Video Article

The Effect of Ultraviolet Radiation on the Chemical Bath Deposition of Bis(thiourea) Cadmium Chloride Crystals and the Subsequent CdS Obtention

Luis Eduardo Trujillo Villanueva[1], Felipe Legorreta García[1], Iker Rodrigo Chávez-Urbiola[2], Francisco Javier Willars-Rodriguez[2], Rafael Ramírez-Bon[2], Marius Ramírez-Cardona[1], Leticia Esperanza Hernández-Cruz[1], Edgar Arturo Chávez-Urbiola[3]

[1]Área Académica de Ciencias de la Tierra y Materiales, Universidad Autónoma del Estado de Hidalgo

[2]Área de Materiales Optoelectrónicos, CINVESTAV-IPN

[3]CONACyT-Área Académica de Ciencias de la Tierra y Materiales, Universidad Autónoma del Estado de Hidalgo

Correspondence to: Edgar Arturo Chávez-Urbiola at chavez.urbiola@gmail.com

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Abstract

In this work, the effects on the preparation of bis(thiourea) cadmium chloride crystals when illuminated with ultraviolet (UV) light at a wavelength of 367 nm using the chemical bath deposition technique are studied comparatively. Two experiments are performed to make a comparison: one without UV light and the other with the aid of UV light. Both experiments are performed under equal conditions, at a temperature of 343 K and with a pH of 3.2. The precursors used are cadmium chloride ($CdCl_2$) and thiourea [$CS(NH_2)_2$], which are dissolved in 50 mL of deionized water with an acidic pH. In this experiment, the interaction of electromagnetic radiation is sought at the moment the chemical reaction is carried out. The results demonstrate the existence of an interaction between the crystals and the UV light; the UV light assistance causes crystal growths in an acicular shape. Also, the final product obtained is cadmium sulfide and shows no evident difference when synthesized with or without the use of UV light.

Video Link

The video component of this article can be found at https://www.jove.com/video/57682/

Introduction

An important area of research is single crystals; their growth is aimed at different applications. These can be used as non-linear optical materials applied in the areas of laser technology, in the field of optoelectronics, and for the storage of information[1], which provides an area of opportunity for their investigation. Bis(thiourea) cadmium chloride is a metal-organic material and can be synthesized from two precursors, thiourea and cadmium chloride, obeying the following chemical formula: $2CS(NH_2)_2 + CdCl_2$ $CdCl_2$-$[CS(NH_2)_2]_2$. This metal-organic material has been prepared under different reaction conditions, such as temperature and pH, but never with the assistance of ultraviolet (UV) light.

The influence of pH on the structure of the crystal has been reported; at a pH < 6, it is possible to obtain the formation of monocrystals. These, in turn, are modified depending on the pH range. At an interval of 6 to 4, it is possible to obtain hexagonal structures, for if pH is < 4, an orthorhombic crystalline structure is obtained[2]. The ion dissociation is promoted by the acidic pH Cd^{2+} and Cl^- since it prevents cadmium hydroxide formation [$Cd(OH)_2$]. This stabilizes the cadmium: a cadmium atom joins with two sulfur-free radicals and two chlorines.

Here, the synthesis is carried out using the chemical bath deposition technique (CBD), controlling the different conditions that intervene at the time of the chemical reaction[3]. In CBD, the factors that control the chemical reaction are the following: the solution temperature, the precursor ions, the solution pH, the number of reagents, and the agitation speed, to name a few. On the other hand, the compared technique used here is called photochemical bath deposition (PCBD) because it uses UV light assistance. There have been reports in which UV light assistance has been used to synthesize films of CuS_x[4,5], ZnS[6], CdS[7], and InS[8], among others. Ichimura and Gunasekaran[9] present in their work that sulfate solutions have an absorption edge close to 300 nm. Due to this absorption range, ultraviolet radiation is applied, which results in a similar emission range to that of the absorbed solutions.

Another property of bis(thiourea) cadmium chloride is its degradation when heated. It exhibits an initial decomposition at temperatures of 512 K and above, forming cadmium sulfide (CdS). The degradation reaction is as follows: $[Cd(CS[NH_2])_2]Cl_2 \rightarrow \Delta$ CdS + HNCS + NH_3 + NH_4SCN. This degradation generates thiocyanuric acid and various thiocyanates[10,11]. Also, in the research group, some effects caused by the UV radiation were studied[12]. Last, in this work, a comparative synthesis procedure for bis(thiourea) cadmium chloride crystals is described, as well as the effects of UV light.

Protocol

CAUTION: The chemicals used in this protocol are toxic and carcinogenic; thus, the safety recommendations and procedures must be followed carefully. Wear proper protective equipment and consult any relevant materials safety data sheet (MSDS).

1. Synthesis of Bis(thiourea) Cadmium Chloride

1. **Preparation of the precursor solution**
    1. Pour 500 mL of deionized water into a 1 L beaker with constant agitation; add 0.3 mL of hydrochloric acid at a 36.5% concentration, making sure that the pH of the solution is as close as possible to 3, using a pH meter.
    CAUTION: To avoid any health effects, performing this action inside a fume hood is highly recommended.
    2. Pour 50 mL of the precursor solution prepared as indicated in step 1.1.1 into each of two 100 mL beakers (hereafter, these beakers will be named A and B).
    NOTE: Two experiments (A and B, dependent on the beaker used) are carried out simultaneously. Only experiment B will be exposed to UV light.
2. Weigh 2.29 g of $CdCl_2$ for each beaker (A and B).
CAUTION: Perform this action inside the fume hood as the material used is identified as hazardous. Cadmium is highly toxic and identified as carcinogenic when inhaled; it must be handled carefully.
3. Weigh 1.33 g of $CS(NH_2)_2$ for each beaker (A and B).
CAUTION: Perform this action inside the fume hood as the material used is dangerously unhealthy. Thiourea is highly toxic when inhaled and must be handled carefully.
4. Add 2.29 g of $CdCl_2$ and 1.33 g of $CS(NH_2)_2$ to each beaker (A and B) containing 50 mL of the precursor solution.

2. Comparative Synthesis of Bis(thiourea) Cadmium Chloride

1. **Experimental arrangement without UV light (A).**
    1. Place the beaker (A) on the stirring hot plate and heat it up to 343 K. Set the plate on a moderate stirring speed.
    CAUTION: Perform this action inside the fume hood.
    2. Keep the solution in the beaker (A) moderately stirring for 2 h on the plate at 343 K.
2. **Experimental arrangement with UV light (B).**
    1. Place the beaker B on the plate and heat it up to 343 K. Set the stirring speed on a moderate level and switch on the UV light source.
    NOTE: The experimental arrangement is shown in **Figure 1**.
    CAUTION: Perform this action inside the fume hood.
    2. Keep the temperature and stirring conditions as described in step 2.2.1 for 2 h.

3. Obtaining Bis(thiourea) Cadmium Chloride Crystals

1. Mount 2 glass funnels with filter paper (No. 40, Ø = 125 mm), each one over a 100 mL volumetric flask, for A and B. To avoid the crystal formation at this stage; do not let the solution cool before filtering it.
2. Filter the solutions A and B through the paper, each into their own 100 mL flask.
CAUTION: Perform this action inside the fume hood.
3. Let both solutions inside the volumetric flasks cool to room temperature.
NOTE: The crystals begin to grow in the first minutes inside the volumetric flasks.
4. Prepare the filtering assembly again (step 3.1) with a new filter paper.
5. Filter the solutions with the crystals through the filter paper into separate volumetric flasks.
CAUTION: Perform this action inside the fume hood.
6. Transfer the crystals on the filter paper to the respective watch glass.
NOTE: At this point, there are 2 watch glasses, 1 for A and 1 for B.
7. Confirm the presence of bis(thiourea) cadmium chloride crystals by powder X-ray diffraction (XRD) and Raman spectroscopy, as reported in Trujillo *et al.*[12].

4. Calcination of the Crystals to Obtain CdS

1. Place the crystals obtained in step 3.7 into 2 different crucibles, 1 for A and 1 for B.
2. Preheat an electric laboratory furnace and stabilize its temperature at 773 K or higher.
3. Place the crucibles of step 4.1 inside the preheated furnace.
CAUTION: The released vapors during calcination are toxic. Make sure that the furnace is in a fume hood due to the toxic fumes that it will be exhausted.
4. Let the material stand inside the furnace for 1 h at 773 K. Then, turn off the furnace and let it cool to room temperature. After that, remove the crucibles from the oven.

Representative Results

The UV-Vis diffusion's reflectance absorption spectra in both precursor solutions, A and B, show the existence of a bis(thiourea) cadmium chloride complex—$CdCl_2$-$(CS(NH_2)_2)_2$. This is evidenced by a broad absorption band within the range of 250 - 500 nm in **Figure 2c**. In turn, **Figure 2c** is the combination of the main absorption bands of the isolated $CdCl_2$ and $CS(NH_2)_2$ in the solution as shown in **Figure 2a** and **2b**, respectively. In addition, a secondary band in the range of 600 - 700 nm is notably visible in both reactants' (**Figure 2a** and **2b**) spectra, and it is not detectable in the complex's UV-Vis absorption spectrum (**Figure 2c**). This latter feature is also determinant to assign **Figure 2c** as an example of the characteristic spectrum of complex $CdCl_2$-$[CS(NH_2)_2]_2$.

The Raman spectrum of the crystals obtained in step 3.6 of the protocol is shown in **Figure 3**. It displays the peaks corresponding to the Cd-Cl, N-C-S, and C-S bonds (217 cm^{-1}, 469 cm^{-1}, and 715 cm^{-1}, respectively), which agree with the results by S. Selvasekarapandian *et al.*[14]. On the other hand, P. M. Ushasree *et al.*[3] previously reported that the change in the spectra is due to a higher count of Cl-Cd-S bonds that remain together in the final structure of $CdCl_2$-$[CS(NH_2)_2]_2$. That higher count causes an increase in magnitude on the Raman spectrum when UV is used. This is because of the formation of zwitterion. A zwitterion is an electrically neutral chemical compound that has positive and negative formal charges on different atoms. Selvasekarapandian,*S., et al.*[14] reported that zwitterion maintains the stability of the thiourea and allows the binding to the cadmium ion. Although **Figure 3** exhibits the same bonds for both experiments, for the one without the UV assistance (CBD), such intensities are lower, which indicates a smaller number of bonds.

X-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis were performed on the same powders mentioned above (in step 3.6 of the protocol). Firstly, **Figure 4a** shows the XRD pattern. The pattern fully indexes with the data sheet 18-1962 $CdCl_2$-$[CS(NH_2)_2]_2$, corroborating the presence of the complex. It also shows the preferential growth in (020) and (001) planes when UV light is used, which correspond to sulfur and cadmium atoms within the structure, respectively. Secondly, observing the morphology of the crystals in the SEM images in **Figure 4b** and **4c**, the effect of UV light can be seen: acicular crystals 4x - 6x larger are formed when UV light is used (**Figure 4c**). Thirdly, in **Figure 4b**, typical crystals obtained are shown, and those results are in good accordance with the report by P. M. Ushasree *et al.*[2]. Subsequently, the crystals obtained in step 3.6 of the protocol were analyzed by thermogravimetric analysis (TGA) to determine their behavior before calcination. The obtained TGA analysis displayed in **Figure 5** exhibits a similar behavior for both experiments, when UV is used (PCBD) and when it is not (CBD), and both are in good accordance with the results obtained by V. Venkataramanan *et al.*[1].

Then, to obtain CdS, calcination at 773 K was performed in both experiments in similar conditions to what Ushasree,*P.M., et al.*[3] reported. Next, in **Figure 6a**, DRX of the calcined complex shows no representative differences in the CdS obtained by CBD *vs.* PCBD. By means of SEM, **Figure 6b** and **6c** exhibit a slightly more prominent average particle size for the PCBD (**Figure 6c**) than for the CBD (**Figure 6b**). Therefore, it is concluded that the UV light promotes the incorporation of the sulfur to the cadmium and this causes a preferential growth in the crystalline structure of $CdCl_2$-$[CS(NH_2)_2]_2$. Finally, the CdS obtained after the calcination shows no evident difference.

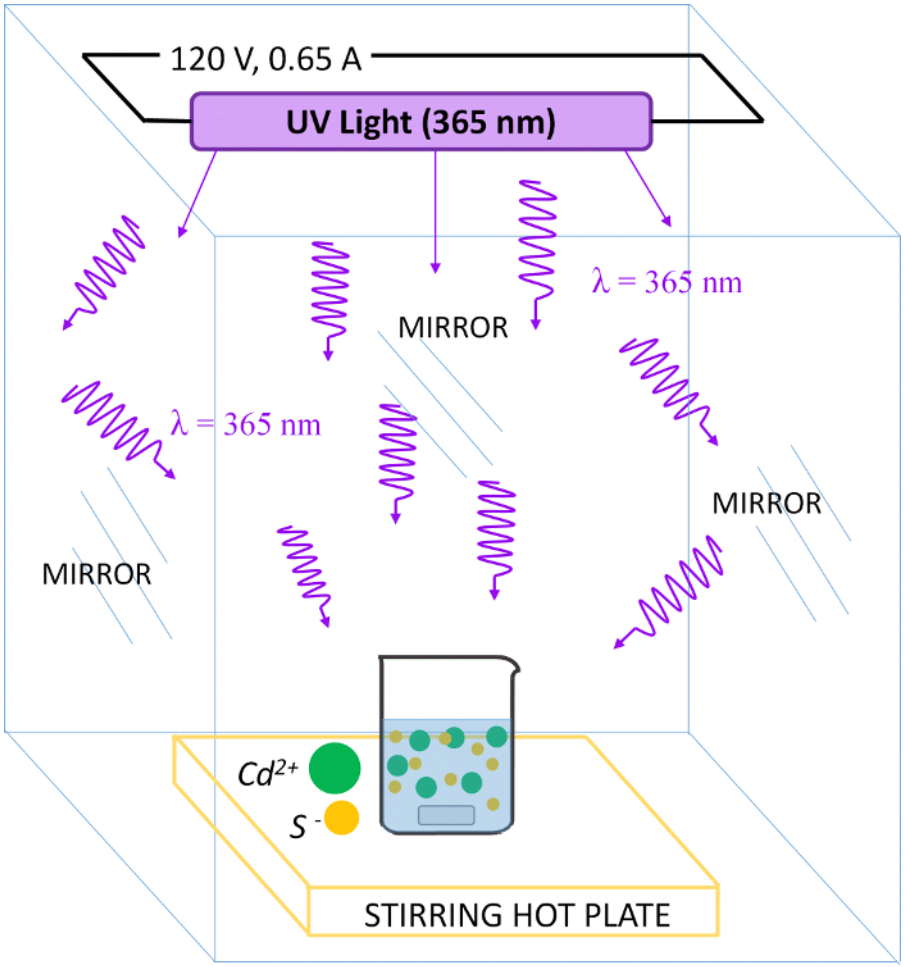

Figure 1: Experimental arrangement with UV light. Please click here to view a larger version of this figure.

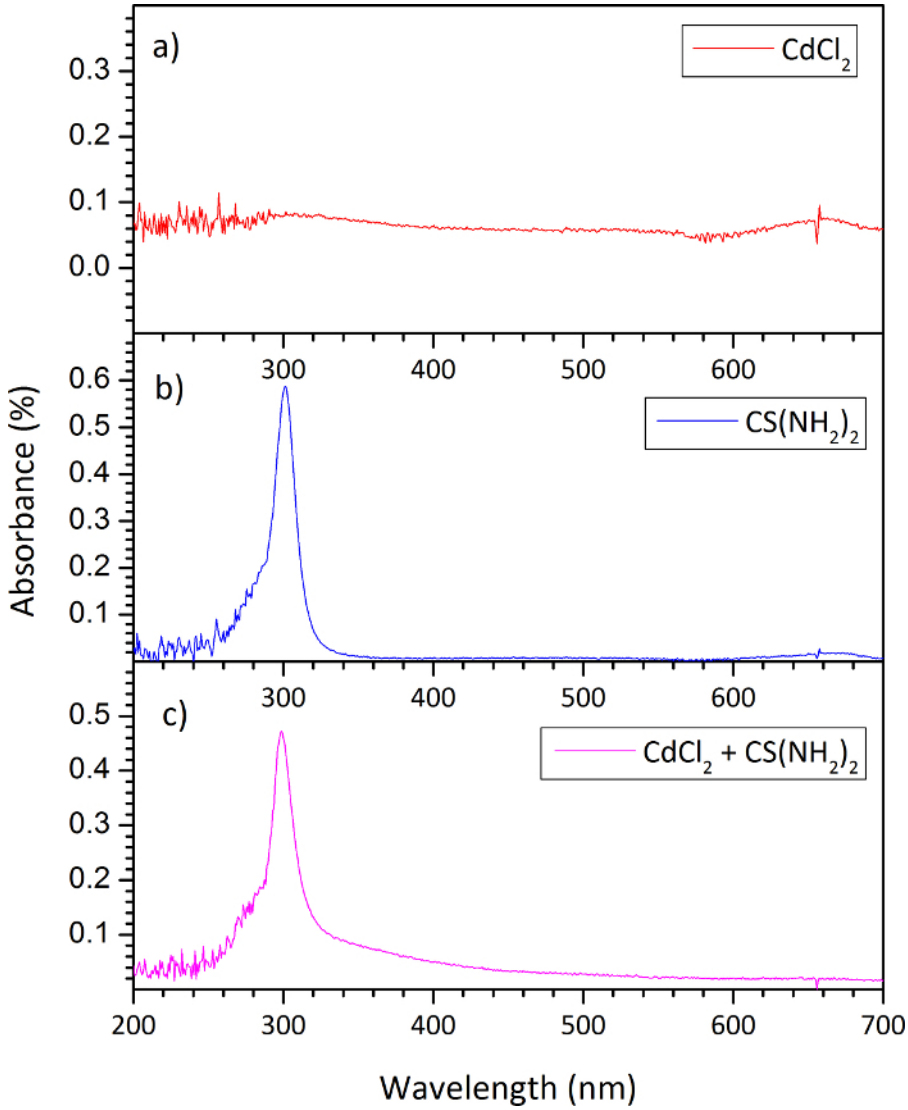

Figure 2: Optical absorption spectra of the precursor solution. (a) CdCl, (b) $CS(NH_2)_2$, (c) $CdCl_2$ + $CS(NH_2)_2$. a), b), and c) shows partial absorption of the UV light. Please click here to view a larger version of this figure.

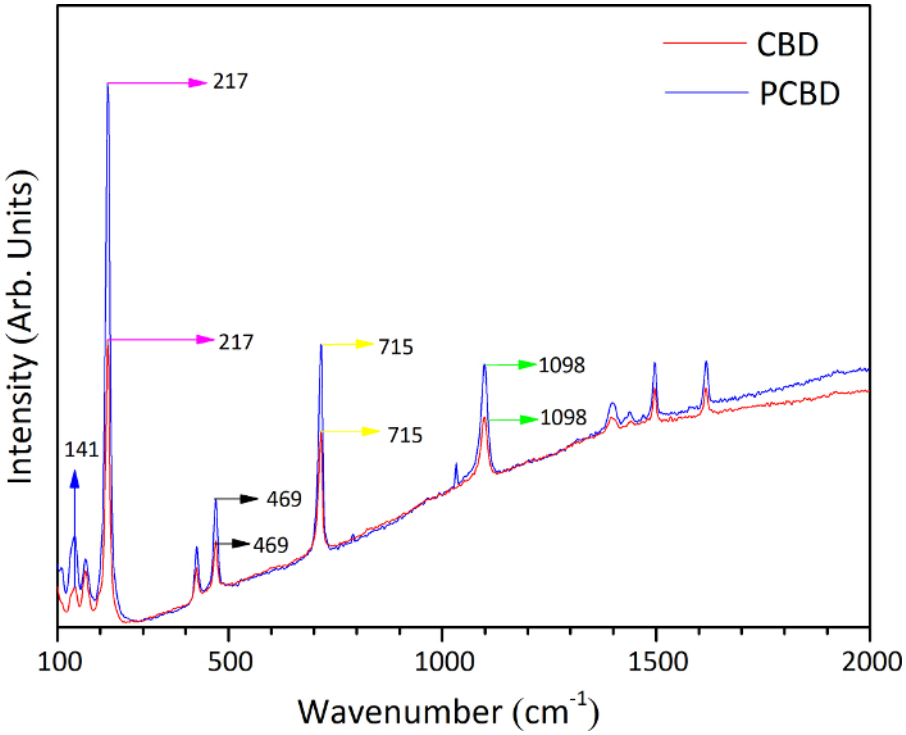

Figure 3: Raman spectra. Spectra comparison of bis(thiourea) cadmium chloride with (PCBD) and without UV (CBD) assistance. Please click here to view a larger version of this figure.

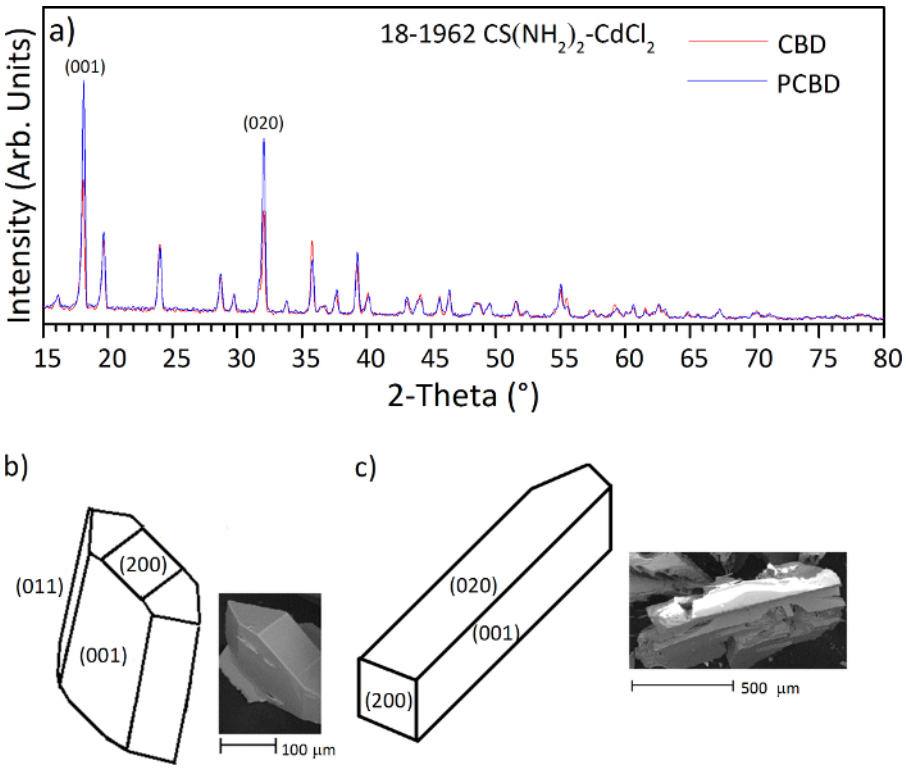

Figure 4: XRD. XRD patterns of bis(thiourea) cadmium chloride CBD and PCBD are shown in a). A scheme of the obtained crystals and SEM images without UV assistance in b) and with it in c). Please click here to view a larger version of this figure.

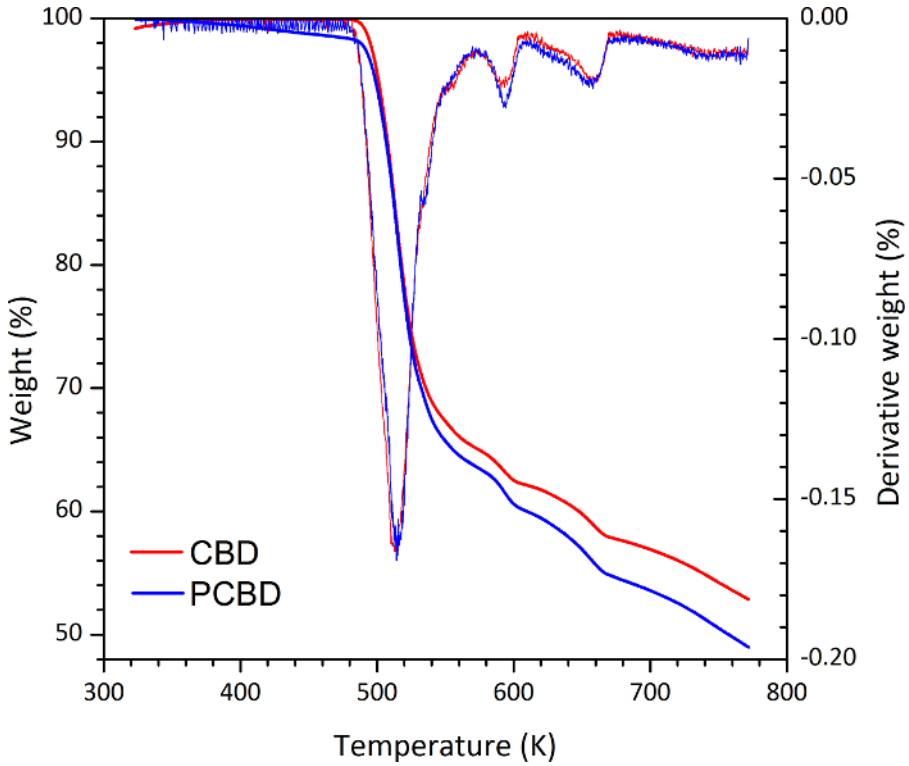

Figure 5: Thermogravimetric analysis. TGA comparison of bis(thiourea) cadmium chloride crystals obtained by CBD and PCBD (Experiments A and B respectively). Please click here to view a larger version of this figure.

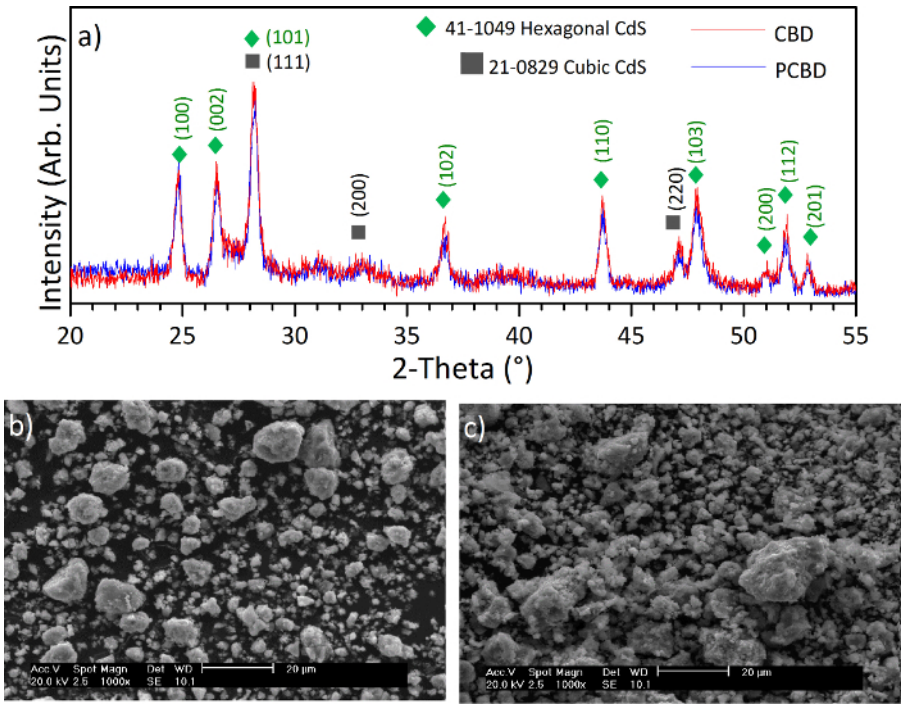

Figure 6: Obtained CdS. In a) the XRD comparison of CBD *vs.* PCBD is displayed. b) and c) exhibits SEM images of the final product obtained after calcination at 773 K. Please click here to view a larger version of this figure.

Discussion

The discussion presented in this section focuses only on the protocol and not on the results already shown in the representative results.

One of the most critical parts of the protocol is the preparation of the precursor solution. It is fundamental to maintain an acidic pH to avoid the $Cd(OH)_2$ formation. If the pH is not acidic, it leads to the direct formation of CdS due to the thiourea dissociation and the $Cd(OH)_2$ formation.

The second most important step is step 3.2, the filtering of the solutions that must be performed before the solutions cool down because otherwise, the cooling-off causes the formation of the crystals to start.

In this protocol, the rapid growth of $CdCl_2$-$[CS(NH_2)_2]_2$ is reported, which occurs in a time less than 10 min. Other researchers (see Ushasree *et al.*[2,3]) report growing times up to 45 days for single crystals.

Due to the relatively low control in the reaction, it is not possible to generate single crystals. In contrast, this technique induces several defects in the crystal when the UV light is used. Because the UV light causes defects in the crystal, any application that may need a defects incorporation can be a potential application. Future research may include the control of the defects in the crystal using different light sources. Also, to perform doping, using the $CdCl_2$-$[CS(NH_2)_2]_2$ with different semiconductors, those defects could be useful to finally incorporate nanoparticles or quantum dots to the CdS.

The method of the synthesis of $CdCl_2$-$[CS(NH_2)_2]_2$ using UV light when the reaction is performed (PCBD) is reported in an extensive and detailed way for the first time in this protocol.

Disclosures

The authors have nothing to disclose.

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