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Fluorescence Microscopy Study of CdS quantum dots Obtained by Laser Irradiation from a Single Source Precursor in Polymeric Film

F. Antolini^a, M. Lanzi^b, G. Raciukaitis^{c*}

^a ENEA, Fusion and Nuclear Security Dept., Photonics Micro and Nanostructures Laboratory Via E. Fermi 45, 00044 Frascati (Rome), Italy

^b Dipartimento di Chimica Industriale, Università di Bologna, V.le Risorgimento 4, Bologna, Italy

^c Center for Physical Sciences and Technology, Savanoriu Ave. 231, LT-02300 Vilnius, Lithuania

Abstract

Recently the quantum dots (QDs) synthesis from single source precursors (SSPs) showed a potential interest for patterning formation of nano-composites. In this approach the SSPs have to be mixed with a matrix that afterwards is treated selectively to obtain the desired nanocomposite. The study of the generation of the QDs from the SSPs is, therefore, crucial for the definition of its behaviour within the polymeric matrix.

The formation of the CdS QDs via thermolysis of the cadmium diethyldithiocarbamate (CdDDTC) was performed and studied in the presence of a non coordinating solvent such as octadecene (ODE) in presence of myristic acid (MA) as ligand.

The precursor is then studied in combination with the poly(methyl methacrylate) (PMMA) polymer for the generation of the CdS QDs under the laser irradiation within a film. The effect of the laser has been studied both on neat PMMA and on the polymer/precursor blend film with the aid of the fluorescence microscope.

The results are used to identify the optimal laser parameters to obtain the decomposition of the precursor and to evaluate the effect of the laser irradiation on the polymer.

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Nomenclature

CdDDTC	cadmium diethyldithiocarbamate
CdS	Cadmium Sulfide
ODE	Octadecene
MA	Myristic Acid
PMMA	Poly(Methyl MetAcrylate)
QDs	Quantum Dots
QD-LED	Quantum Dot Organic Light Emitting Diode
SSP	Single Source Precursor

1. Introduction

Nanoparticles of semiconductor materials especially those of metal chalcogenides (CdS, ZnS, CdSe, etc) [1, 2] have been extensively investigated due to their promising applications for light emitting diodes (LED) and QD-LED [3, 4], photovoltaic devices [5, 6] and/or different biologic procedures [7, 8]. These types of quantum dots (QDs) are characterised by chemical and optical stability, properties that can be easily modulated just by varying their size (and shape) without changing their final chemical composition [1, 2].

Commonly, the inorganic QDs are combined with polymers in order to obtain nanocomposites materials [9, 10] with superior characteristics. In the framework of the nanocomposites synthetic strategies, the literature data have reported an ex-situ approach [11] based on physical dispersion of an inorganic component (nanoparticles) into an organic matrix (polymers) and, an in-situ route [12, 13] when the QDs colloids are grown directly within a polymer matrix (by thermal, chemical or optical decomposition of proper precursors), allowing optimal polymer/QDs interaction and uniform distribution of nanocrystals within the polymer matrix.

The generation of QDs directly in a polymeric matrix can be done in a space-selective way by using an external laser source [14] on a polymer doped with a metallorganic single source precursor (SSP). This methodology reported for the first time in [15] opened the way to the direct laser patterning of QDs and represents a promising pathway for spatially controlled fabrication of new devices like QD-LEDs [16].

The potential advantages of the SSP [17] strategy include: *i*) a preformed bond between the metal centre and the chalcogenides leads to the formation of a material with fewer defects; *ii*) the precursor synthesis is achieved in few chemical steps by using non-volatile and/or less hazardous intermediaries which leads to the formation of a stable precursor under ambient conditions; *iii*) more important QD synthesis is achieved at relatively low baking temperatures. All of these characteristics are appealing for industrial purposes, because they can ensure convenient and low cost routes for inorganic materials preparation. Recently, SSPs like cadmium thiolates [12, 18, 19], cadmium xanthates or cadmium selenolates [20] have been used as fillers inside a polymeric matrix to obtain nanocomposites via laser induced decomposition of the precursor directly inside the polymer.

In this work another SSP, namely cadmium-diethyldithiocarbamate (CdDDTC), belonging to the class of carbamates, has been used as a filler within the poly(methyl methacrylate) (PMMA) polymer to test its ability to form the CdS QDs under laser radiation. The CdDDTC has been already investigated by other authors as source of CdS QDs by its thermal decomposition in solution [21, 22, 23], as a reagent for shell growth around CdSe QDs [24], or in combination with polymers [25] but not under laser radiation. First its thermal decomposition has been tested in solution by using a not coordinating solvent such as octadecene (ODE), in presence of a capping agent such as the myristic acid (MA) to improve the QDs optical properties.

Then the same precursor has been mixed with PMMA to form a film that has been irradiated by UV laser (266 nm 100 KHz). The effect of the laser patterning has been analysed by means of a fluorescent microscope under normal and UV light. The preliminary results suggest the formation of semiconductor CdS QDs with photoluminescence in the region 550 650 nm (yellow/orange) induced by laser patterning.

2. Experimental

All the chemicals are commercially available and were used without further purification unless indicated. Cadmium nitrate tetrahydrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\geq 99.0\%$), sodium diethyldithiocarbamate trihydrate ($(\text{Et})_2\text{NCS}_2\text{Na} \cdot 3\text{H}_2\text{O}$), octadecene (ODE, 90.0%), myristic acid (MA) were purchased from Sigma-Aldrich. Poly(methyl-methacrylate) (PMMA), an optically transparent and chemically inert polymer, was used as matrix for the in-situ CdS QDs formation. All procedures for the CdS QDs preparation were carried out using standard techniques under controlled atmosphere (nitrogen or vacuum). Octadecene (ODE 90%) employed in the experiments was dried at 120 °C under vacuum 30 min then under nitrogen for 30 minutes before use.

2.1 Synthesis of single-source precursor

The synthesis of the cadmium diethyldithiocarbamate (Figure 1) single-source precursor (namely $\text{Cd}(\text{DDTC})_2$) followed the general requests of the single-source precursor approach, in which the final product has to contain all the elements in an individual molecule.

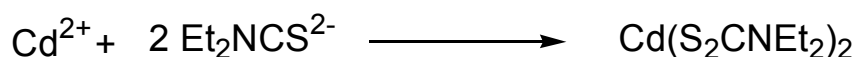


Fig. 1. Formula for the synthesis of the cadmium diethyldithiocarbamate

Accordingly, a cadmium diethyldithiocarbamate complex was prepared starting from a 0.1 M of $\text{Cd}(\text{NO}_3)_2$ and 0.2 M of $(\text{Et})_2\text{NCS}_2\text{Na}$ solutions in ethanol. Then, two aliquots were mixed and stirred with the formation of an abundant precipitate. The white powder was washed several times with ethanol and dried in air at 60 °C. The molecule is slightly soluble in chloroform and other common organic solvents.

Elem. analysis: Found: Cd, 22.27%; C, 28.54%; H, 4.97 %; S, 30.60%; N, 7.50 %. Calculated: Cd, 27.45%; C, 29.41%; H, 4.90 %; S, 31.37%; N, 6.86%.

FTIR (KBr, cm^{-1}): 2978 (antisymmetric str. $-\text{CH}_3$); 2965 (antisymmetric str. $-\text{CH}_2-$); 2930 (symmetric str. $-\text{CH}_3$); 2869 (symmetric str. $-\text{CH}_2-$); 1496 ($-\text{CH}_2-$ deformation); 1377 ($-\text{CH}_3$ deformation); 1269 (C-N stretching); 1203 (C=S str.); 777 ($-\text{CH}_2-$ rocking).

$^1\text{H-NMR}$ (CDCl_3 , ppm): 3.92 (8H, q, H16+H12+H14+H9); 1.32 (12H, t, H17+H13+H15+H10).

$^{13}\text{C-NMR}$ (CDCl_3 , ppm): 203.3 (C4+C6); 51.6 (C12+C16+C9+C14); 12.8 (C13+C17+C15+C10).

2.2 QDs formation in solution and their optical characterisation

The formation of the CdS nanoparticles via thermolysis of the $\text{Cd}(\text{DDTC})_2$ precursor was performed in a reaction flask in the presence of a non coordinating solvent (ODE) in presence of myristic acid (MA). An amount of 20.5 mg (0.05 mmol) of $\text{Cd}(\text{DDTC})_2$ precursor, 68.5 mg (0.3 mmol) of MA and 3 ml of ODE were loaded in a pyrex tube under nitrogen at 250 °C under stirring for 60 minutes.

The reaction was stopped cooling the tube 5-10 minutes at room temperature, then in water. The solution was then poured in a tube containing 9 ml of acetone then centrifuged at 4000 rpm for 10 minutes. The precipitate is re-dissolved in 1 ml of chloroform then 4 ml of acetone were added. The suspension was centrifuged at 15.000 in eppendorf for 10 minutes. The washing was repeated once again. The final precipitate is then dissolved in chloroform ready for the optical analysis.

The as-prepared MA-capped CdS nanoparticles were analysed with UV-Vis and PL spectroscopy. The absorption spectra were measured with a UV-Vis spectrophotometer (Cary 100 Scan) diluting 20-50 μL of QDs solution in 3 mL of chloroform so that the absorbance of QDs at 360 nm is about 0.1. The PL signal (emission interval 370 nm 680 nm) was measured on the same cuvette by using an Edinburgh FLS920 spectrometer equipped with an Edinburgh Xe900 450W Xenon arc lamp. The excitation wavelength is set at 360 nm. All the spectra were corrected for the detector response.

2.3 Film formation laser treatment and fluorescence microscopy characterisation

Film formation: The PMMA/CdDDTC film has been prepared by drop casting. A volume of 6 ml of PMMA 25 mg/ml in chloroform has been mixed and stirred with 50 mg of CdDDTC until its dissolution. The solution is then dropped in a Petri dish and leaved to dry over night. After drying the film is removed from the Petri dish and treated with laser.

Laser treatment and optical microscopy characterisation

Most of the laser-patterning experiments were performed using the laser micro-processing system with picosecond laser working at 266 nm wavelength. The systems parameters are reported in Table.1.

The samples after laser irradiation were examined by using the optical microscope Nikon 80i epi-fluorescence microscope equipped with a Hg-lamp excitation and with UV-2A filters (excitation filter 330 – 380 nm emission filter long band pass above 420 nm).

Table 1. Laser system parameters

Laser	PL10100 (<i>Ekspla</i>)
Wavelength	266 nm
Pulse length	10 ps
Rep. rate	100 kHz
Max average power	800 mW@100 kHz
Optics	
Beam control	Pockel cells with polarizer
Sample positioning	XY stage
Objective	100 mm
Spot size (diameter)	28.2 μ m

3. Result and discussion

The suitability of the Cd(DDTC)₂ single-source precursor for the generation of semiconductor nanocrystals was initially tested in a synthetic colloidal approach, when capped-CdS nanoparticles were successfully prepared by thermolysis of Cd(DDTC)₂ precursor into a hot non coordinating solvent ODE in presence of a capping agent, namely myristic acid. The decomposition scheme of the CdDDTC is illustrated in figure 2 and it has already shown that the decomposition temperature interval of CdDDTC is included between 200 and 350 °C [22] when carried out without solvent.



Fig. 2. Formula of the thermolysis of the CdDDTC forming the CdS

Subsequently, the MA-capped CdS nanoparticles were prepared by the dispersion of the Cd(DDC)₂ single-source precursor in ODE containing the myristic acid (MA) as capping agent at 250 °C.

The use of a non coordinating solvent like ODE should ensure a temperature of QD formation near to the decomposition temperature of the molecule itself and a control of the nanoparticle nucleation and growth by adding the proper type and concentration of ligand. Moreover it is well known that the optical properties of the QDs and their PL quantum yield are strictly correlated with surface ligands. The role of the ligands is to modulate the surface defects of QDs. The dangling bonds on the exposed surfaces of the QDs can be passivated by the ligands so that deep trap emission states can be consequently modulated [26]. In metal chalcogenide QDs, chalcogen filled states and metal derived empty states can lead to mid gap states that work as an ideal passivation system for both of them

[27]. The selection of MA as ligand is motivated because in the work by Ouyang et al. [28] it is shown that the best PL intensities were obtained with a ligand having a chain length included between 12 (C_{12}) and 16 (C_{16}) carbon atoms and with a molar ratio not exceeding 12 with respect to Cd. In these conditions the PL emission shown in figure 3 is sharp (FWHM 19.4 nm) and with a low emission at high wavelength. This indicates that the surface defects are well passivated by the MA. The absorption shoulder and the PL emission maximum at 448 nm and 460 nm respectively are very close and confirm the band edge emission (figure 3) of the synthesised QDs. The calculated size of the QDs is 5.2 nm [29].

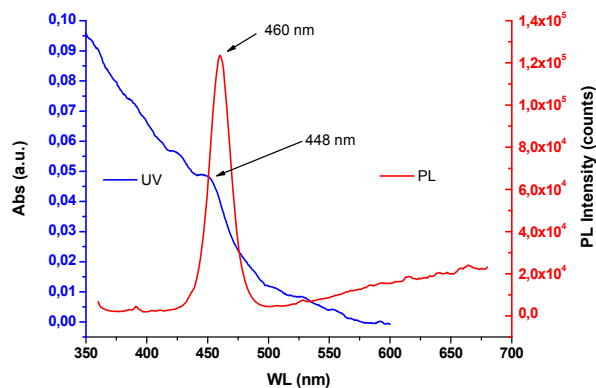


Fig. 3. UV-Vis and PL spectra of the CdS QDs growth at 250 °C for 60 minutes

After the study of the CdDDTC in solution, the precursor decomposition has been studied within the PMMA polymer film. First the effect of the laser source has been tested on the neat PMMA carrying out a matrix of points of different combinations of energies and pulse number (figure 4a and b). Each point represent a specific pulse energy (columns) associated to a number of pulses (rows) released on the polymer surface.

In figure 4a is reported the effect of the laser pulse observed under the microscope with visible light while in figure 4b the same sample is observed under UV light with long band pass filter (above 420 nm). The black dots in figure 4a suggest that the laser ray has burnt the polymer. The same black dot under the UV light emits a blue light. This means that the polymer has been modified in some fluorescent molecule. The fluorescence is also observable when apparently under the visible light the PMMA is unchanged (yellow circle). This means that the fluorescence is more sensitive technique to detect the polymer changes under the laser beam.

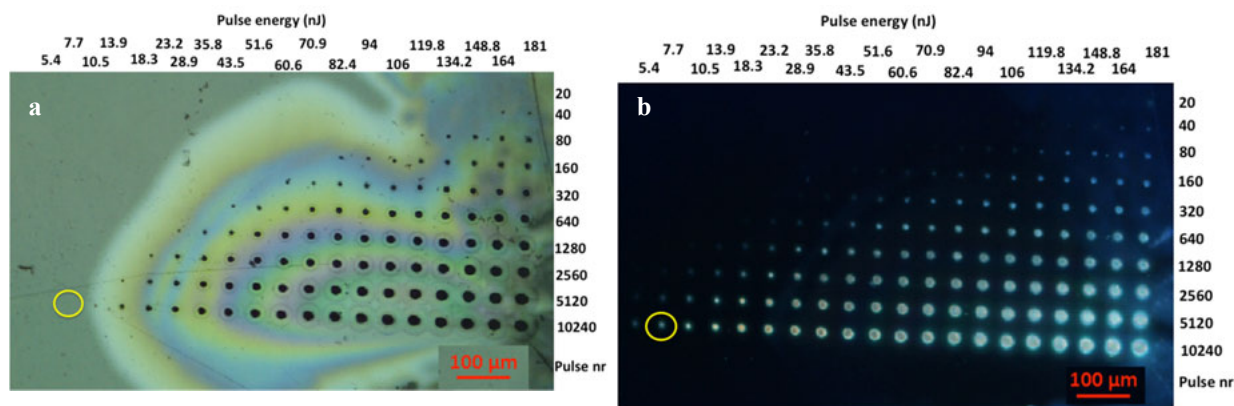


Fig. 4. Matrix of number of pulses (rows) and pulse energies (columns) observed in (a) bright field and (b) under UV light. The yellow circles indicate the same area in the two images.

This effect is confirmed in the experiment showed in figure 5 where is reported the effect of the laser lines in the polymer both under the normal and UV light. Apparently under normal light the polymer seems unchanged (figure

This happens because in some regions the precursor is at the surface of the film so the laser energy is enough to modify it (red rectangle figure 7b). In other areas where the precursor is embedded in the film, the laser energy is adsorbed partially by the polymer so that only a few amount of the precursor can produce the CdS (yellow rectangle figure 7b). Finally if the precursor is too distant from the surface only the polymer will be modified and only a blue photoluminescence is detected (blue rectangle figure 7b) due to the polymer modification.

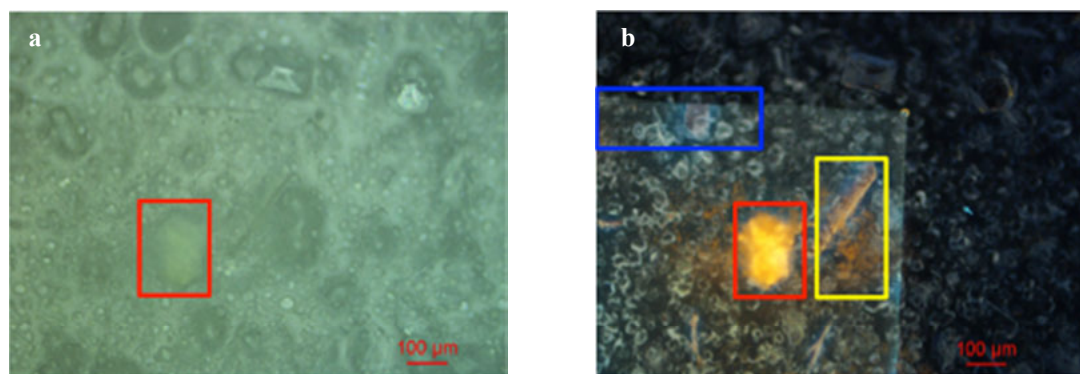


Fig. 7. Laser writing of lines on PMMA film (Pulse energy 13 nJ, speed 2.5 mm/s, hatch 2.5 μm) observed in (a) bright field and (b) under UV light (UV-2A filters). The red rectangle indicates the same region under normal and UV light. Yellow and blue rectangles indicate two different regions with faint orange and blue emission respectively.

4. Conclusions

The optical properties of the CdS QDs obtained in solution from the decomposition of the CdDDTC show that the photoluminescent signal of CdS QDs is almost due to the band edge emission (PL max at 460 nm) with low emission due to the defect band (500 – 700 nm). In other works the use of complex solvents [22] or amine ligands (oleylamine) [23] did not block formation of the defect emission (strong band between 600 – 700 nm) that is practically absent when it is used the myristic acid as ligand. This is probably due to the fact that the carboxylic group bear by the MA is more effective to fix the cadmium dangling bonds at the QDs surface than the amine group or other agents presents in olive oil as stated in ref. 22 and ref. 23.

When the CdDDTC is used in combination with PMMA under the laser radiation it is possible to obtain a photoluminescent yellow/orange signal that suggests the formation of the nanostructured CdS with surface defects. This strategy is a powerful method to obtain patterned nanocomposites for application in optoelectronic devices [16]. In that case the 266 nm laser if in one side is effective in CdDDTC modification on the other side it is not the better wavelength because is adsorbed by the PMMA. Indeed the PMMA is modified by laser source and only changing the laser wavelength as shown recently by Smirnov et al. [31], a similar precursor dissolved in PMMA can be irradiated with a laser at 365 nm with CW laser without damaging of polymer.

Further work is in progress to improve the interaction of laser and the polymer/precursor blend in order to avoid the polymer damage, to improve the precursor solubility in the matrix and the optical properties of QDs within the matrix.

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