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Influence of concentration of poly (Vinylpyrrolidone) on copper doped ZnS nanoparticles prepared by co- precipitation method

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Abstract: **Copper doped ZnS nanoparticles capped with different amounts (0.25g and 1g) of poly(Vinylpyrolidone) (PVP) have been synthesized in aqueous solution by a simple chemical precipitation method. The synthesized particles were characterized by X-ray diffraction (XRD), and the morphology of the product was studied by scanning electron microscopy(SEM) and EDAX. The functional groups of the synthesized particles were identified by Fourier transform infrared spectroscopy(FT-IR). XRD studies confirmed the formation of cubic Cu:ZnS nanoparticles.The average particle size decreases as the concentration of PVP increases and the PVP at 1g due to decreasing particle size. This was due to less attraction between conduction electrons and metal ions for smaller particle size corresponding to fewer atoms that made up the metal nanoparticles.**

Index Terms: capping agent, coprecipitation, EDAX Nanoparticles, Poly(vinylpyrolidone)

I INTRODUCTION

Nanomaterial have been the subject of intense research because of their special physical, and chemical properties that can change between the molecular and bulk limitse Researcher have been taking enormous interest to synthesize nanometre sized semiconductor materials because optical and electric properties depends on the size of the materials. ZnS belongs to II-VI group semiconductor Nps with remarkable optical properties. Several techniques have been employed so for to prepare doped nanocrystals they are hydrothermal method, sol-gel method, auto-combustion and chemical precipitation method. In previous research paper, we have reported synthesis of ZnS nanoparticles doped with Ag trough simple chemical precipitation method using poly (vinyl alcohol) PVA as a capping agent [1-3]. In condinuation of our research work here with we report the polymer assisted synthesis of cupper doped ZnS nanoparticles and their charecterisation [4-5].

Recently, researcher developed new approaches to synthesise nanoparticles by controlling the particle size . The main aim of controlling nanoparticle size and there obtaining a desired shape is to get the best dimension for their application. Usually, the shape, size and size distribution of nanoparticles can be controlled by changing the production approaches reducing agents and stabilizers.

Different organic materials can be used as reducing agents and stabilizer in producing nanoparticles. The most popular and important material, which can be used in the synthesis of nanoparticles is PVP which can be used in various aspects in the synthesis of nanoparticles are for example to stabilize the surface of particles, to control the rate of growth nanoparticles growth and dispersion andalso as a reducing agent. Literature reports suggest that PVP and metal interact via the carbonyl group and nitrogen atom of the pyrrolidine [6-7]. Various transition metal ions such as Cu2+, Mn2+, Pb2+, Ni2+, Cd2+, Co2+, Eu2+, Sm3+, Tb3+, Er3+ etc., used as dopant in nanocrystalline ZnS

host has been reported, but very few reports available on Cu doped ZnS nanocrystals. Therefore, to study the effect of copper on ZnS Nps we have chosed copper as a dopent and also studied the capping agent activity at different concentrations.

Based on the above concept, we designed a simple method for synthesizing copper doped ZnS Nps with different concentration of PVP by co-precipitation method. PVP plays an important roles as a capping agent and in controlling the nanoparticle size, decreases speed of agglomeration and improves the crystallinity of nanoparticles.[8-9].

II MATERIALS AND METHOD

ZnS Nps were prepared by chemical co-precipitation method using analytical grade reagent Zinc acetate dihydrate (Zn(CH3COO)2.2H2O), sodium sulfide (Na2S.XH2O), Poly(vinylpyrrolidone) (PVP), Cupric acetate as source materials. Deionized water is used throught out the preparation process.

A. Experimental section

Semiconducting Nps of ZnS, copper doped ZnS using capping PVP agent. Synthesized by chemical co-precipitation method. Analytical grade zinc acetate, and sodium sulphide (Na2S) and cupric acetate used has a source to synthesis ZnS and Cu:ZnS Nps using PVP as surfactant for controlling nanoparticle size, these chemical are used as such without further purification. In this process, 0.5 M of aqueous solution of cation source zinc acetate (A) and 0.5M anion source sodium sulphide (B) are first dissolved in distilled water to obtain a mixed solution into two different beakers. Subsequently, solution A stired continuously. After the reaction of 30min, a equimolar aqueous solution (B) was been poured drop wise into the above solution with vigorous stirring resulting in colloidal solution after that, the precipitated sample was removed from the solvent using the filter paper. The sample washed with deionized water for several times. Finally, it was dried in an oven at 120 ◦C for 6 hour. The dried sample crushed into fine powder. For preparing Cu:ZnS Nps with PVP a certain amount of 0.05M of cupric acetate was added into aqueous solution of zinc acetate and sodium sulphide. The resultant solution was stirred magnetically at 60 ◦C until a homogeneous solution was obtained, then different concentration of (0.25 and 1 g) of PVP in 50 mL of deionized water was added drop by drop to the above mixture. The entire mixture was stirred magnetically until a precipitate was formed [11]. The precipitated sample was removed from the solvent using filter paper, washed with deionized water for several time, the product was dried in a hot air oven at 120 ◦C for 6 hour.

III RESULT AND DISCUSSION

A. Characterization of catalyst

The synthesized Nps was characterized by the following method

1) X-Ray diffraction measurements

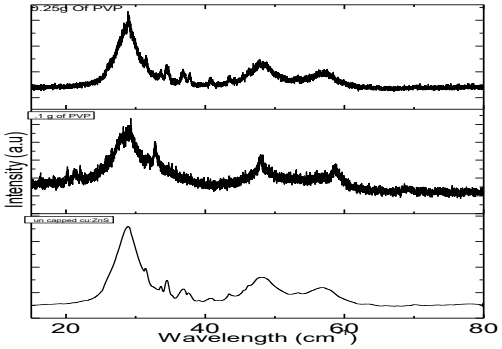

Fig.1 The XRD pattern for (A) UncappedCu: ZnS, (B) 1g of PVP capped Cu:ZnS, and (C) 0.25g PVP capped Cu-doped ZnS Nps

The X-ray diffraction of uncapped Cu doped ZnS and 0.25g PVP capped Cu doped ZnS and 1g of PVP capped Cu:ZnS are shown in Fig.1. Three diffraction peaks in XRD pattern of all the of synthesized Nps related to the lattice planes (111), (220), and (311) which corresponds to the standerd (card No.00-005-0566) and indicate cubic zinc blende structure . Interestingly, we observed. That the uncapped Cu:ZnS nanoparticles diffraction patterns did not show any phase change and impurity peak[12]. In case of capped PVP Cu:ZnS Nps the intensity decreased when compared to uncapped Cu:ZnS nanoparticles, which indicated the capped Nps reduced in crystallinity . Reduction in crystallity of capped nanoparticles could be due to the lattice disorder and the strain which induced by the vacancies or the substitution of the Cu ions in the ZnS crystal lattice.

2) UV-visible spectroscopy

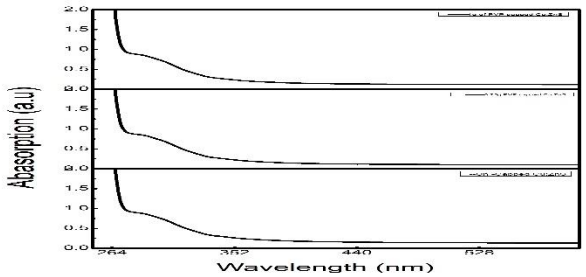

Figure.2 UV spectra for (A) Uncapped Cu: ZnS, (B)1g of PVP capped Cu:ZnS, and (C) 0.25g PVP capped Cu-doped ZnS Nps

Fig.2 showed a strong absorption peak of pure ZnS, capped and uncapped Cu doped ZnS nanoparticles at 282, 290 and 298 nm respectively. The sharp fall in the absorption is due to narrow size distribution of the Nps. The absorption edge has blue shift in the spectrum of Nps after doping with copper metal.The slight shift in the absorption edge is due to quantum confinement effect produced due to increased nucleation rate with doping resulting in construction of smaller particles. Absorption spectrum of semiconductors plays an important role to investigate their band gap energy. The value of the band gap obtained for un-capped Cu doped ZnS is 4.5 eV, the band gap for capped and 0.25g PVP capped Cu:ZnS nanoparticles are 4.1 eV and that of 1g PVP capped Cu:ZnS Nps 4.3 Ev[13]. The band gap increases with the decrease in the particles size. The increase in band gap with reduced particle size, indicate the strong quantum confinement effect, which were higher than the bulk value.

3) Fourier transform infrared spectroscopy

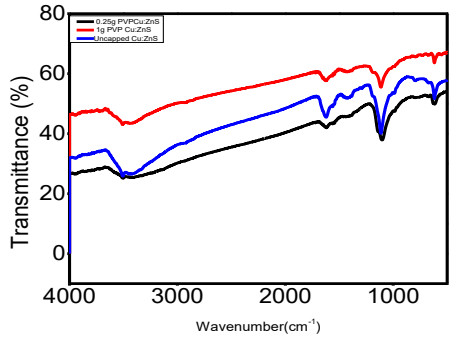

Figure.3 The FTIR pattern for (A) Uncapped Cu: ZnS, (B) 1g of PVP capped Cu:ZnS, and (C) 0.25g PVP capped Cu-doped ZnS Nps

Fourier transform infrared spectroscopy (FTIR) is a technique used to identify the component of a sample and give information relating to type of chemical bonds present between diverse compounds and polymers. Spectra were employed for the detection of functional groups/chemical species which were present in the synthesized samples. It also interprets that the variation in vibrational, absorption bands. The FTIR spectra Cu:ZnS samples are shown in Fig.3.The sharp and strong peak also shown that the samples were highly crystalline in nature.. In this work, the effect of PVP concentration on the structural properties of the Cu:ZnS Nps that were produced with different PVP concentration synthesized by chemical co precipitation method. The absorption bands at 500 to 650 cm-1 indicate formation Zn-S stretching. The absorption band around 2920 cm-1 are attributed to -C-H vibration which is observed due to doping of copper and spectra in the 3420 to 3500 cm-1 indicate OH stretching[14-15]. The peaks in the range 1098 to 1126 cm-1 observed are to the formation of micro structural Cu:ZnS in the samples. It is clear that the spectrum is in comparison with different concentration of PVP, there is incomplete removal of PVP when heating and thus there is a broad band belong to C-N bond stretching at which indicate the presence of the PVP trace in the sample . The appeared band values are in good agreement with the reported literature.

4) SEM and EDAX analysis

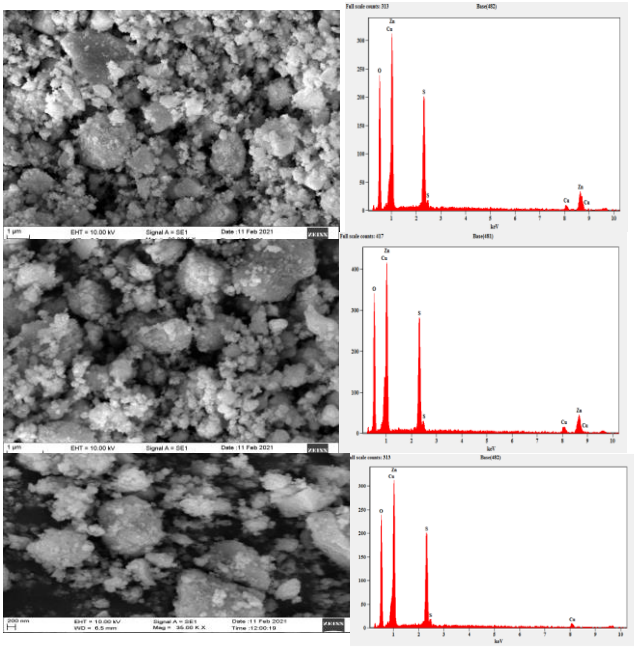

Fig.4: SEM and EDAX images of (A) Uncapped Cu: ZnS, (B)1g of PVP capped Cu:ZnS, and (C)0.25g PVP capped Cu-doped ZnS Nanoparticle

The SEM and EDAX images are shown in fig.4 are morphology of the synthesized nanoparticles. The SEM has been used to characterize the size , shape and morphologies of formed nanoparticles. The SEM image shows spherulitic structure. In the synthesis of Nps via co-precipitation method , the copper ions interact with PVP in the form of Cu(PVP)+, due to these, the metal particles were capped upon nucleation and copper ions will stabilize with the Nps complexstructure. This stabilization of copper ions reduces the nucleation process and also larger particle production and , further increasing the concentration of capping agent from 0.25 to 1 g, more number of copper ions interact with capping agent (PVP) and the growth of particle size also controlled as shown in fig.4. The capped Nps exhibit less agglomeration and better morphology than uncapped Cu: ZnS [16]. The fig. 4 showed that the Nps are spherical shape and uniform in size distribution. From the EDAX, the elemental analysis confirm the presence of copper, sulphur and zinc metals without any impurity in the synthesized nanoparticlesand also indicate the percentage of zinc and sulphur in the ZnSNps, The elemental composition of uncapped and PVP and the capped Cu doped ZnS is shown in fig.4 EDX spectra .

CONCLUSION

The effect of PVP concentration on the structural properties of the Cu:ZnS Nps that were produced with different concentration via coprecipitation method was studied by XRD or X-Ray diffraction. The structure of the Nps have been determined by XRD measurement which indicate that zinc blende structure. From EDAX the elemental analysis confirms the presence of copper, sulphur and zinc ions in the synthesized nanoparticles without any impurity. FTIR spectra confirm the functional groups of the synthesized nanoparticles. The result of optical absorption indicated that the capping agent are not only reduce the particle size but also enhance the optical properties of nanoparticles

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