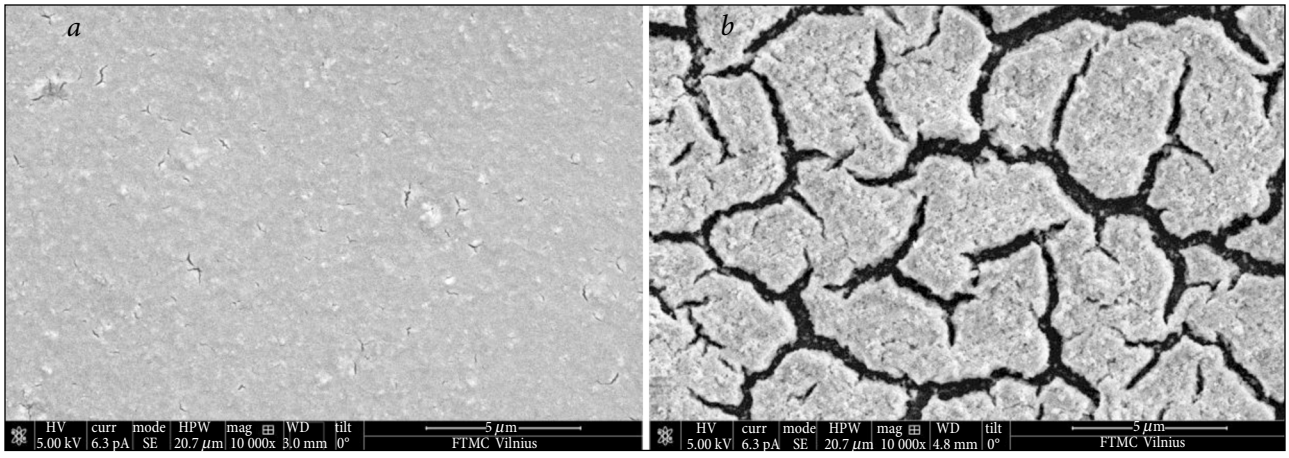

Fig. 4. FESEM views of CdS, formed on the glassy carbon from the ethylene glycol (*a*) and 2-propanol (*b*) solutions by spin-coating. The CdS nanocrystals were prepared from the reaction mixture containing 0.1 mol l^{-1} $Cd(NO_3)_2$, 0.2 mol l^{-1} CH_4N_2S, 0.005 mol l^{-1} EDTA; pH 8.5. Parameters of microwave synthesis: $t = 100$ °C; P = 100 W, τ = 10 min

CONCLUSIONS

It has been found that the size and structure of CdS particles synthesized by means of microwave synthesis depend on the alkalinity of the reaction mixture and the microwave power. The average size of CdS crystallites, obtained from the reaction mixture with pH 7.98 and 9.22, was 9.2 and 2.0 nm, respectively.

The synthesized CdS nanoparticles have a band gap of 2.5–2.7 eV. Higher band gap energy has CdS nanoparticles prepared from the reaction mixture with pH of 8.72 and 8.94.

ACKNOWLEDGEMENTS

The work was carried out within the project VP1-3.1-ŠMM-08-K-01-009 that is partly supported by the National Programme "An Improvement of the Skills of Researchers" launched by the Lithuanian Ministry of Education and Science.

Received 26 May 2015
Accepted 15 June 2015

References

1. H. Uda, H. Yonezawa, Y. Ohtsubo, M. Kosaka, H. Sonomura, *Sol. Energ. Mat. Sol. C.*, **75**, 219 (2003).
2. H. Ren, L. Zhang, X. Wan, Y. Bi, Y. Zhang, *Thin Solid Films*, **518**, 3700 (2010).
3. K. L. Choy, B. Su, *Thin Solid Films*, **388**, 9 (2001).
4. R. Castro-Rodríguez, J. Mendez-Gamboa, I. Perez-Quintana, R. Medina-Ezquivel, *Appl. Surf. Sci.*, **257**, 9480 (2011).
5. S. Aksay, M. Polat, T. Özer, S. Köse, G. Gürbüz, *Appl. Surf. Sci.*, **257**, 10072 (2011).
6. M. Biçer, A. O. Aydın, İ. Şişman, *Electrochim. Acta*, **55**, 3749 (2010).
7. S. Higashimoto, K. Kawamoto, H. Hirai, et al., *Electrochem. Commun.*, **20**, 36 (2012).
8. M. Innocenti, S. Cattarin, M. Cavallini, F. Loglio, M. L. Foresti, *J. Electroanal. Chem.*, **532**, 219 (2002).
9. K. Zarębska, M. Skompska, *Electrochim. Acta*, **56**, 5731 (2011).
10. P. Shahbazi, A. Kiani, *Sol. Energ. Mat. Sol. C.*, **134**, 165 (2015).
11. N. S. Kozhevnikova, A. A. Rempel, F. Hergert, A. Magerl, *Thin Solid Films*, **517**, 2586 (2009).
12. F. Liu, Y. Lai, J. Liu, et al., *J. Alloy. Compd.*, **493**, 305 (2010).
13. M. Kim, S. Lee, S. H. Sohn, *Thin Solid Films*, **519**, 1787 (2011).
14. N. Preda, M. Enculescu, F. Gherendi, E. Matei, M. E. Toimil-Molares, I. Enculescu, *J. Phys. Chem. Solid.*, **73**, 1082 (2012).
15. B. Ghosh, K. Kumar, B. K. Singh, P. Banerjee, S. Das, *Appl. Surf. Sci.*, **320**, 309 (2014).
16. J. Nicholas Alexander, S. Higashiya, D. Caskey Jr, H. Efstathiadis, P. Haldar, *Sol. Energ. Mat. Sol. C.*, **125**, 47 (2014).
17. C. D. Lokhande, B. R. Sankapal, H. M. Pathan, M. Muller, M. Giersig, H Tributsch, *Appl. Surf. Sci.*, **181**, 277 (2001).
18. M. Sasagawa, Y. Nosaka, *J. Electroanal. Chem.*, **536**, 141 (2002).
19. K. G. Rao, V. K. Ashith, *J. Phys. Chem. Solid.*, **77**, 14 (2015).
20. J. Zhu, M. Zhou, J. Xu, X. Liao, *Mater. Lett.*, **47**, 25 (2001).
21. G. Tai, W. Guo, *Ultrason. Sonochem.*, **15**, 350 (2008).
22. B.-Y. Hu, Z.-Z. Jing, J.-F. Huang, J. Yun, *Trans. Nonferrous Met. Soc. China*, **22**, 89 (2012).
23. I. A. Lopez, A. Vazquez, I. Gomez, *Rev. Mex. Fis.*, **59**, 160 (2013).
24. J. Tauc, R. Grigorovici, A. Vancu, *Physica Status Solidi B*, **15**(2): 627 (1966).

L. Tamašauskaitė-Tamašiūnaitė, G. Grincienė,
B. Šimkūnaitė-Stanynienė, L. Naruškevičius, V. Pakštas,
A. Selskis, E. Norkus

CdS NANOKRISTALITŲ FORMAVIMAS TAIKANT MIKROBANGŲ SINTEZĘ

S a n t r a u k a

Darbe CdS nanodalelės buvo sintetinamos greituoju kaitinimo mikrobangose būdu. Gautųjų CdS nanodalelių morfologija, struktūra ir sudėtis buvo apibūdinta Lauko emisijos skenuojančios elektronų mikroskopijos bei Rentgeno spindulių difrakcijos metodais. Plonų plėvelių, suformuotų iš gautųjų CdS nanokristalų ant stiklo pagrindo, optinės savybės buvo ištirtos ultravioletinės-matomos šviesos spektro dalies spektrofotometriniais matavimais.

Nustatyta, kad greitojo kaitinimo mikrobangose būdu susintetintų CdS dalelių dydis ir struktūra priklauso nuo reakcijos mišinio šarmingumo ir mikrobangų stiprio. Susintetintų CdS nanodalelių E_b yra nuo 2,5 iki 2,7 eV.