Research Journal of Recent Sciences ____ ISSN 2277-2502
Vol. **2(ISC-2012),** 102-105 **(2013)** *Res. J. Recent. Sci.*

Growth and Characterization of Cobalt Sulphide Nanorods

Ariponnammal S. and Srinivasan T.
Department of Physics, Gandhigram Rural Institute, Deemed University, Gandhigram, Dindigul District, TamilNadu, INDIA

Available online at: www.isca.in
Received 21st November 2012, revised 24th December 2012, accepted 19th January 2013

Abstract

Uniformly distributed cobalt sulphide (CoS) nanorods with diameter of 139nm and 0.7µm long have been synthesized by using inexpensive chemical precipitation method. The X-ray powder diffraction study has shown the amorphous nature of the as prepared CoS nanorods. The scanning electron microscope reveals the morphology of the nanorods having nearly spherical head and elongated to flat tail tip just similar to nail shape. These kinds of structure are useful in laser and field emission applications. The analysis of EDAX has shown the presence of nearly equal percentage of cobalt and sulphur along with oxygen peak. This shows the formation of cobalt sulphide with slight hydrous nature. The hydrous nature is confirmed by FTIR study which has shown the presence of O-H bond. The UV-VIS transmission spectrum of CoS nanorods shows high absorption in the ultra-violet region at about 350nm which makes the material to be suitable for UV filters. The room temperature photoluminescence at excitation wavelength of 320nm exhibits two bands of which one violet emission observed at 413nm is broad and other blue emission band at 493nm is comparatively sharp. These two emissions are originated from Co vacancy related defects or their complexes.

Keywords: Nanorods, CoS, SEM.

Introduction

Semiconducting nanostructures are promising candidates for future electronic and photonic devices. They have unique physical and chemical properties and can be used as elementary units of opto electronic devices[1]. In nanostructures, the density of states of carrier is concentrated at some specific energy levels, which enable enhancement of exciton oscillator strength and light emitting efficiency. As a result, the performance of nanostructure based optical devices is expected to improve and to be less temperature dependent. So far, many semiconducting materials have been grown into nanostructures[2-5]. Among these, cobalt sulphide (CoS) form a II-IV compounds with considerable potential for application in electronic devices[6]. It can be used in solar energy as absorbers[7], ultra high density magnetic recording[8], anodes for Li-ion batteries[9] and catalysts for hydrodesulphurization and dehydrodearomatization[10]. And also, the cobalt sulphide also finds novel applications in selective coatings and solar cells, optical filters, temperature sensors, optical wave guides and IR detectors[11-21]. It is of particular interest that the properties of cobalt sulphide are strongly dependent on the particle size, shape, distribution and surface. Therefore, the crystal structure and opto-electronic properties of CoS may be varied depending on the micro environment of layered inorganic matrices. It is also notable that the properties, morphologies and stochiometric compositions were affected by various synthetic routes[22]. In the continuing search for different synthetic routes for nanostructures, the synthesis of CoS nanorods has been made by simple chemical precipitation method and it's analysis has been presented in this paper.

Material and Methods

The CoS nanorods were prepared by the simple chemical precipitation method at room temperature. All chemicals were of analytical grade and used without further purification. In this synthesis, 100 ml of aqueous solution of the reactants was prepared using 0.1 M $CoCl_2$ and 0.1 M Na_2S as the reactant materials. Freshly prepared aqueous solution of 0.1M Na_2S was mixed drop by drop in the 0.1 M $CoCl_2$ solution using vigorous stirring. As the reaction was started the reaction system suddenly changed from pale orange to dark black and the stirring was continued upto 2 hours. The precipitate was then washed several times with ethanol and centrifuged. The precipitate collected from centrifugation was dried at 60ºC for few hours and then kept in dissicator. It is dark black in colour. This dried CoS powder was further characterized by XRD, SEM, EDAX, FTIR, UV-VIS and Photoluminescence spectrum.

The powder XRD was performed by using Richseifert diffractometer. The SEM images were taken on a JEOL JSM-6390 model (made in Japan) scanning electron microscope. The EDAX spectrum was recorded by OXFORD INCAPENTAx3 model made in England. The FTIR spectrum was recorded using Perkin Elmer spectrum BX model spectrophotometer by KBr pellet technique in the range 400–4000cm^{-1} at a resolution 2 cm^{-1}. The UV-Visible absorption spectrum was recorded using Perkin Elmer Lamda 35 spectrophotometer in the spectral range 200 to 1100nm. The PL emission spectrum was recorded by VARIAN Cary Eclipse Fluorescence Spectrophotometer employing 150 Watts Xe arc discharge lamp as the excitation source.

Results and Discussion

XRD: The figure1 has shown the recorded powder XRD for the sample. It has shown only increased background and does not show any peaks which confirms the amorphous nature of the sample.

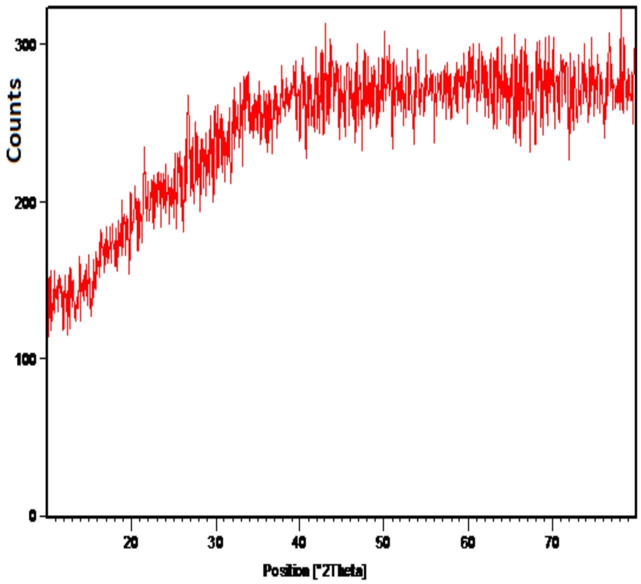

Figure-1
X-ray powder diffraction pattern of CoS nanorods

SEM: The SEM images (figure2) of as prepared CoS has shown uniformly distributed cobalt sulphide (CoS) nanorods with average diameter of 139nm and 0.7µm long. The scanning electron microscope reveals the morphology of the nanorods having nearly spherical head and elongated to flat tail tip just similar to nail shape. These kinds of structure are useful in laser and field emission applications.

EDAX: The CoS is one of the more complicated metal sulphide systems with a number of phases and differing chemical compositions[6]. The diversity in the stochiometry of cobalt sulphides poses a challenge for the control of size and shape in small particle synthesis which is exacerbated by potential coexistence of the strongly reducible cobalt ion and oxidizable sulphide ion[23]. The energy dispersive x-ray spectrum (figure 3) has shown that the Co and S are present in the atomic percentage of 19.38 and 13.67 with intensity correlation 0.8736 and 0.8960 respectively. The analysis of EDAX has shown the presence of nearly equal percentage of Cobalt and Sulphur along with oxygen peak of intensity correlation 1.1532. This shows the formation of cobalt sulphide with slight hydrous nature. The hydrous nature is confirmed by FTIR study which has shown clearly the presence of O-H bond.

FTIR: The figure 4 shows the FTIR spectrum of the CoS and table 1 presents the observed absorption frequencies and their assignments in relation to their characteristic vibrational modes. The broad trough positioned in between 3650-2729cm^{-1} corresponds to O-H bonding which confirms the hydrous nature. The bands observed at 832.6 and 609.91 are characteristic bands of sulphides[24-25].

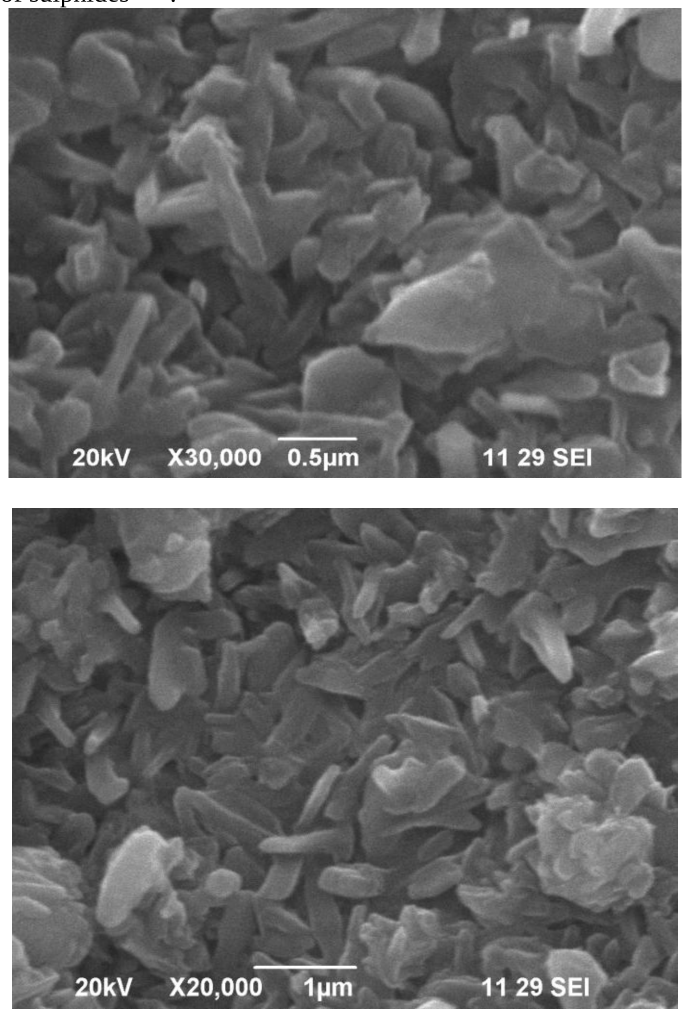

Figure-2
SEM images of CoS nanorods with two different magnification

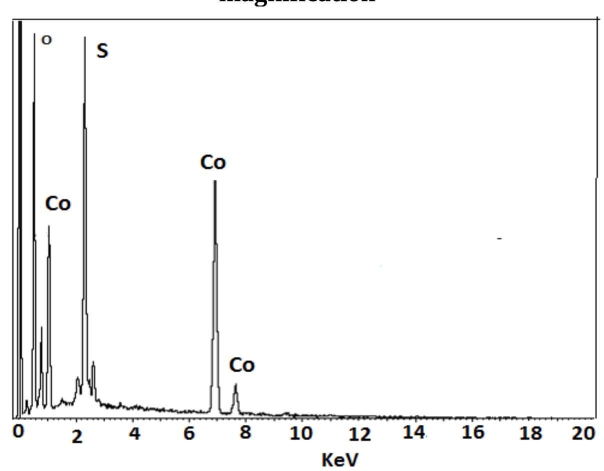

Figure-3
EDAXpattern of as prepared CoS

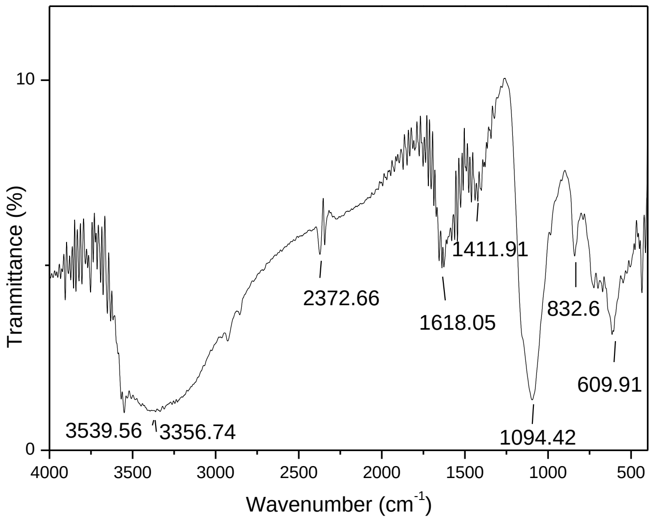

Figure-4
FTIR spectrum of CoS

Table-1
The assignment of FTIR bands of CoS

Sl. No.	Frequency of bands	Assignment[24-25]
1	3539.56	O-H stretching
2	3356.74	O-H stretching
3	2372.66	O-H stretching
4	1618.05	O-H stretching
5	1411.91	O-H stretching
6	1094.42	O-H stretching
7	832.60	Sulphides
8	609.91	Sulphides

UV-Visible: The transmission spectrum of CoS recorded in the UV-Vis region is shown in figure 5. It shows that the cobalt sulphide nanorods have high absorption in the ultra-violet region at about 350nm than in any other region of the spectrum. This makes the material to be suitable for devices for good absorption of UV radiation that is, it can be used as a UV filters. The spectrum shows moderate transmittance in the visible region. The observed wide transmission in the entire visible region (300 to 1100 nm) enables it to be a potential candidate for optoelectronic applications**.**

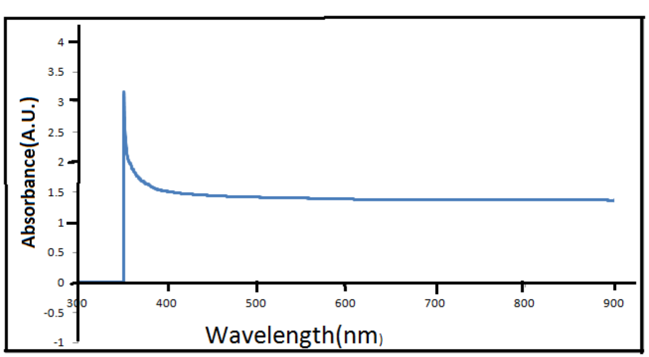

Figure-5
UV-VIS spectrum of CoS

Photoluminescence: The photoluminescence spectrum of CoS nanorods recorded at an excitation wavelength of 320nm at room temperature is shown in figure 6. Cobalt is a transition metal impurity. It is a fast diffuser and gives rise to both radiative and nonradiative centres [26]. The PL spectrum comprises two bands of which one broad violet emission peak is observed at 413nm and other strong blue emission is observed at 493nm. Bhattacharjee et al have attributed 418nm peaks to S^{2-} vacancy [27-29]. Yanagida et al [30] have observed defect related longer wavelength luminescence at about 420nm. It has been reported that 422.87nm peak has been classically termed as self activated luminescence and known to be due to the recombination of carriers between S vacancy related donor and valance band [31]. The strong blue peak observed at 493nm may arise due to native point defects.

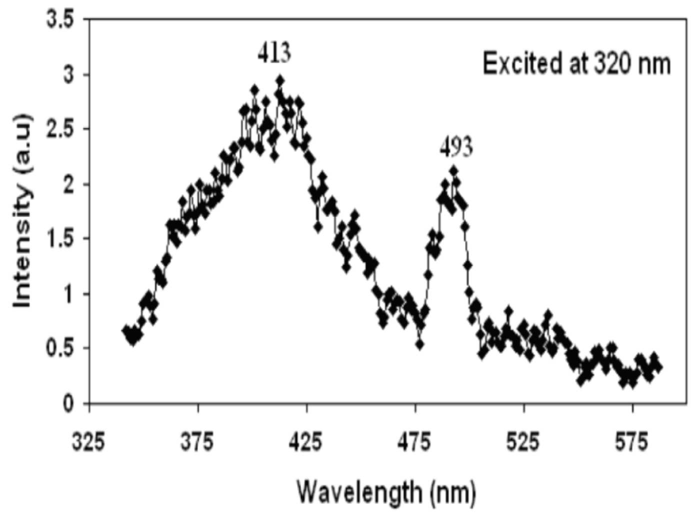

Figure-6
PL spectrum of CoS

Conclusion

The powder XRD has confirmed the amorphous nature of the sample. The SEM of as prepared CoS has shown that the CoS has been synthesized as nanorods of uniform distribution with average diameter of 139nm and 0.7µm long. The morphology of the nanorods are nearly spherical head and elongated to flat tail tip just similar to nail shape. The analysis of EDAX has shown the presence of nearly equal percentage of Cobalt and Sulphur with slight hydrous nature. The hydrous nature is confirmed by FTIR study which has shown the presence of O-H bond. The high absorption in the ultra-violet region at about 350nm makes the material to be suitable for UV filters and the wide transmission in the entire visible region enables it to be a potential candidate for optoelectronic applications**.** The room temperature photoluminescence at excitation wavelength of 320nm exhibits two bands of which one violet emission observed at 413nm is broad and other blue band at 493nm is comparatively sharp. These emissions are originated from Co vacancy related defects or their complexes.

References

1. Jun Zhou, Young Ding, Shao Z. D-eng, Li Gong, Ning S.Xu and Zhong L. wang Three –Dimensional Tungsten Oxide Nanowire networks, *Adv.mater*, **17,** 2107-2110 (**2005**)

2. Hu J.T., Odom T.W. and Lieber C.M., Chemistry and Physics in One Dimension: Synthesis and Properties of Nanowires and Nanotubes, *Acc. Chem. Res.,* **32,** 435-445**(1999)**

3. Wu Y. and Yang P., Germanium nanowire growth via simple vapor transport, *Chem. Mater.,* **12,** 605-607 (**2000**)

4. Yazawa M., Koguchi M., Mutto A., Ozawa M. and Hiruma K., Effect of one monolayer of surface gold atoms on the epitaxial growth of In As nanowhiskers, *Appl. Phys. Lett***., 61,** 2051-2053**(1992)**

5. Chen C.C. and Yeh c., Large-Scale Catalytic Synthesis of Crystalline Gallium Nitride Nanowires**,** *Adv. Matter.* **12,** 738-741 (2000)

6. Karthik Ramasamy, Weerakanya Maneerprakorn, Mohammad A. Malik and Paul O' Brien, Single-molecule precursor-based approaches to cobalt sulphide nanostructures, *Phil. Trans. R. Soc.* **A368**, 4249-4260 **(2010)**

7. Smith G.B., Ignatiev A. and Zajac G. Solar selective black cobalt : preparation, structure and thermal stability, *J. Appl. Phys.* **51**, 4186-4197 **(1980)**

8. Whitney T.M., Jiang J.S., Searson P. and Chien C., Fabrication and magnetic properties of arrays of metallic nanowires, *Science,* **261**, 1316-1319 **(1993)**

9. Yue G.H., Yan P.X., Fan X.Y., Wang M.X., Qu D.M., Wu Z.G., Li C. and Yan D, Structures and properties of Cobalt disulphide nanowire arrays fabricated by electrodeposition, Electrochem., Solid State lett., **10,** D29-D30 **(2007)**.

10. Feng Y.G., He T. and Alonso-Vante N. *In situ* free-surfactant synthesis and ORR-electrochemistry of carbon-supported Co_3S_4 and $CoSe_2$ nanoparticles, *Chem. Mater*. **20**, 26-28 **(2008)**

11. Yu Z., Du J., Guo S., Zhang J. and Matsumoto Y., CoS thin films prepared with modified chemical bath deposition, *Thin Solid Films,* **415,** 173-176 **(2002)**

12. Cruz-Vazquez C., Inoue M., Inoue M.B., Bernal R. and Espinza _Beltran F.J., Electrical and spectroscopic properties of amorphous copper sulfide films treated with iodine, lithium iodide and sodium iodide, *Thin Solid Films* **, 373,** 1 -5 **(2000)**

13. Ortega-Borges R., Lincott D., Mechanism of Chemical Bath Deposition of Cadmium Sulfide Thin Films in the AmmoniaThiourea System: In Situ Kinetic Study and Modelization, *J. Electrochem. Soc*. **140,** 3464-3473 **(1993)**

14. Deshmukh L.P. and Holikatti S.G., A CdS:Sb photoelectrode for photoelectrochemical applications*, J. Phys. D: Appl. Phys***., 27,** 1786 -1790 **(1994)**

15. Basu P.K. and Pramani K.P., Chemical deposition of thin film of CoS*, J. Mater. Sc i: Lett*., **5,** 1216-1218 **(1986)**

`

16. Donald Okli N. and Cecilia okoli N., Optical growth and characterization of cobalt sulphide Thin films Fabricated using the chemical Bath Deposition Technique, *J. Natural Sci. Res.*, **2,** 5-8 **(2012)**

17. Deshmukh L.P. and Mane S.T., Liquid Phase Chemical deposition of Cobalt Sulphide Thin Films: Growth and properties, *Digest J. Nano materials and Biostructures,* **6**, 931-936 **(2011)**

18. Sifuentes C., Ybarmenkov, Strodumov A., Filipov V., Lipovskii A., Application of CdSe-nanocrystallite-doped glass for temperature measurements in fiber sensors, *Opt. Eng*., **39,** 2182-2186 **(2000)**

19. Stegeman G.I. and Seaton C.T., Nonlinear integrated optics , *J. Appl. Phys*., **58,** R57-R79 **(1985)**

20. Ezema F.I. and Osuji R.U., Band gap shift and optical characterization of chemical bath deposited CdSSe thin films on annealing, *Chalcogenides Lett*., **4** , 69 -75 **(2007)**

21. Mishack E. Ekuma et al., Synthesis and characterization of chemical bathdeposited CDCOS thin film, *chalcogenide Lett*., **7**, 31-38 **(2010).**

22. Nithima Khaorapapong , Areeporn onatam makoto Ogawa, Very slow formation of copper sulfide and cobalt sulfide nano partices in montmorillonite, *App. Clay sci.,* **51,** 182 -186 **(2011)**

23. Bao S. J., Li Y., Li C. M., Bao Q., Lu Q. and Guo, Shape evolution and magnetic properties of cobalt sulfide, *J. Cryst. Growth Des.,* **8,** 3745-3749 **(2008)**

24. Silverstein, Basster and Morrill, Spectrometric identification of organic compounds, John Wiley and Sons, USA, 91 (**1991**)

25. Jag Mohan, Organic Spectroscopy, Narosa Publishing House, New Delhi, 61-62 (**2000**)

26. Pal D. and Bose D.N., Study of photoluminescence and computation of configuration coordinate diagram of Cu related deep levels in InP, *Bull. Mater. Science*, **20,** 401-407 (**1994**)

27. Baibaswata Bhattacharjee and Chung-HsinLu, Multicolor luminescence of undoped zinc sulfide nanocrystalline thin films at room temperature, *Thin Solid films*, **514,** 132-137 **(2006)**

28. Fang Yang, Wilkinson M., Austin E.J. and O'Donnel K.P., Origin of the Stokes shift: A geometrical model of exciton spectra in 2D semiconductors , *Phys. Rev. Letts.,* **70,** 323-326 **(1993)**

29. Yanagida S., Yoshida M., Shiragami T., Pac C., Mori H. and Fujita H., Semiconductor photocatalysis. I. Quantitative photoreduction of aliphatic ketones to alcohols using defect-free zinc sulfide quantum crystallites, *J. Phys. Chem.,* **94**, 3104-3111 **(1990)**

30. Jayanth I.K., Chawla S., Chander H. and Haranath D., Structural, optical and photoluminescence properties of ZnS: Cu nanoparticle thin films as a function of dopant concentration and quantum confinement effect, *Cryst. Res. Technol.,* **42**, 976 -982 **(2007)**