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One-pot Synthesis of Soluble Nanoscale CIGS Photoactive Functional Materials

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Abstract Promising alternatives for solar energy utilization are thin film technologies involving various new materials. This contribution describes an easy and inexpensive synthetic method that can be used to prepare soluble nanoscale triphenyl phosphine-coordinated CIGS (TPP-CIGS) photoactive functional materials. This complex is stable in the solid state under the irradiation of the ambient light, but its solution becomes a little bit unstable under the illumination of the low intensity laser.

Keywords Nanomaterials · Optical materials · Gallium · Indium · Copper

Introduction

Nanoscale materials and devices are a rapid growing field of research with large impact for knowledge, technology, and economy, and for environment as well. The performance of most of the optoelectronic and photonic devices, e.g., nanocrystalline photovoltaic cells, photo-electrochromic devices, OLED, PLED and others, may be improved by incorporating nanotechnology during the materials synthesis and device fabrication [1]. Promising alternatives for solar energy utilization are thin film technologies involving various new materials, which are currently attracting considerable attention. Of all the thin film photovoltaic materials, the ternary semiconducting materials such as $CuInSe_2$, $CuInS_2$, and $CuGaSe_2$ [CIS and CGS], and their multinary alloy $Cu(In,Ga)_x(S,Se)_y$ [CIGS] have been recognized to be the most promising materials designed for high-efficiency photovoltaic devices due to their high absorption coefficient, radiation stability, and low gap of these materials [2]. The highest energy conversion efficiency of these materials-based solar cells has reached up to 19.5% (692 mV, 35.2 mA/cm^2, FF 79.9%) at NREL [3]. Very recently new $CuIn_xB_{1-x}Se_2$[CIBS] thin film materials have been fabricated that have the potential to overcome the bandgap limitations and exceed the energy conversion efficiency of the $CuIn_xGa_{1-x}Se_2$ class of materials [4]. The main problems preparing these materials are, however, that almost all the preparation technologies for these alloy materials involve high temperature and high cost. It would thus be very desirable if one could use a reliable, simple, and low-temperature synthetic method to prepare soluble CIS and/or CIGS functional materials.

The first structurally characterized molecular precursor compounds $(Ph_3P)_2CuIn(QR)_4$ (Q = S,Se; R = ethyl, isobutyl) was synthesized by Hirpo and his coworkers [5]. These materials have higher solubility in common organic solvents, which makes them good candidates for solution spray pyrolysis for thin film deposition at relatively low temperature. In the single crystal structure of

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$(Ph_3P)_2CuIn(QR)_4$, which feature tetrahedrally coordinated indium and copper atoms bridged by thio(seleno)lates forming a planar "$CuIn(QR)_4$" core, the terminal ligands are two phosphines on the Cu and two thiolates or selenolates on the In. Five years later, Czekeliu et al. developed a simple low cost colloidal route to nanocrystalline ZnO/$CuInS_2$ bilayers on indium tin oxide (ITO) glass [6]. The triphenyl phosphite ($(PhO)_3P$) coordinated $CuInS_2$ (CIS) complex was prepared in a three-step synthesis in acetonitrile solution. The resulting deep red solutions were stable against aggregation and oxidation, which allowed further handing in air. Following Czekeliu's research work, Arici and his co-workers [7] incorporated $(PhO)_3P$-stabilized nanoparticles of $CuInS_2$ into polymer matrices to fabricate $CuInS_2$-based hybrid solar cells, which show better photovoltaic response with external quantum efficiencies up to 20%. In this contribution, we use one-pot synthetic method to prepare soluble triphenyl phosphine (TPP)-coordinated CIGS (TPP-CIGS) nanorods (see Eq. 1).

$$2CuI + 2InCl_3 + 2GaCl_3 + 7\left[(CH_3)_3Si\right]_2S \xrightarrow[170\,^{\circ}C,\,Ar]{TPP,\,DMA} Cu_2In_2Ga_2S_7TPP_2 + 12(CH_3)_3SiCl + 2(CH_3)_3SiI \tag{1}$$

Experimental

General

All chemicals were purchased from Aldrich and used without further purification. Organic solvents were purified, dried, and distilled under dry nitrogen. The operations for synthesis prior to the termination reaction were carried out under purified argon. The UV/Vis spectral measurements were carried out with a JASCO model V570 DS spectrophotometer. Steady-state fluorescence spectra were measured on a Shimadzu RF-5300 PC spectrofluorophotometer. The sample for the fluorescence measurement was dissolved in the dry toluene, filtered, transferred to a long quartz cell, and then capped and bubbled with high pure argon (without O_2 and moisture) for at least 15 min before measurement. MALDI-TOF-MS measurements were performed on a Bruker REFLEX III-S (preparation method of sample: the samples were dissolved in dry THF, then mixed 1:1 (0.8 μl each) with a methanol solution of α-cyano-4-hydroxycinnamic acid as matrix); Elemental Analyses: Carlo-Erba Elemental Analyser 1104, 1106. Transmission electron microscopy (TEM) image was recorded on a Hitachi H-800 TEM system operated at 100 kV. The differential scanning calorimetry (DSC) curve was obtained on the Perkin-Elmer DSC-7 instrument.

The redox values were measured using the differential pulse voltammetry (DPV) technique by applying BAS CV-50W Voltammetric Analyzer (Japan). A platinum disk electrode was used as working electrode, while a platinum wire served as a counter electrode. An Ag/AgCl electrode was used as a reference electrode. All measurements were carried out in different solvents containing 0.1 M tetra-butylammonium perchlorate [(*n*-Bu)4$NClO_4$] as a supporting electrolyte. The scan rate used is 0.1 V s^{-1}.

Sample Preparation

In a typical synthesis, to the stirred solution of CuI (1.0 mmol), $InCl_3$ (1.0 mmol), $GaCl_3$ (1.0 mmol) and Ph_3P (3.0 mmol) in anhydrous *N*, *N*-dimethylacetamide (DMA, 100 ml) was added dropwise an excess of hexamethyldisilathiane (10.8 mmol) in DMA over 2 h at 170 °C under argon. The reaction mixture was then heated under reflux for 20 h. The resulting solution was filtered to remove the insoluble materials; the filtration was evaporated to dryness under high vacuum to give brown-black solid.

Results and Discussion

The MALDI-TOF-mass spectrum of the resulting complex shows a number of peaks at $m/z = 1274, 1256, 1258, 1242, 1230$, and so on. The peak at $m/z = 1274$ can be logically assigned to $\{[Cu_2In_2Ga_2S_7(Ph_3P)_2]^+ + {}^7Li^+ + {}^{23}Na^+\}$. It can be commonly observed that $[M^{n+}$ ($n = 1, 2, 3...$) $+ {}^{23}Na^+]$ adduct peak appears in FD, FAB, and MALDI-MS spectra. Most importantly, the appearance of $[M^{n+} + Na]$ adduct peak in MS mainly depends on the intrinsic nature of parent compound, e.g., affinity for impurity sodium cations. If the parent compound structure has a very high affinity for Na^+, it will result in the production of abundant $[M^{n+} + Na]$ ions even when sodium cations are only present as impurities.

This compound is soluble in some common organic solvents such as acetone, chloroform and others, and stable in the solid state at room temperature. Figure 1 compares the influence of the long-term UV irradiation on the UV/Vis absorption spectrum of TPP-CIGS in chloroform. When the solution of TPP-CIGS complex in chloroform is exposed to the UV light for several days, the absorption intensity decreased gradually with increased exposure to the ultraviolet light, but the band position is almost unchanged. This result is associated with the partial removal of the organic ligands "TPP" under the UV illumination. Furthermore, the absorption band at 264 nm of pure TPP in $CHCl_3$ was not detected in the UV/Vis absorption spectrum of the TPP-CIGS complex in which its main absorption bands are located at 320 and 400 nm in the same solvent. Upon the excitation with a laser of 350 nm,

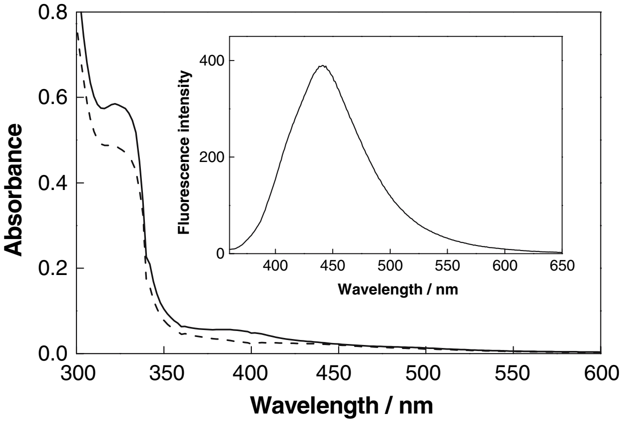

Fig. 1 Steady-state absorption spectra of TPP-CIGS (0.2 mM) in chloroform before (solid line) and after (dashed line) long-term UV irradiation. Inset: Steady-state fluorescence spectrum (0.1 mM) in chloroform. $\lambda_{ex} = 350$ nm

its fluorescence spectrum exhibits a strong emission band at 441 nm, while the pure TPP displays an emission band at 315 nm at the same conditions. Smirnov et al. [8] systematically studied the spectral-luminescent properties and the nature of electron states of Ph_3M (M = N, P, As, Sb, and Bi). Photo-dissociation occurred when these Ph_3M molecules are irradiated with ultraviolet light. The fluorescence spectrum of the products of photo-dissociation shows a weak broader emission band centered at 400 nm. In our work, we did not observe this fluorescence band in chloroform. These findings further support the formation of TPP-CIGS complex.

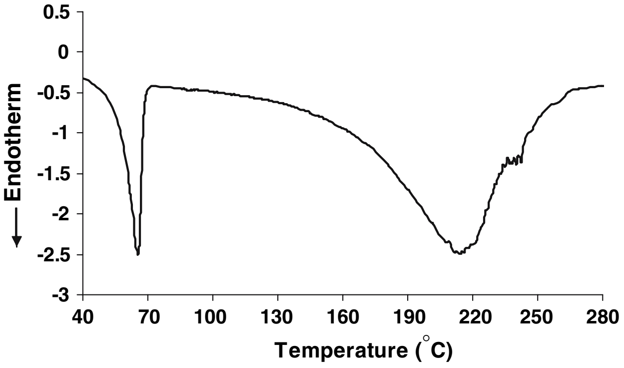

Fig. 2 DSC curve of TPP-CIGS complex

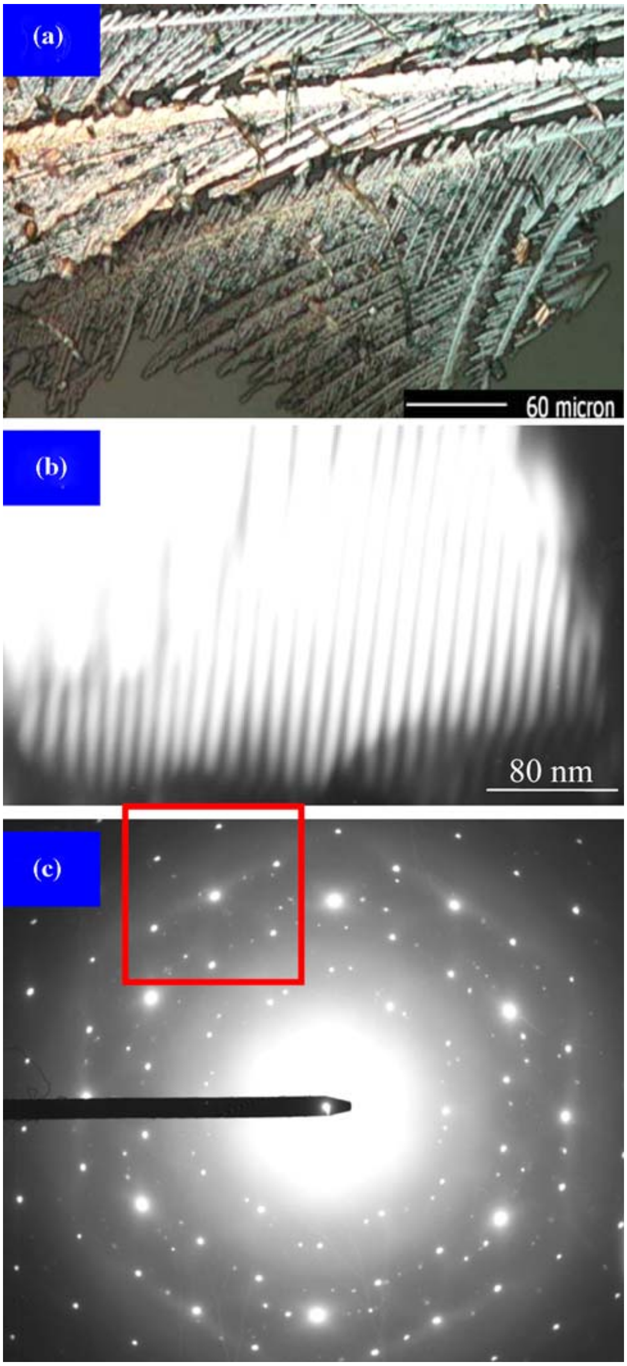

Fig. 3 (**a**) Polarized optical light microscopy photograph, (**b**) TEM image, and (**c**) electron diffraction pattern of TPP-CIGS thin film

As shown in Fig. 2, DSC thermogram of the TPP-CIGS complex shows two endothermic peaks: one is located at 65.45 °C and another at 214.14 °C. Upon heating at 100 °C for several minutes, the solid crystalline phase of this complex is transformed into a viscous birefringent liquid. Basically, the HOMO/LUMO values of materials can be experimentally estimated by the onset of the redox potentials [9] taking the known reference level for ferrocene, 4.8 eV below the vacuum level, according to the following equation: HOMO/LUMO $= -[E_{\text{onset}} - E_{\text{ox.(ferrocene)}}]$ -4.8 eV. In our electrochemical experiments, ferrocene exhibits an oxidation peak with an onset of 103 mV vs. Ag/AgCl. From the onset values of the oxidation potential (E_{ox}) and reduction potential (E_{red}) of TPP-CIGS complex, which are 564 mV and −682 mV, respectively, the HOMO/LUMO values are calculated as

−5.26 eV and −4.02 eV, respectively. The HOMO-LUMO gap is 1.24 eV.

As shown in Fig. 3, the polarized optical image of TPP-CIGS complex, which was taken at room temperature, shows a typical image of a feather-shaped texture. Transmission electron microscope (TEM) image of this complex looks like a comb in which the rods pack parallel to each other and stack together. The average width of each rod is about 9.4 nm. The electron diffraction pattern displayed in Fig. 3c exhibits a pattern composed of hexagonal-lattices, this suggesting the highly ordered structure of TPP-CIGS complex, which is favorable for the hole and/or electron transportation in the photovoltaic cells.

In summary, we have synthesized a soluble triphenylphosphine-coordinated CIGS complex with highly ordered structure by one-pot synthetic method. This complex is stable in the solid state under the irradiation of the ambient light, but its solution becomes a little bit unstable under the illumination of the low intensity laser. The HOMO-LUMO gap of this complex is about 1.24 eV. The further studies on the photovoltaic properties of this complex and the influence of the different organic ligands on the materials structure and performance are currently in progress.

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