Category: Photovoltaics

Synthesis of $AgInS_2$ nanoparticles Directly in Poly (3-hexyl thiophene) (P3HT) Matrix: Photoluminescence quenching studies

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***Abstract*—Inorganic semiconductor $AgInS_2$ nanoparticles and P3HT/$AgInS_2$ composite was synthesized by decomposition of silver indium xanthate. The synthesized nanoparticles and composite were characterized by XRD and UV-Vis spectroscopy. PL quenching of the composite demonstrate that the electron transfer from polymer to inorganic NPs through ex-situ solution blending is less efficient in PL quenching as compared to in-situ synthesis.**

***Index Terms*— Nanoparticles, Photovoltaics, Luminescence**

I. INTRODUCTION

Organic-inorganic solar cells combine the desirable characteristics of both organic and inorganic components included within a single material. Such composites show advantages of inorganic nanoparticles like tunable band gap property, stability as well as the polymer properties like solution processing, fabrication of devices on large and flexible substrates for low-cost roll-to-roll fabrication process [1]. Recently, organic–inorganic hybrid solar cells have been demonstrated employing various nanocrystal materials [2]. Synthesis of new materials that do not contain toxic heavy metals such as cadmium and lead are currently under investigation due to the environmental and regulatory acceptance concerns. Materials such as bismuth sulfide, cuprous oxide, iron disulfide, copper indium sulfide (CIS), silver indium sulfide have been recently investigated for photovoltaic applications as environmentally friendly alternatives since they do not rely on toxic heavy metal compounds.

I–III–VI_2 semiconductor nanoparticles, such as $AgInS_2$ (AIS) nanoparticles have attracted intense attention due to their promising applications in solar cells, light-emitting diode (LED), and biological labeling due to their large absorption coefficients, adjustable band gap, low toxicity and higher PL QY [3]. Silver-indium sulfide $AgInS_2$ has a band gap between 1.87 and 2.03eV, which makes it as a promising material for applications in photovoltaics. $AgInS_2$ generally crystallize in orthorhombic phase at room temperature, however nanocrystals of other phases may be prepared using chemical routes [4]. At present, the research on hybrid solar cells is focused on (a) The development of new fabrication routes for hybrid thin films and (ii) the development of alternative inorganic electron acceptors that exhibit light harvesting properties superior to the typically used cadmium-based materials. The hybrid polymer/inorganic nanocomposites are generally prepared by two processing routes. In the first process, namely *the ex-situ approach*, the inorganic nanoparticles are synthesized in a first, separate step. Then the nanoparticles are purified and usually subjected to a ligand exchange step. After that, they are dissolved together with the polymer giving the coating solution for the active layer. In the *in situ approach* the nanoparticles are formed directly from precursors in the conjugated polymer matrix. Having a suitable precursor, this approach is the conceptually simplest one, as the synthesis of the nanostructures is carried out already in the active layer or the coating solution omitting an extra process for the generation of the inorganic nanostructures and avoiding stabilizing ligands. The *in situ* approach yields into nanostructures without capping agents directly in intimate contact with the conjugated polymer. Additionally, particle to particle distance is typically shorter facilitating charge transport. Since the in-situ method consists of the synthesis of nanoparticles in the polymer matrix, it can allow better nanoparticle dispersion in the polymer itself reducing the difficulty generally encountered in ex-situ dispersed heterojunction such as the solid state miscibility and stability. In both of the processes, nanoparticles are required to be homogeneously dispersed in the polymer to constitute an interpenetrating network in order to obtain efficient exciton separation and charge transport in the active layer.

Recently a new approach was reported for the fabrication of hybrid metal sulfide–polymer composites based on the in-situ thermal decomposition of a single source metal xanthate precursor in a polymer [5]. Such strategy was demonstrated for the fabrication of CdS:P3HT and $CuInS_2$:polymer nanocomposite films and efficient charge photogeneration at the donor–acceptor heterojunction was demonstrated. [5-6] In this route, metal xanthates are dissolved together with a conjugated polymer in an apolar organic solvent. The advantages of metal xanthates are that they decompose at temperatures significantly below 200°C and that their solubility can be tuned by varying the alkyl moiety of the xanthate group. Additionally, co-ligands like pyridine can be introduced to optimize decomposition temperature and solubility. Despite their relatively low decomposition temperatures, they are stable over a long time at room temperature, even in solution For the preparation of the nanocomposite layer, the solution containing metal xanthates and conjugated polymer is coated onto a substrate and the dried layer is subjected to a mild thermal annealing step at temperatures of about 160-200°C, which is compatible with many conjugated polymers, with roll-to-roll fabrication processes, and with the use of flexible substrates. During this annealing step, the metal xanthates decompose and the metal

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sulfide nanoparticles are formed in the polymer matrix. All the by-products of the decomposition reaction are volatile and evolve from the layer, so that no remaining side-products could be detected in the active layer.

In this paper, we report the successful synthesis of $AgInS_2$ semiconductor nanoparticles (NPs) and P3HT/AIS NP composite at relatively moderate temperature using a similar approach of thermal decomposition of silver indium ethyl-xanthate precursor. High quality $AgInS_2$ nanocrystals were synthesized by a simple one-pot noninjection route using low-cost, air-stable silver indium ethyl xanthate as the starting material. With simple variation of the reaction recipe (growth temperature and time), the absorption and emission wavelength and crystalline size of the resulting $AgInS_2$ NPs can be conveniently tuned. The hybrid nanocomposite was fabricated in-situ with the addition of P3HT polymer during synthesis. Photoluminescence properties of the composite were monitored and the results demonstrate that the in-situ synthesis resulted in better polymer PL quenching as compared to the ex-situ synthesized nanoparticles. The basic aim of this work was (a) demonstration of different sized AIS nanoparticle using a ligand free route (b) direct synthesis of AIS nanoparticles in polymer matrix without using any surfactant and (c) a comparative study of in situ and ex-situ synthesized AIS nanoparticles in P3HT luminescence quenching.

II. EXPERIMENTAL DETAILS

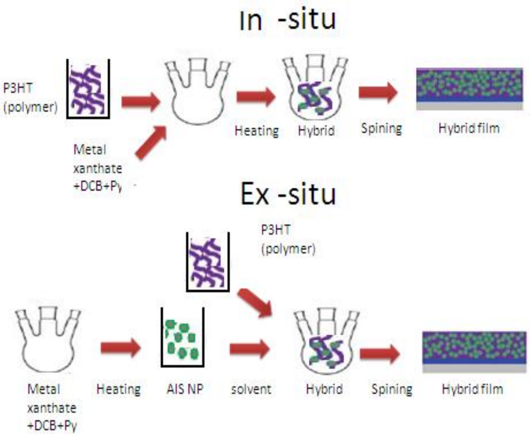

FIG.1.Nucleation and growth process of $AgInS_2$ NPs by in-situ and ex-situ method.

Silver indium xanthate precursors were synthesized by usual chemical methods.

(a) In situ synthesis: For in-situ synthesis of P3HT: AIS hybrid, different weights fractions of organic precursor (xanthate AIX) were mixed in 5ml DCB to which 5mg of P3HT was added. The reaction mixture was stirred for 10 min at room temperature and ½ ml pyridine was added to dissolve all the components. The solution was heated at 120ºC for 30 min under the nitrogen atmosphere.

(b) Ex situ synthesis: AIX was mixed in 5 ml DCB in three necked flask, a small amount of pyridine was added into the solution, and solution was continuously stirred at room temperature for 10 min, afterwards the solution was heated to 120ºC for different time periods (1 to 30min) under the nitrogen atmosphere and consequently different sized AIS NPs were obtained. The polymer-AIS composite was prepared in the form of colloidal solution by adding known concentration of AIS nanoparticles to P3HT dissolved in DCB.

The X-ray diffraction (XRD) studies were carried out by using Rigaku Miniflex- II diffractometer (CuKα=1.54A°). Absorption spectra were recorded using UV 1800 Shimadzu UV Spectrometer.

III. RESULTS & DISCUSSIONS

AIS nanoparticles

AIS nanoparticles were prepared by metal xanthate decomposition to sulfide in presence of pyridine. The crystal structure of $AgInS_2$ NPs was analyzed by powder XRD. The XRD patterns of AIS nanoparticles, synthesized at 120ºC for 30 min., is shown in Fig.2 (a). Sharp peaks located at 2θ = 25.8, 27.3, 29.37, 45.02, 48.32 and 52.87º are observed which belong to the (120), (121) (201), (320), (203) and (322) planes of orthorhombic AIS phase (JCPDS-5-7322). Here it is to be notices that we were able to prepare pure orthorhombic phase of AIS NPs at such a low temperature of 120ºC.The peak are relatively broadened which indicates the size of NPs very small.

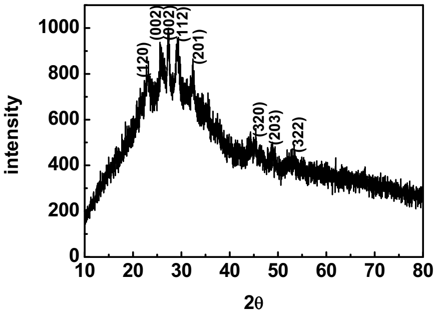

FIG.2. XRD spectra of AIS NPs obtained at 120ºC for 30 min

The optical property of AIS NPs was studied by examining the UV-Vis spectra of different nanoparticles, and is an important property for their photovolataic applications. Fig.2 (b) shows the absorption spectra of the dispersed AIS nanoparticles in chloroform. The band gap energy, *Eg,* was calculated using the Tauc's relation,$(\alpha h\nu)^{1/n}=A(h\nu-Eg)$, where *A* is a constant and *n* is equal to 1/2 for direct allowed transitions. Since, AIS is a direct band gap material, the band gap was derived from the plot of $(\alpha h\nu)^2$ *verses (hν)*.

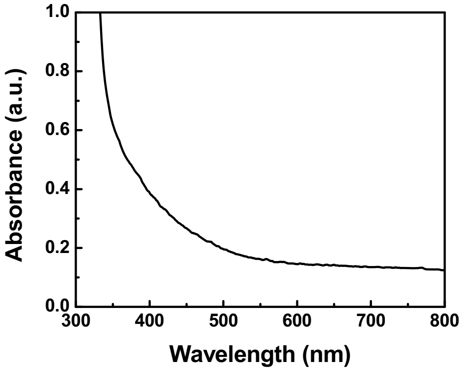

FIG.2(b). Absorption spectra of AIS Nps synthesized at a temperature of 120ºC for 30 min.

Band gap was obtained by extrapolating the linear part of the $(\alpha h\nu)^2$ to intercept the energy axis (hν = 0) and an absorption band gap Eg = 2.3 eV was obtained, which is slightly larger than that of the bulk ortorhombic phase, due to the quantum confinement of nanoparticles. Recently AIS was investigated for applications to organic hybrid solar cells [7], due to its appropriate band positions.

AIS-P3HT composite: In-situ synthesis

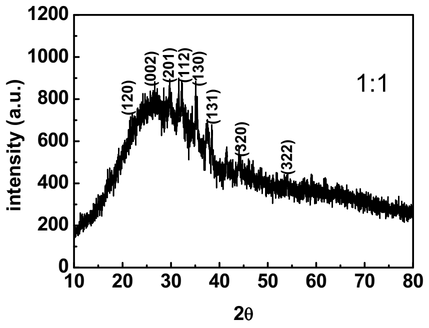

FIG.3(a). XRD spectra of P3HT-AIS nanocomposites (1:1)

In situ formation of $AgInS_2$ in P3HT matrix was realized by thermal decomposition of matal xanthates in presence of P3HT polymer. X-ray diffraction studies were performed to confirm the in situ formation of AIS NCs in the P3HT matrix, as shown in **Fig 3a** for polymer to NP weight ratio of 1:1. The sharp peaks can be assigned to different planes of orthorhombic AIS (JCPDS-5-7322), similar to the peaks observed without P3HT addition as shown in Fig. 2 a. As the AIS NPs ratio increased, these peaks gradually sharpen with increased intensity and approached the 2θ values for the XRD pattern without P3HT additive (not shown here). Since the polymer concentration was small, no XRD peak was observed belong to P3HT phase.

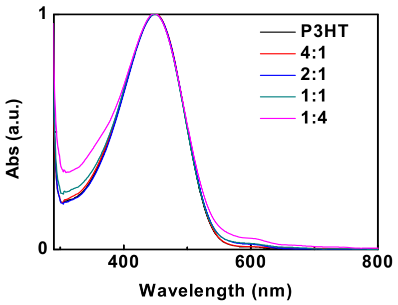

FIG.3(b).UV spectra of P3HT-AIS nanocomposites synthesized for different concentration of AIS

The UV-vis absorption spectra of P3HT: $AgInS_2$ hybrids are shown in Fig. 3b. A blank reaction of P3HT without any added AIS precursors was also carried out to understand the effect of reaction temperature on P3HT stability, and based on absorption measurements, no degradation of P3HT was observed. The pristine P3HT film exhibits a typical absorption spectrum ranging from 400 to 600 nm (Fig. 3b). Absorption spectrum of P3HT: AIS nanocrystal hybrid exhibits adsorption tail above 600 nm that was not present in pristine P3HTand the intensity of this absorption tail increases with the concentration of AIS additive, indicating that this is the characteristic absorption of the AIS material having a small peak near 620 nm. Obviously, the hybrid shows better absorption ability below 470 nm and above 570 nm (Fig. 3b). The band gap of AIS Nps is however near to P3HT polymer, and can be derived from the peak in the absorption spectra, i.e. 620 nm or 2 eV.

Photoluminescence quenching

Fig. 4 (a) shows the photoluminescence emission spectra of P3HT and P3HT: AIS composites as a function of CIS concentration (in situ). P3HT and its nanocomposites exhibited PL emission peak at 580 nm, which suggests that the luminescence is due to the radiative decay of the excitons from the polymer. However, a reduction in the PL intensity was observed in P3HT: AIS nanocomposites as compared to pure P3HT which reduces further on increasing the weight ratio of AIS. The reduction of PL intensity is due to the AIS nanoparticles formation in polymer matrix which facilitates an efficient charge transfer from the polymer to the AIS NPs. When the photogenerated excitons are dissociated in the polymer, the probability for recombination will be reduced due to electron transfer from the donor (P3HT) to acceptor (AIS).

From the photoluminescence emission spectra of P3HT and P3HT: AIS composites, it was observed that the reduction in PL intensity increases with increase in AIX precursor concentration which implies that with increase in AIS NCs concentration, there is an increment in the charge transfer from polymer to AIS nanoparticles.

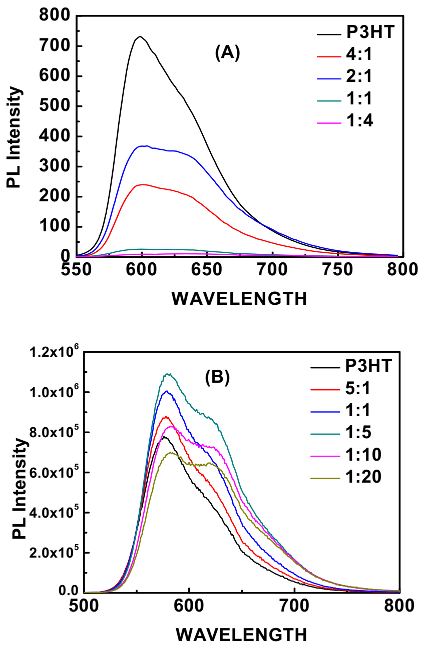

FIG.4.PL quenching spectra of P3HT-AIS nano composites synthesized at different concentration of AIS (a) in situ and (b) ex situ method.

To confirm that an in-situ synthesis gives better charge transfer as compared to ex-situ synthesis, we perform PL quenching of P3HT though blending of AIS nanoparticles by increasing the weight ratio of AIS in P3HT:AIS composite from 1:0.2 to 1:15 weight ratio using AIS nanoparticles synthesized at 120ºC for 30 minutes.

The PL spectrum of P3HT shows that the PL emission is quenched on adding the AIS nanoparticles. This is a good indication of the interaction between the two components in the excited state. In particular if we consider the polymer as a donor and the nanoparticles as acceptors, photoluminescence quenching is expected through charge transfer. The photoluminescence intensity of P3HT polymer hybrid with varied mass fractions of AIS nanoparticles were shown in Figure 4(b) along with the PL spectra for the pure polymers. Both types of hybrids were excited at 480 nm. Photoluminescence quenching was more pronounced in the in-situ hybrids where the PL was quenched by almost 90% even for 1:1 polymer to NP weight ratio. On the other hand in case of ex-situ synthesized nanoparticles, for the initial AIS NP addition, PL was enhanced and even for P3HT: AIS=1:10 the PL was reduced by 20-30% only. Here, it might be observed that even after addition of a large amount of AIS particles, the PL quenching of the polymer is not complete, which might be due to some aggregation of CIS NPs formed in solution, which causes most of the nanoparticle not in direct contact with polymer when CIS amount is large. By charge transfer spectra of in situ and ex situ spectra, we also observed that the charge transfer is more efficient in in situ as compared with ex situ.

The effective charge separation and transfer in *in situ* as compared to *ex situ* hybrid formation suggests that the in situ synthesis method is a promising approach for the fabrication of active layer in organic–inorganic hybrid photovoltaic devices. Most importantly, the presented material AIS Nps is an n-type semiconductor that can act as an accetor material which does not contain toxic heavy metals and therefore can lead to the development of non-toxic polymer-NP (hybrid) solar cells.

IV. CONCLUSIONS

An efficient generic ligand free synthesis method to $AgInS_2$ NCs was demonstrated that can be utilized to synthesize in-situ polymer –NC composite. This is an important step towards environmentally friendly manufacturing which has been gaining increasing interest. The use of in-situ route allows for a highly reproducible and effective synthesis protocol that is fully adaptable for mass production and can be easily employed to synthesize a variety of metal sulfide QDs.

V. REFERENCES

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