



Localized formation and size tuning of CdS nanocrystals upon irradiation of metal precursors embedded in polymer matrices

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ABSTRACT

We present a method of spatial and dimensional controlled formation of CdS quantum dots into polymer matrices by light irradiation. The initial samples consist of Cd thiolate precursors doped in TOPAS polymer matrix. Under pulsed UV laser irradiation the precursors are photolysed driving to the nucleation of CdS nanocrystals, with increasing size and concentration, related to the number of UV pulses. The formed quantum dots are localized in the irradiated area, while the host polymer remains macroscopically unaffected by the UV irradiation. In this study we investigate how the formation of the nanocrystals (size, dimensions, and concentration) is affected by the use of different irradiation conditions (wavelength, number of pulses), revealing information about the different pathways followed during the formation. The change of the size of the dots results in the change of the peak of their emission due to the quantum size effect, which is studied by fluorescence measurements. The results are reinforced by TEM microscopy and by XRD measurements. The main advantages of the presented method are the size tuning of the produced dots and their spatial confinement inside the host matrix, not possible by the other methods used until now (thermal annealing, mixing etc.).

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The fabrication of nanocomposites of polymers containing inorganic semiconductor nanoparticles (NPs) is of great research interest due to their potential application as highly technological materials. In particular, the incorporation of semiconductor NPs into solid polymer matrices results to the prevention of the degradation and the aggregation of the NPs [1], while the formed nanocomposites can be easily processed and manipulated into thin films or any other desired form. On the top, the nanocomposites can combine special properties of both the polymeric and inorganic components, such as the mechanical and thermal properties of the former, and the special optical and electronic features of the later [2]. In particular, the formed materials can exhibit extraordinary optical properties that are strongly depended on the size and the shape of the dots [3], since the absorption/emission of the latter can be tuned with their size [4]. This is due to the quantum size effect, i.e. the variation of the semiconductor band gap energy with the size of the dots, when this gets smaller than the Bohr exciton radius [4,5]. In this case, the optical absorption/emission is shifted towards smaller wavelengths with the decrease of the nanoparticles' dimensions. Therefore, the nanocomposite structures can be

used in new promising applications in many fields, such as in optoelectronics [6–8], and sensor devices [9].

Much of the recent research on nanocomposites is focused on discovering new preparation routes of NPs incorporated into a condensed phase material, with sizes in the quantum regime. One of the most common preparation ways is the in situ NP formation in the polymer matrix after the thermal decomposition of a metal precursor [10–12]. The main disadvantage of this approach is the lack of localized NP formation inside the matrix. Another interesting approach is the in situ NP synthesis with gas treatment, after polymerization of NP-precursor containing resins [13–15]. In this case size controlled nanoparticles are formed in localized areas inside the polymer, but the procedure is pretty complicated and time consuming.

Our approach involves the in situ localized formation of nanodots in the quantum size regime, by the use of pulsed UV laser irradiation on a polymer-precursor film. The NPs size is controlled by the number and the energy of the incident laser pulses, while the polymer matrix remains macroscopically unaffected. Since the nanoparticles are formed from the very first pulses of some nanoseconds (ns) duration each, the overall procedure takes place in few hundreds of ns interaction time (τ). Recently, it has been demonstrated the formation of cadmium sulfide (CdS) dots in the quantum size regime

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starting from a metal precursor embedded in a polymer matrix, by this procedure [16]. This work opened up new perspectives for the nanocomposite study since this fast and easy way to form size controlled nanodots in well defined areas in a polymer matrix can be expanded to the study of various metal precursors, polymer matrices, and irradiation conditions. In the present work we compare two different irradiation wavelengths 266 and 355 nm, starting from one metal precursor, and we reveal the differences in the formation procedure of the CdS nanodots.

Nanocomposite films containing 20% per weight cadmium bis-dodecanthiolate precursor, (C12), and 80% of TOPAS (thermoplastic cyclo-olefin copolymer consisting of ethylene and norbornene chains) were prepared as described in Ref. [10]. These films were irradiated under air atmosphere with Nd:YAG laser pulses operating at the third and fourth harmonic, (wavelengths 355 and 266 nm, respectively, pulse duration 8 ns, fluence 25 mJ cm^{-2} , and repetition rate 2 Hz). The laser beam was focused perpendicularly onto the film surface at an area of 0.2 cm^2 , and the fluence was low enough so as not to cause macroscopic damage to the films. As shown in Fig. 1 the first laser wavelength used for the irradiation experiments ($\lambda_1 = 266 \text{ nm}$) is strongly absorbed by the sample since it coincides with the absorption peak of the C12-TOPAS film, while the second wavelength, ($\lambda_2 = 355 \text{ nm}$), is very weakly absorbed. Moreover for both the irradiation wavelengths, the bare TOPAS film is not absorbing.

For the verification of the existence and the crystal structure identification of the formed nanoparticles after irradiation, X-ray diffraction measurements (XRD) were performed by using a 3 kW Bragg-Brentano diffractometer. The study of the films before and after irradiation verified the phase changes of the precursors to CdS nanocrystals. Fig. 2 demonstrates one of the XRD diffraction patterns of a C12-TOPAS film irradiated with 20 pulses at 266 nm. Three diffraction peaks of the wurtzite CdS structure are revealed, while the (002) wurtzite (JCPDS, PDF No.80-0006) coincides with the (111) zincblende peak (JCPDS, PDF No.80-0019). Thus, it is assumed the coexistence of wurtzite and zincblende phases of CdS. This is verified by theoretical simulations done as described in Ref [11], by considering spherical nanoparticles with mixed zincblende and wurtzite phases (45:55, respectively).

The evolution of the CdS formation under various number of laser pulses is followed by conducting spatially resolved photoluminescence measurements with a confocal microscope (Leica TCS-SP5, excitation wavelength 405 nm). Fig. 3a,b demonstrates

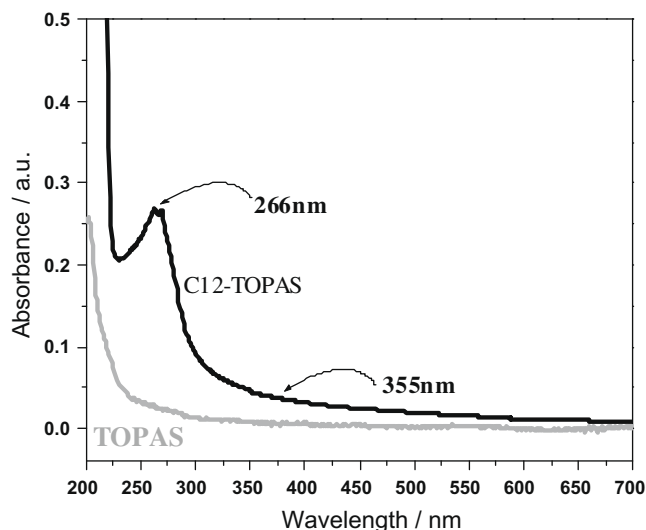


Fig. 1. Absorption spectra of the TOPAS polymer and of the C12-TOPAS solutions.

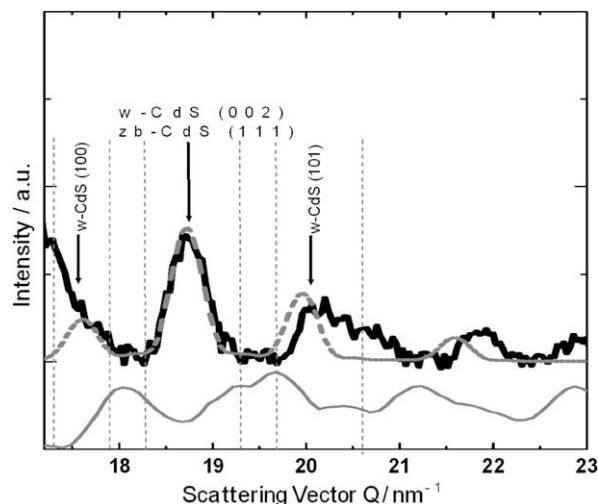


Fig. 2. XRD diffraction pattern of the C12-TOPAS film, before (gray line) and after 20 incident laser pulses at 266 nm (black line). The peak at 17.25 nm^{-1} refers to the diffraction signal of the polymer. The dashed gray line corresponds to the simulated diffraction pattern.

the fluorescence images of the irradiated areas of two films, after 10 and 80 pulses at $\lambda_1 = 266 \text{ nm}$, and in the inset are shown indicative fluorescence spectra from the two areas. After 10 pulses ($\tau = 80 \text{ ns}$) the density of the fluorescent particles appears very small, (Fig. 3a), with dominant emission peak close to $\lambda = 440 \text{ nm}$. After 80 pulses ($\tau = 640 \text{ ns}$), the fluorescent area appears much denser, while the emission is shifted towards higher wavelengths, with a peak at about 510 nm (Fig. 3b).

Fig. 3c illustrates the evolution of the emission for films irradiated at $\lambda_2 = 355 \text{ nm}$ with increasing number of pulses. At 0 pulses the emission is very broad and corresponds to the C12 precursors. After 10 irradiation pulses the spectra changes dramatically while by increasing the irradiation pulses, a red shift of the emission is observed. It is known by the quantum size effect, that the CdS dots when are smaller than 7–9 nm have different emission spectra depending on their size [4], showing a blue shift upon decreasing dimensions [17]. On the contrary when the size becomes equal or larger than 7–9 nm, they exhibit bulk properties with emission peak slightly above 500 nm (bulk bandgap energy, $E_g = 2.4\text{--}2.45 \text{ eV}$) [4,11]. Thus, the observed shift of the emission peak can be attributed to the increasing size of the formed CdS nanoparticles with increasing number of UV pulses, until the size where the quantum confinement effect is not anymore valid is reached.

Fig. 4 shows the evolution of the CdS emission energy by increasing the incident pulses for irradiation with wavelengths of 266 and 355 nm. In both cases, the CdS emission energy starts from $\sim 2.85 \text{ eV}$ and is decreasing by increasing the number of the incident pulses, until is stabilizes close to the E_g . The main difference between the two irradiation wavelengths is that the NPs are formed faster in the case of irradiation with 266 nm. The first indication of formation of small CdS nanocrystals with bandgap energy of about 2.85 eV is after 6 pulses ($\tau = 48 \text{ ns}$) for irradiation at 266 nm, and after 10 pulses ($\tau = 80 \text{ ns}$) for 355 nm. Also, the bulk material emission with $E_g \sim 2.4 \text{ eV}$ is reached after 40 incident pulses ($\tau = 320 \text{ ns}$) of 266 nm, although the existence of smaller nanodots sizes is still apparent, while the same behaviour is observed after 200 pulses ($\tau = 1600 \text{ ns}$) for films irradiated at 355 nm.

The reason for the faster CdS NPs formation in the case of irradiation with 266 nm can be attributed to the fact that the specific wavelength is at the peak of the C12-TOPAS absorption. The

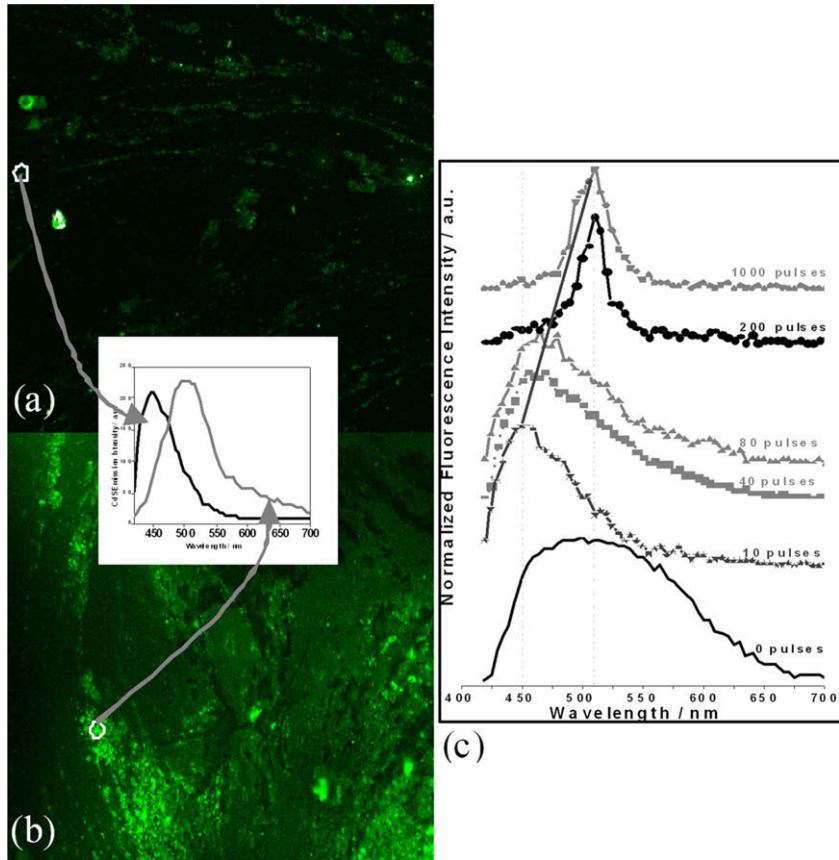


Fig. 3. Fluorescence images of the C12-TOPAS film after 10 pulses (a), and 80 pulses (b) at 266 nm. Inset: Local fluorescence spectra. (c) Fluorescence spectra evolution after irradiation at 355 nm.

photons absorbed by the precursor cause the C–S chemical bond breakage as described by Eq. (1) [16].



On the contrary, the precursor absorption at 355 nm is very low. Therefore, the efficiency of the precursor nucleation to give CdS nanodots is also expected to be low, leading to an increased number of photons needed for the NPs formation. Consequently, the CdS formation under irradiation at 355 nm needs a greater number of laser pulses compared to 266 nm, making the procedure slower. It should be mentioned here that the abovementioned results have been achieved under irradiation with the same laser fluence.

In the strong-confinement regime, the bandgap energy shift is related to the radius of the semiconductor nanocrystals by the Brus equation [5]

$$\Delta E_{\text{CdS}} = \left(\frac{\hbar^2 \pi^2}{2R_{\text{CdS}}^2} \right) \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8e^2}{\epsilon R_{\text{CdS}}} \quad (2)$$

where ΔE_{CdS} is the bandgap energy shift from the bulk value; R_{CdS} the CdS radius; m_e^* and m_h^* the effective masses of the charge carriers (electron and hole, respectively); \hbar the Planck's constant; and ϵ the dielectric constant. By taking the value of the ΔE_{CdS} from the experimental data, the CdS diameter is calculated. At the initial pulses the diameter starts from 4 nm and is increasing by increasing the laser pulses, until the bulk material is reached, with sizes equal or higher than 8 nm.

In order to verify the NPs sizes calculated by Eq. (2), the nanocomposite films were studied with transmission electron microscopy (TEM) (Jeol-Jem 1011 operating at 100 kV). The irradiated areas were dissolved in chloroform, and few drops were placed

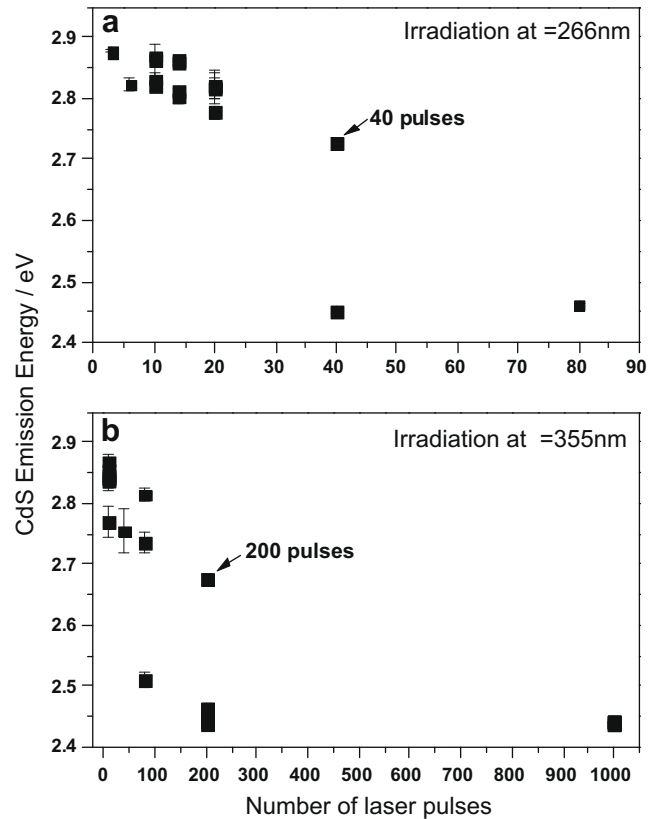


Fig. 4. Emission energy evolution of the CdS nanodots upon increasing number of UV pulses ($\lambda_1 = 266$ nm, (a), and $\lambda_2 = 355$ nm, (b)).

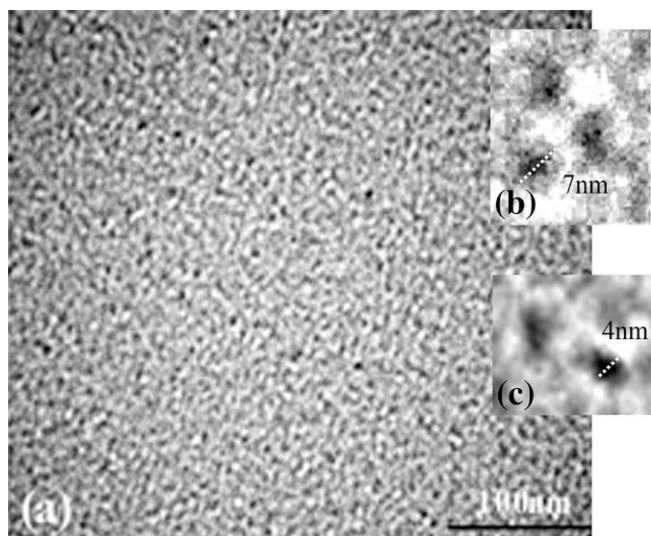


Fig. 5. (a) TEM image of CdS nanodots formed after 40 pulses at 266 nm, fluence 25 mJ/cm² and its magnification (b). (c) Magnification of a TEM image taken from a sample after irradiation with 6 pulses at 266 nm.

onto carbon-coated copper grids. After the solvent evaporation the grids were transferred to the TEM microscope and analyzed. Fig. 5a shows the TEM image of the C12-TOPAS film irradiated with 40 pulses at 266 nm. CdS nanoparticles with sizes close to the bulk (7–9 nm) can be clearly seen in the magnified image of Fig. 5b. For less incident pulses the sizes of the formed NPs are smaller and coincide with these calculated by the Brus equation. Indeed, Fig. 5c shows the magnified TEM image of CdS nanoparticles formed after irradiation with 6 pulses at 266 nm. In this case, the mean size of the NPs is 4 nm, in perfect agreement with the calculated value from the Brus equation.

In summary, we demonstrate that upon pulsed UV irradiation it is possible to form areas with nanocrystals of specific size in polymer films. The initial films consist of a polymer matrix doped with

metal precursors, while the appropriate selection of the UV wavelength defines the formation and the size evolution of the nanodots. In all the cases studied, the polymer remains macroscopically unaffected. This is an alternative technique of micro/nanopatterning of NPs into polymers where the nanocomposite areas are formed in situ. By selecting the number of the irradiation pulses it is possible to define the optical properties of the nanocomposites that depend on the size of the formed NPs. The technique presented is really fast and efficient since the overall procedure takes place in few hundreds of nanoseconds that is the interaction time of the photons with the samples, and opens up new ways for the nanocrystal patterns fabrication into polymer matrices.

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