



Synthesis and Optical Characterization of Sodium Dodecyl Sulfate Assisted Zinc (II) BIS (8-Hydroxyquinoline) Rod - Like Structures

V. Bharathi Devi^{1,2}, P. Arulmozhichelvan¹, P. Murugakoothan^{1*}

¹MRDL, PG and Research Department of Physics, Pachaiyappa's College, Chennai – 600 030, India.

²Department of Physics, Dr. M.G.R. Educational and Research Institute University, Maduravoyal, Chennai - 600 095, India

Abstract

Highly luminescent zinc (ii) bis (8-hydroxyquinoline) nanorods were synthesized via simple precipitation method using sodium dodecyl sulfate (SDS) as a surfactant. The sodium dodecyl sulfate assisted zinc (ii) bis (8-hydroxyquinoline) [Znq2:SDS] nanorods were analyzed by powder X-ray diffraction (PXRD) to confirm the crystalline nature of the particles. Thermo gravimetric analysis (TG) and differential thermal analysis (DTA) were carried out to find the thermal stability of the Znq2:SDS nanorods. The morphology and presence of elements were studied by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX). The functional groups of the particles were confirmed by FTIR spectroscopy. The optical properties of the particles were studied by UV-vis-NIR spectral study. The band gap of the particles was calculated. The synthesized Znq2:SDS nanorods were confirmed by photoluminescence studies for OLED applications as emission and electron transport layers.

Key words : Znq2: SDS, nanorods, Thermal stability, SEM, FTIR, UV-vis – NIR.

1. Introduction

Organic electroluminescent materials have been the subject of intense research for use in light emitting diodes (LEDs) [1]. When compared with liquid crystal display (LCDs), organic light emitting diodes (OLEDs) require lower energy input, have a wider viewing angle with improved color contrast and can be made much thinner [2]. Now a days bright and efficient organic light – emitting devices (OLED) have attracted considerable interest due to their potential application to flat panel display [3]. Recently high luminance and high efficiency were realized in OLEDs with a multi-layer structure, including emitting materials, such as the metal-chelate complex [4]. Thus, the 8-hydroxyquinolinato ligand is currently used by many researchers because of its thermal stability, carrier mobility and improved performance [5- 6]. In particular, research on a Zn complex as an emitting, as well as electron transport material [7-11]. Zinc (ii) Bis (8 – hydroxyquinoline) (Znq2) has been investigated as an electroluminescent and electron transporting material in organic light emitting diodes. In this paper we report synthesis and studies on Znq2: SDS nano rods which can be used as an electron transport layer. Sodium dodecyl sulfate has acted as a surfactant which modifies the surface of nano rods and prevents the growth of particle to a larger size.

2. Materials and Methods

2.1. Materials

Zinc acetate ($\text{ZnC}_4\text{H}_6\text{O}_4$), 8-Hydroxyquinoline (8Hq) and Ammonia (NH_3) all of Merck brand, were used as starting materials. All these chemicals were of high purity and no further purification was done. Sodium dodecyl sulfate ($\text{NaC}_{12}\text{H}_{25}\text{SO}_4$) was used as the surfactant.

2.2. Synthesis Of Znq2: Sds Nanorods

Initially, 4.3175 g of zinc acetate was dissolved in 100 mL of water and stirred using magnetic stirrer for 1 hour at room temperature. In this solution, 0.0345 g of SDS dissolved in 20 mL of water was added. The 8Hq solution was separately prepared by dissolving 5.442 g of 8Hq in a mixed solvent of ammonia (0.04 mL) and water (100 mL) and then it was added drop by drop to the above solution under continuous stirring. Yellow precipitate was formed immediately. The precipitate was filtered and dried in vacuum oven for 6 hours.

2.3. Characterization Studies

Powder X-ray diffraction (PXRD) analysis was carried out using a Rich Seifert X-ray diffractometer with $\text{Cu K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation to observe the crystallinity of the sample. The TG-DTA thermograms of the samples were recorded using a SEIKO DSC200 instrument under nitrogen atmosphere at a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$. Scanning electron microscope (SEM) was employed for morphological study using a CARI ZEISS MA15/EVO18 operated at 30 kV with Energy Dispersive X-ray analyser (EDAX). The FTIR spectrum of Znq2:SDS nanorods was recorded in the range of $4000\text{--}400 \text{ cm}^{-1}$ using a BRUKER 66 V FTIR spectrophotometer by KBr pellet method in order to study the metal complex coordination. The optical absorption spectrum of the sample was recorded in the range between 200-800 nm using Labindia 3032 UV-vis-NIR spectrophotometer. The photoluminescence study was done using a JOBIN YVON FLUROLOG-3-11 spectrofluorometer with an excitation wavelength (λ_{ex}) of 380 nm to confirm the OLED property of the Znq2:SDS particles.

3. Results and Discussion

3.1. Powder X- Ray Diffraction Analysis

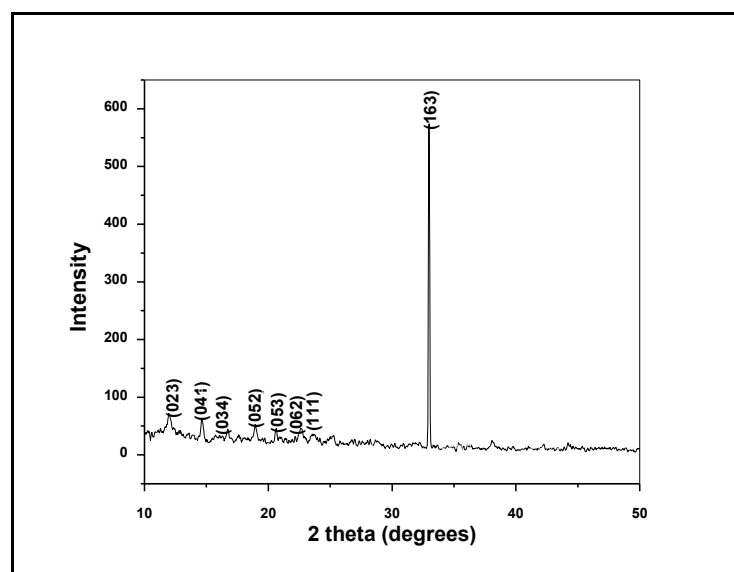


Fig.1. PXRD pattern of Znq2: SDS

The Powder – X - ray diffraction (PXRD) pattern of Znq2:SDS nano rods prepared using simple precipitation method is shown in Fig.1. The peaks at scattering angle (2θ) of 11.8° , 14.6° , 16.7° , 18.9° , 20.6° , 22.4° , 23.6° and 32.9° corresponds to (023), (041), (034), (052), (053), (062), (111) and (163) crystal planes

respectively. It also shows that the particle has an orthorhombic phase with lattice constant $a = 3.85 \text{ \AA}$, $b = 24.93 \text{ \AA}$, $c = 28.72 \text{ \AA}$ and $v = 2756 \text{ \AA}$ [12, 13].

3.2. Thermal Analysis

Thermal stability of the Znq2: SDS nano rods was determined by thermo gravimetric analyzer (TGA) unit of SEIKO model TG/DTA 6200. The TG and DTA thermograms of the synthesized Znq2: SDS nano rods are shown in Fig.2. The TG thermogram shows 3 stages of weight loss of Znq2: SDS. The first stage occurs from 153°C to 205°C with the weight loss of 42.4%. The second stage occurs from 205°C to 430°C with the weight loss of 14.8%. The third stage occurs from 430°C to 570°C with the weight loss of 28.1%. From the TG curve it is clear that the sample is stable up to 153°C . The endothermic peak observed in DTA thermogram at 201°C coincides with the first stage weight loss of Znq2: SDS. The observed endothermic of Znq2: SDS is attributed to the absorption of energy for the breaking of bonds during decomposition.

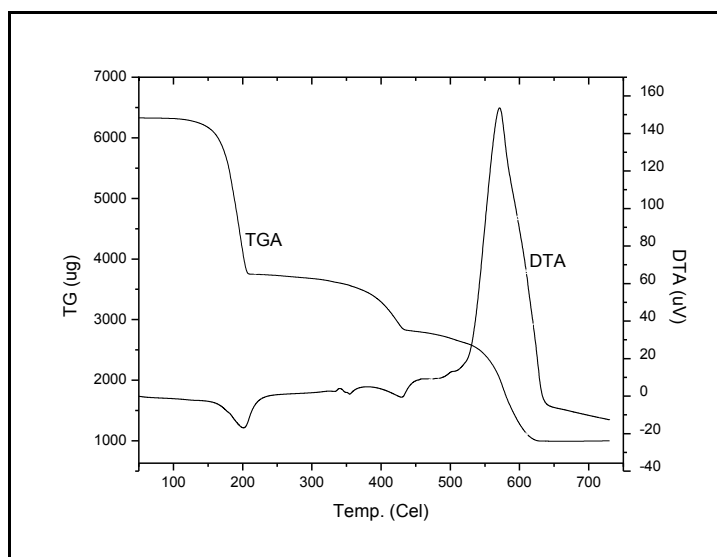


Fig.2. Thermal analysis of Znq2:SDS

3.3. Sem and Edax Analysis

The surface morphology of the Znq2: SDS nano rods was analyzed using SEM. Fig.3 (a) shows the scanning electron micrograph of Znq2: SDS nano rods. It reveals that the synthesized sample is composed of nano rods with maximum thickness of about 230.9 nm.

Fig.3 (b) shows the EDAX spectrum of Znq2: SDS nano rods. This indicates that the particles are indeed made up of zinc, carbon, sodium, sulfur and oxygen. It suggests that the obtained product is a pure Znq2: SDS devoid of impurities.

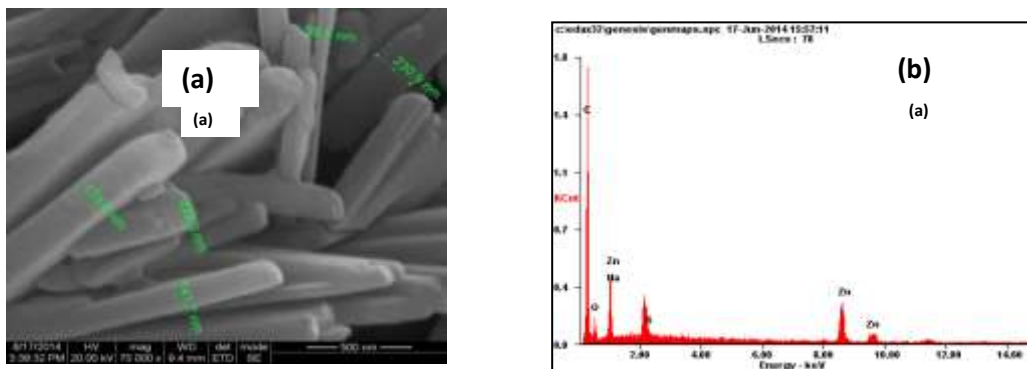


Fig.3. (a). SEM image and (b) EDAX pattern of Znq2: SDS

3.4. FTIR ANALYSIS

The FTIR spectrum of Znq2:SDS nano rods are shown in Fig.4. The plane ring deformation of 8 hydroxyquinoline is observed at 820 cm^{-1} and 911 cm^{-1} . The metal bonding with the quinoline molecules is observed at 1330 cm^{-1} , 1390 cm^{-1} , 1577 cm^{-1} and 1598 cm^{-1} [14]. The bands at 1461 cm^{-1} and 1495 cm^{-1} are corresponded to the vibrations of the pyridyl and phenyl groups of 8 hydroxyquinoline [15]. The O-H vibration bands are detected at 3046 cm^{-1} - 3379 cm^{-1} [16]. The characteristic absorption band of Zn-O is observed at 462 cm^{-1} , which further support that the as – prepared product is pure Znq2: SDS.

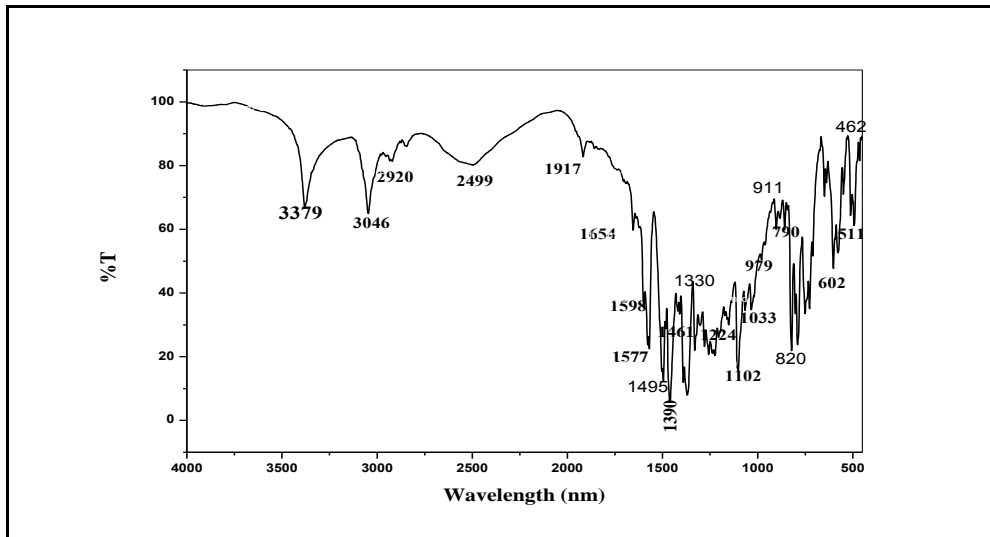


Fig.4. FTIR spectrum of Znq2: SDS

3.5. UV-VIS – NIR SPECTRAL ANALYSIS

UV-vis-NIR absorption spectrum of Znq2: SDS nano rods is shown in Fig.5 (a). From this spectrum it is observed that the absorption maximum occurs at 271 nm with a shoulder at 320 nm and the cutoff wavelength at 368 nm. The optical band gap was determined from the optical absorption edge and using the Tauc's relation. Fig. 5(b) shows the Tauc's plot of Znq2: SDS nano rods. The optical band gap of Znq2: SDS nano rods was determined using the Tauc's relation [17-18].

$$A_{hv} = (hv - E_g)^n$$

Where n is $\frac{1}{2}$ for allowed direct, 2 for allowed indirect, $\frac{3}{2}$ for forbidden direct and 3 for forbidden indirect transitions, A is the absorbance, E_g is the band gap corresponding to a particular absorption occurring in the material and $h\nu$ is the photon energy. The direct optical band gap for Znq2:SDS E_g was obtained from extrapolation of the linear part of the Tauc's plot as 3.3 eV.

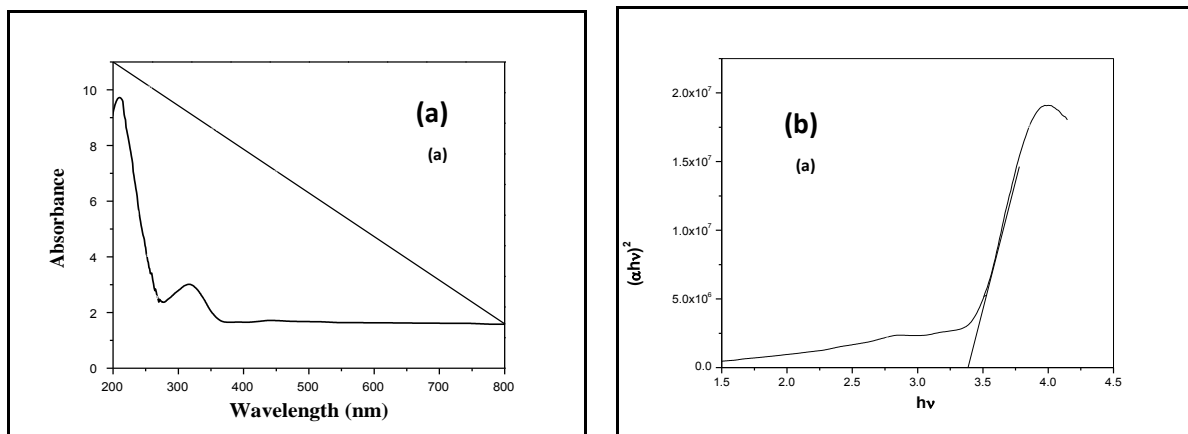


Fig .5. (a) UV-Vis absorption and (b) Tauc's plot of Znq2: SDS

3.6. Photoluminescence Analysis

The photoluminescence (PL) emission spectrum of Znq2:SDS nano rods is shown in Fig.6. The prominent PL emission peak is observed at 538 nm in green region of the spectrum. It shows that Znq2: SDS is not only suitable for organic light emitting diode (OLED) it is also useful for solid state lighting application [19].

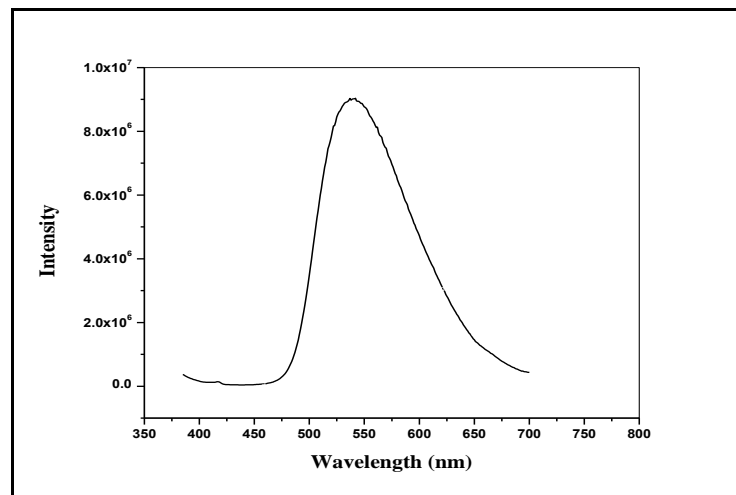


Fig .6. Photoluminescence spectrum of Znq2: SDS

4. Conclusion

Znq2 particles were synthesized by simple precipitation method using SDS as a surfactant. The crystal structure, morphology, absorption, functional groups and emissive properties of Znq2: SDS nano rods were studied by PXRD, HRSEM, UV-vis, FTIR and PL analyses. The TG –DTA analysis of the powder sample suggests that the synthesized sample is stable up to 153°C. The observed optical properties of the Znq2: SDS nanorods suggest that this compound is a potential candidate for application in organic light emitting devices, such as OLEDs.

References

1. Abhijith ,T., Shamjid, P., and Reddy, V.S, Synthesis of Silver Nano particles for Organic Bistable Memory Device Applications, International Journal of ChemTech Research, 2015, 7(2): 1000-1004.
2. Periyasamy Murugan, Efficient green light-emitting diodes based on substituted triphenylamine derivatives and its structural elucidation, International Journal of ChemTech Research, 2015, 8(7): 172-176.
3. Tang , C., VanSlyke, S, Organic electroluminescent diodes , Journal of Applied Physics Letter, 1987, 51: 913- 915.
4. Tang, C. W., Van Slyke, S.A., Chen, C.H, Electroluminescence of doped organic doped Organic thin films, Journal of Applied Physics Letters, 1989, 65(9): 3610 – 3616.
5. Jang, Y.K., Kim, D.E., Kim, W.S., Kwon, O.K., Lee, B.J., and. Kwon, Y.S, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2006, 331: 284-285.
6. Byoung-Sang Kim , Dong-Eun Kim , Gyu-Chae Choi Jun-Woo Park , Burm-Jong Lee and Young-Soo Kwon , Electron Transport Properties of Zn (phen)q Compared with Alq3 in OLED, Journal of Electrical Engineering & Technology, 2009, 4(3): 418- 422.
7. Naiying, D.U., Qunbo, M.E.I., and Mangeng, L.U, Quinolate aluminum and zinc complexes with multi-methyl methacrylate end groups : synthesis, photoluminescence, and Electroluminescence characterization, Synthetic Metals, 2005, 149: 193-197.
8. Zeng, H.P., Wang, G.R., Zeng , G.C., and Li, J, The synthesis characterization and Electroluminescent properties of zinc (II) complexes for single –layer organic light emitting Diodes, Dyes and Pigment, 2009, 83: 155 -161.

9. Vandna Nishal, Amit Kumar, Partap, S., Kadyan, Devender Singh, Ritu Srivastava, Ishwar Singh and Modeparampil N. Kamalasanan, synthesis characterization and Electroluminescent characteristics of Mixed-ligand Zinc(II) complexes, *Journal Of Electronic Materials*, 2013, 42(6): 973-978.
10. Jarald Brigit Gilda1, M.J., Anbarasu, S., Samson , Y., and Prem Anand Devarajan, The Influence of Benophenone substitution on the Physico – Chemicl Characteriations of 8- Hydroxyquinoline NLO single crystals, *Journal of Minerals and Materials Characterization and Engineering*, 2012, 11:769-773.
11. Bharathi Devi, V., Arulmozhichelvan, P., Murugakoothan, P, Synthesis and Electroluminescence characterization of annealed Znq2 particles with CTAB, *International Journal of Chem Tech Research*, 2014, 6(3): 2138-2140.
12. Aravinth, K., Anandha Babu, G., and Ramasamy, P. Growth of <201> 8-hydroxyquinoline organic crystal by czochral ski Method and its characterizations, *Journal of Thermal Analysis and Calorimetry*, 2012 , 110:1333-1339.
13. Mae, R.J., Gordon , L, The infrared spectra of chelate compounds—I: A study of some Metal chelate compounds of 8-hydroxyquinoline in the region 625 to 5000 cm⁻¹, *Talanta* , 1963,10: 851-859.
14. M. Nagpure,I. M., Duvenhage, M., Shreyas, S., Pitale, Ntwaeaborwa, O.M., Terblans, J.J., Swart, H.C, Synthesis, Thermal and Spectroscopic Characterization of Caq2 (Calcium 8- Hydroxyquinoline) Organic Phosphor, *Journal of Fluorescence*, 2012, 22: 1271–1279.
15. Hong-Cheng Pan , Fu-Pei Liang, Chang-Jie Mao, Jun-Jie Zhu and Hong-Yuan Chen Highly Luminescent Zinc (II) – Bis –(8hydroxyquinoline)complex Nanorods: sonochemical Synthesis, Characterizations, and Protein Sensing, *Journal of Physical Chemistry B*, 2007, 111: 5767-5772.
16. Guifeng Liu, Shihua Ma , Hongwei Zhao, Te Ji , Zengyan Zhang and Wenfeng Wang , Terahertz absorption spectra of 8-hydroxyquinoline and its some metal complexes, *Journal of Molecular Structure* , 2009,936: 56-59.
17. Tauc, J., Grigorovici,R., and Vancu, A, Optical properties and Elecronic structure of Amorphous germanium , *physica status solidi (b)* , 1996 ,15(2): 627–637.
18. Aparna Misra, Pankaj Kumar, Dhawan , S., Kamalasanan, M.N., and Subhas Chandra, Bright- blue organic electroluminescent device based on bis (2-methyl 8-quinolinolato) (triphenyl siloxy) aluminium , *Indian Journal of Pure & Applied Physics* , 2005, 43: 522-526.
19. Michael Colle, Jurgen Gmeiner, Wolfgang Milius, Harald Hillebrecht, and Wolfgang Brutting, Tunable Photoluminescence from tris (8-hydroxyquinoline) aluminum (Alq3), *Advanced Function Materials*, 2003, 13: 237-239.
