Study of the Characteristics of Nanocrystal CdS , CdSe , CuO and Nanocomposite CdS-PTh ,CdSe-PTh by XRD-Analysis

Aurobinda Acharya[1] , Bairagicharan Panda[2], Mamun Mohanty[3] ,Gourisankar Roy[4*]

[1]Tata Consultancy Service,Kalingapark, Bhubaneswar,Orissa, India

[2]Dept of Physics, R.I.H.S Bhograi, Balasore, Orissa, India

[3]124/126, Satyanagar, Bhubaneswar, Orissa, India

[4]Govt (Auto) College, Bhawanipatna ,Orissa, India

gsroy2004@gmail.com

Abstract: In this piece of work we have synthsized the nanocrystaline CdS by Microemulsion Mediated Sonochemical Route, CdSe by Wet Chemical Synthesis and CuO by Combined Precipitation-Pyrolysis Method then by Oxidative Polymerization of Thiophene we have synthesized polythiophene and nanocomposite CdS-PTh and CdSe-PTh and studied their phase identification by X-ray Diffractometer.

[Aurobinda Acharya, Bairagicharan Panda, Mamun Mohanty ,Gourisankar Roy. **Study of the Characteristics of Nanocrystal CdS, CdSe , CuO and Nanocomposite CdS-PTh ,CdSe-PTh by XRD-Analysis**. Researcher. 2011;3(1):108-112]. (ISSN: 1553-9865). http://www.sciencepub.net.

Keywords: X-ray Diffraction(XRD), Nanocrystal, Nanocomposite

1.Introduction

Semiconductor nanocrystals exhibit unique size and shape-dependent optical properties due to the quantum confinement effects and thus may find a wide range of applications in optoelectronic devices, photocatalysis, solar energy conversion and biological imaging and labeling. The II-VI semiconductor nanocrystals, such as CdSe, CdTe and CdS nanocrystals, are the group of nanostructures that have been mostly investigated because of their high luminescence efficiency and easily adjustable luminescence[1-4] from ultraviolet to near infrared region by nanocrystals sizes showing the prospective for optoelectronic devices and biological imaging as well as labeling applications. As a direct wide bandgap (2.42 eV) semiconductor, CdS nanocrystals may be potentially used in optoelectronics of nonlinear optics and light emitting diodes. The Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nano-scale this is often not the case. Size-dependent properties are observed such as quantum confinement in semiconductor nanoparticles, surface plasmon resonance in some metal particles and super para magnetism in magnetic materials. The properties of materials change as their size approaches the nanoscale and the percentage of atoms at the surface of a material becomes significant. Modification in the electronic levels occurred very strongly due to the limited number of atoms in the particles. Such materials in these regime exhibit novel physical and chemical properties due to the large surface to volume ratio as well as size quantization effect in semiconductor nanoparticles. Due to finite size of the nanoparticles the continuous energy band of the bulk crystal transforms into a series of discrete states resulting in widening of the effective band gap. The nanoparticles frequently display photoluminescence and sometimes display electroluminescence [5-7]. Additionally, some nanoparticles can form self-assembled arrays. Because of these favorable properties, nanoparticles are being extensively displays studied for use in optoelectronic. With the decreasing crystal size, CuO nanocrystals exhibit some unique properties like change in ionic character, ferromagnetic response etc. Investigation of electronic properties of CuO nanocrystals will provide more insight into the electronic correlation and also the electronic coherent states [8-10]. As Copper oxide has more industrial applications like solar energy storage, semiconductors and catalysis, it attracts researchers to study its behavior at various size regimes. Doped

semiconductors are extensively investigated to obtain basic information on impurity states in quantum dots and to examine their potential applications in novel light-emitting devices. It is well known that the quantum confinement effect modifies the electronic structure of nanocrystals when their diameter is comparable to or smaller than the diameter of the bulk exciton. We have synthesized the CdS, CdSe and CuO nanocrystals as well as CdS-PTh and CdSe-PTh nanocomposites and studied their phase identification by X-ray Diffractometer.

2.Theory

The fractional decrease in intensity I of an X-ray beam as it passes through a substance is proportional to the distance traversed by the beam 'x'. Therefore $-dI/dx = -\mu dx$, where 'μ' is the linear absorption coefficient. This constant is dependent on the material properties, its density and the wavelength of X-rays. Integrating this equation gives: $I_x = I_o \exp(-\mu x)$, where 'I_o' is the intensity of the incident beam and 'I_x' is the intensity of the transmitted beam after passing through distance 'x'. Only a small range of characteristic x-rays are widely used for diffraction. Mainly K_α lines are used. A diffraction pattern records the X-ray intensity as a function of 2θ diffraction angle. The peaks in X-ray diffraction pattern are directly related to the atomic distances. For a given set of lattice plane with an inter plane distance of 'd', the condition for a diffraction peak to occur can be simply written as $2d\sin\theta = n\lambda$ which is known as the Bragg's law. The positions and the intensities of the peaks are used for identifying the underlying structure or phase of the material. This phase identification is important because the material properties are highly dependent on structure. We can calculate the particle size of the sample from XRD analysis using debye Scherrer's formula $d = 0.9\ \lambda / \beta \cos\theta$ where 'λ' is the wave length of X-rays, β is the FWHM of diffraction peak and θ is the angle to the corresponding peak.

3. Experimental Work

The experimental work has been done in Centre for Materials for Electronics Technology (C-MET), Pune. We have discussed in brief the preparation of CdS , CdSe and CuO nanocrystals as well as CdS-PTh and CdSe-PTh nanocomposites.

3.1 Synthesis of Nanocrystaline CdS (Sonochemical Route):

In this procedure, 95 ml of distilled water and 5 ml of CTAB (surfactant) were added together and divided into two 50 ml aliquots. Then 0.01 M solutions of cadmium nitrate and ethylene diamine tetraacetic acid (EDTA) were prepared in one aliquot and 0.01 M solutions of sodium thiosulphate were prepared in another aliquot. These solutions were added together slowly (drop by drop) under stirring and then irradiated at 20 KHz frequency for 1 hour in an ultrasonic bath. The products of greenish-yellow precipitates were collected. These products were filtered and washed thoroughly with distilled water followed by ethanol and then dried in a vacuum oven at 70° C for 5 hours and ground these to get powder form of nanocrystalline CdS.

3.2 Synthesis of Nanocrystalline CdSe: (Wet Chemical Synthesis)

In this procedure, first 0.4 M Se metal powders were dissolved in 0.4 M sodium sulphite solution. The solution was carried out at 60 C under stirring for 4-5 hours. Then the undissolved particles were filtered out after the solution cooled to the room temperature. That solution was sodium selenosulphate used as a selenium source. Second, in 35 ml of distilled water and 15 ml of isopropanol, 0.1 M of cadmium sulphate solution was prepared. The prepared sodium selenosulphate solution was added drop wise to the stirred cadmium sulphate solution. After one hour, the products of dichromate coloured precipitates were collected and then washed with distilled water followed by absolute ethanol. The products were dried in a vacuum oven at 70°C for 6 hours. Finally the powders of nanocrystalline CdSe were collected.

3.3 Preparation of Copper Oxide Nanocrystals

The synthesis of Copper oxide nanocrystals is done by a combined precipitation-pyrolysis method, which involves initially preparing precursors and finally decomposing the precursors in a furnace with different annealing temperatures, which lead to the final products of copper oxide nanocrystals.

3.3.1 Procedure for Preparing Precursor A

Preparation of precursor A involves the following reaction. 0.3 M of aqueous ammonium carbonate is prepared by dissolving 4.714 g of ammonium carbonate in 100 ml distilled water. Similarly, 0.05 M of aqueous copper acetate is prepared by dissolving 4.991g of copper acetate in 500 ml of distilled water. Now, 50 ml of freshly prepared aqueous ammonium carbonate is rapidly added to 300 ml of aqueous copper acetate, and precipitate is formed. After a reaction time of 1minute, the precipitate formed is separated by a centrifuge process. Then they are washed with distilled water and ethanol to remove possible

remnant ions in the final products, which are dried in air at 600 C and kept ready for further reaction.

3.3.2 Procedure for Preparing Precursor B

0.3 M of aqueous sodium hydroxide is prepared by dissolving 4.714 g of sodium hydroxide in 100 ml distilled water. Similarly, 0.05M of aqueous copper acetate is prepared by dissolving 4.991 g of copper acetate in 500 ml distilled water. 50 ml of prepared aqueous sodium hydroxide is mixed rapidly with 300 ml of aqueous copper acetate. After a reaction of 1 min the precipitate is formed which is separated by centrifuge process, and then washed with distilled water and ethanol. It is then dried in air at 600 C.

3.3.3 Thermal Decomposition of Precursors

Thermal decomposition of the precursors in a furnace with different annealing temperatures led to the final product of CuO nanocrystals and nanorods. Sample (S2) was prepared at 2000C by using precursor A under constant nitrogen flow. Annealing at temperatures 3000C, 4000C, and 5000C, samples (S3), (S4), and (S5) are prepared respectively from precursor A. without nitrogen flow the final product obtained was copper oxide nanocrystals. Sample (S6) was prepared by using precursor B with the reactant copper sulphate at an increased concentration 0.15 M, which is obtained by dissolving 3.742g of copper sulphate in 100 ml of distilled water and at an annealing temperature of 3000C. Here the final product obtained was copper oxide nanorods.

3.4 Synthesis of Polythiophene (PTh):(Oxidative Polymerization of Thiophene)

Here 0.1 M of thiophene was dissolved in 25 ml of acetonitrile or methanol (non-aqueous media) with 1ml of CTAB as surfactant. Then 0.3 M of lithium perchlorate was added as a supporting electrolyte to increase the bath conductivity and also added 0.1 M of ferric chloride as an oxidant to the above stirred solution. Again stirred the above mixture for 2 hours and kept several hours for polymerization. Then the products of black coloured precipitates were collected. These products were washed thoroughly with acetonitrile to remove any residual ferric chloride. These products were dried in a vacuum oven at 70°C for 10 hours to get powder form of polythiophene .

3.5 Synthesis of CdS / PTh Nanocomposite:

In a typical procedure, 50 ml of methanol, 45 ml of distilled water and 5 ml of CTAB stock solution were added together and then divided into two equal volumes. 0.1 M of thiophene, 0.3 M of lithium perchlorate and 0.1 M of ferric chloride solutions were prepared in one part. Again 0.1 M of cadmium nitrate, 0.1 M of EDTA and 0.1 M of sodium thiosulphate solutions were prepared in another part. Then these solutions were mixed slowly under stirring for 1 hour and irradiated 20 KHz frequency for 1 hour in an ultrasonic bath. The products of brown coloured precipitates were collected and then washed thoroughly with ethanol. The final products were dried in a vacuum oven at 70°C for 10 hours and ground to get CdS/polythiophene nanocomposite powders.

3.6 Synthesis of CdSe / PTh Nanocomposite:

Here first Se metal powders were dissolved in 0.4 M sodium sulphite solution at 60□C under stirring for 4-5 hours and then the undissolved particles were filtered out after the solution cooled to the room temperature. That solution was sodium selenosulphate used as a selenium ion source. Second, 50 ml of methanol, 45 ml of distilled water and 5 ml of CTAB stock solution were added together and then divided into two equal volumes. 0.1 M of thiophene, 0.3 M of lithium perchlorate and 0.1 M of ferric chloride solutions were prepared in one part. Again 0.1 M of cadmium nitrate and the above prepared sodium selenosulphate solutions were prepared in another part. These solutions were mixed slowly under stirring for 1 hour and irradiated 20 KHz frequency for 1 hour in an ultrasonic bath. The products of blackish-brown coloured precipitates were collected and then washed thoroughlywith absolute ethanol. The final products were dried in a vacuum oven at 70°C for 10 hours. Finally CdSe/polythiophene nanocomposite powders were collected.

4. Results and Discussion

X-Ray Diffraction (XRD) Analysis:

Phase identification was carried out by X-ray Diffractometer (X-Ray generator, Regaku Miniflex, Japan) employing a scanning rate of 2°/minute in diffraction angle 2θ range from 10° to 80° and CuK_{α} radiation (λ=1.5405 A°).

The X-ray diffraction curves for different prepared materials are discussed here. Figure 1 gives the XRD pattern of nanocrystalline CdS prepared by microemulsion mediated sonochemical synthesis. The XRD pattern of nanocrystalline CdS contains 3 main peaks at diffraction angle 26.55˚, 43.87˚ and 51.91˚ corresponds to the Miller indices (101), (110) and (112).

This XRD pattern matched with the JCPDS data (JCPDS No. 6 - 314) of hexagonal CdS. The broadening of the peaks indicates the inorganic component CdS is in nanometer scale. Figure 2 shows the XRD pattern of CdS/polythiophene nanocomposite. Here the more diffraction peaks are due to the presence of polythiophene in CdS/polythiophene nanocomposite. It confirms the successful polymerization of thiophene monomer and the formation of nanocomposite material.

Figure 3 gives the XRD pattern of as-prepared nanocrystalline CdSe synthesized by wet chemical route. After thermal annealing of the prepared CdSe, we can get the clear diffraction peaks because of the increase in grain sizes of the material. The above XRD pattern matched with JCPDS data (JCPDS No. 8 - 459) of hexagonal and cubic CdSe. Figure 4 shows the XRD pattern of CdSe/polythiophene nanocomposite. Here also some extra diffraction peaks are due to the presence of polythiophene in CdSe/ polythiophene nanocomposite. Figure 5 and figure 6 shows the XRD pattern of CuO nanocrystal synthesized at different tempreture. The mean crystalline sizes of the samples estimated using scherrer formula and are in the range of 5 to 15nm. The XRD data clearly demonstrate the growth of nanocrystals as the thermal treatment temperature increases. The FWHM increases as the sample size decreases.

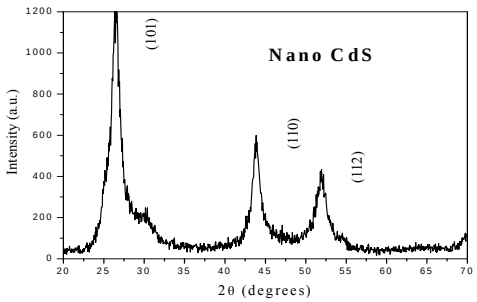


Figure 1: XRD pattern of nanocrystalline CdS

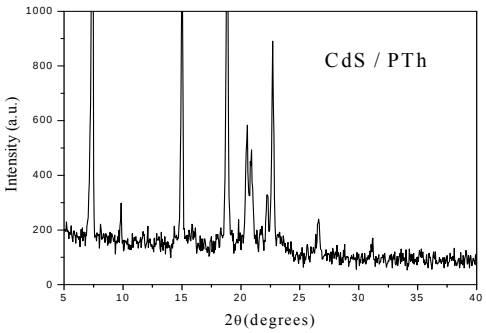
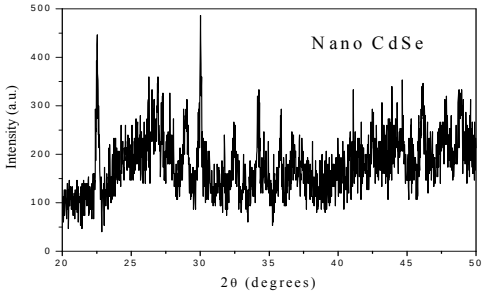


Figure 2: XRD pattern of CdS / Polythiophene nanocomposite



Figur

e 3: XRD pattern of nanocrystalline CdSe

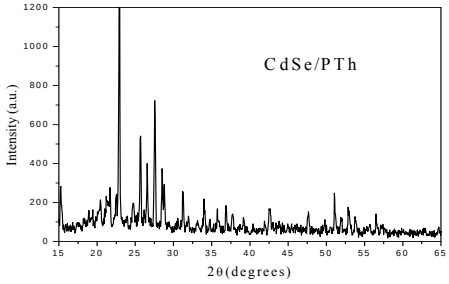


Figure 4: XRD pattern of CdSe / Polythiophene nanocomposite

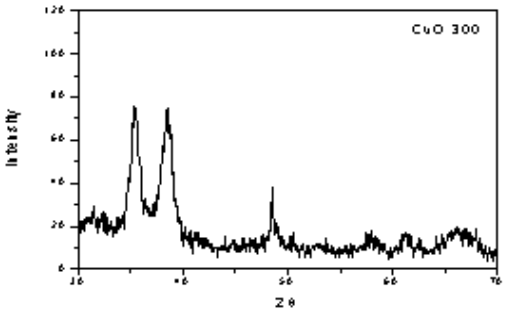


Figure 5: XRD pattern of CuO prepared at 300 ^{0}C

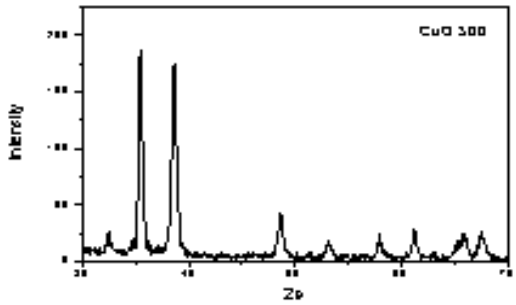


Figure 6: XRD pattern of CuO prepared at 500 ^{0}C

3. Conclusion

In conclusion, it is summarized that CdS/polythiophene and CdSe/polythiophene

nanocomposites are successfully synthesized in room temperature and pressure. The inorganic CdS and CdSe nanocrystals are of uniform size and nearly monodispersive, which are disordered and mixed with polythiophene. In XRD, the broadening of peaks indicates the inorganic components are in nanometer scale. Some extra peaks in nanocomposites may be assignable to the dopants. In case of CuO the XRD data demonstrates the growth of nano crystal with increase of thermal treatment temperature.

References

[1] Zhanyu Wu, Yili Zhao, Fangping Qiu, Yapeng li, Shuwei Wang, Bao Zhang, Bohan Yang, Yefei Zhang, Ruotian Gao, Jingyuan Wang "Synthesis and characterization of water-soluble, stable and highly luminescent itaconic acid/methacrylic acid" copolymer-coated CdSe/CdS quantum dots" Journal of Luminescence,2009;129(10);p 1125-1131.

[2]Alexandra E. Raevskaya, Alexander L. Stroyuk, Stephan Ya. Kuchmiy "Preparation of colloidal CdSe and CdS/CdSe nanoparticles from sodium selenosulfate in aqueous polymers solutions" Journal of Colloid and Interface Science,2006;302(1);p 133-141.

[3]Qiang Wang, Daocheng Pan, Shichun Jiang, Xiangling Ji, Lijia An, Bingzheng Jiang "Luminescent CdSe and CdSe/CdS core-shell nanocrystals synthesized via a combination of solvothermal and two-phase thermal routes"Journal of Luminescence,2006; 118(1);p 91-98.

[4]Yung-Tang Nien, Badruz Zaman, Jianying Ouyang, In-Gann Chen, Chii-Shyang Hwang, Kui Yu"Raman scattering for the size of CdSe and CdS nanocrystals and comparison with other techniques" Materials Letters,2008; 62(30);P 4522-4524.

[5] Umme Farva, Chinho Park "Influence of thermal annealing on the structural and optical properties of CdSe nanoparticles" Solar Energy Materials and Solar Cells; 2010, 94(2),p 303-309.

[6] Ming Sun, Haizhou Yu, Wen Yang, Li Qi, Fan Yang, Xiurong Yang "Shape evolution of CdSe nanocrystals in vegetable oils: A synergistic effect of selenium precursor" Colloids and Surfaces A: Physicochemical and Engineering Aspects;2009,350(1-3),p 91-100

[7] C. Dridi, M. Haouari, H. Ben Ouada, A.-P. Legrand, J. Davenas, M. Bernard, J.-J. André, A. Haj Saïd, F. "Mattoussi Spectroscopic investigations on hybrid nanocomposites: CdS : Mn nanocrystals in a conjugated polymer"Materials Science and Engineering C;2006,26(2-3),P 415-420.

[8] Junwu Zhu, Huiping Bi, Yanping Wang, Xin Wang, Xujie Yang, Lude Lu "CuO nanocrystals with controllable shapes grown from solution without any surfactants" Materials Chemistry and Physics,2008; 109(1), P 34-38.

[9] A.E. Bianchi, S.J. Stewart, G. Punte, R. Viña, T.S. Plivelic, I.L. Torriani "Grain growth of CuO nanocrystal activated by high energy ball milling" Physica B: Condensed Matter, 2007 ,389(1), P135-139.

[10] Chengfa Li, Yidong Yin, Haige Hou, Naiying Fan, Fulong Yuan, Yanmei Shi, Qingling Meng "Preparation and characterization of Cu(OH)2 and CuO nanowires by the coupling route of microemulsion with homogenous precipitation" Solid State Communications; 2010,150(13-14), P 585-589.

11/8/2010