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Photon-induced formation of CdS nanocrystals in selected areas of polymer matrices

Athanassia Athanassiou[a] and Roberto Cingolani
NNL-National Nanotechnology Laboratory, INFM, CNR, Via Arnesano, 73100 Lecce, Italy and IIT-Italian Institute of Technology, Via Morego 30, Genova, Italy

Elsa Tsiranidou
Institute of Electronic Structure and Laser (IESL), FORTH, 711 10 Heraklion, Crete, Greece and Chemistry Department, University of Crete, 71003 Heraklion, Crete, Greece

Costas Fotakis
Institute of Electronic Structure and Laser (IESL), FORTH, 711 10 Heraklion, Crete, Greece and Physics Department, University of Crete, 71003 Heraklion, Crete, Greece

Anna Maria Laera, Emanuela Piscopiello, and Leander Tapfer
ENEA, Department Advance Physics Technologies and New Materials, Centro Ricerche Brindisi, SS7 Appia Km 706, 72100 Brindisi, Italy

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We demonstrate light-induced formation of semiconductor quantum dots in TOPAS® polymer matrix with very high control of their size and their spatial localization. Irradiation with UV laser pulses of polymer films embedding Cd thiolate precursors results in the formation of cadmium sulfide nanocrystals well confined in the irradiation area, through a macroscopically nondestructive procedure for the host matrix. With increasing number of laser pulses, we accomplish the formation of nanoparticles with gradually increasing dimensions, resulting in the dynamic change of the spectra emitted by the formed nanocomposite areas. The findings are supported by x-ray diffraction and transmission electron microscopy measurements. © *2007 American Institute of Physics*.

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Appropriate combination of polymer matrices with semiconductor nanoparticles results into the formation of nanocomposite materials that exhibit the unique properties of the nanoparticles (optical, electronic, and magnetic) merged together with, and even enhanced by, special properties of polymers (optical and mechanical). The nature of the polymer matrices makes the nanocomposites easy to process and manipulate, opening the way to the development of devices. Indicative applications of nanocomposite materials are optical filters,[1] photovoltaic solar cells, light emitting devices, photodetectors,[2–7] and gas sensors.[8]

In this work, we demonstrate fabrication of cadmium sulfide (CdS) nanocrystals in TOPAS®, a copolymer of the cyclic olefin 2-norbornene with ethylene, containing Cd thiolate precursors, using UV laser pulses. High control of their size from few to hundred nanometers is accomplished by increasing the number of laser pulses inducing dot nucleation. Our approach improves the quality of the formed nanocrystals, compared to thermal treatment through annealing or infrared radiation of similar precursor-polymer systems,[9–12] where surface defects eventually obscure the nanocrystal emission.[9–12] Furthermore, the formation of the nanocrystals is localized in the irradiation areas, which is not possible in the case of thermal annealing.[9–11,13]

Cadmium bis-dodecanthiolate $Cd(SC_{12}H_{25})_2$ precursors prepared as described in Ref. 10 were dispersed in TOPAS®. The polymer samples with the precursors were irradiated with UV laser pulses at intensity efficient for the formation of nanocrystals, but low enough to ensure prevention of any macroscopic alterations to the host polymer. Optical microscopy ensured that the surface remained intact after irradiation. The irradiation was performed in air using a XeCl excimer laser (308 nm, pulse duration of 30 ns, fluence of 100 mJ cm^{-2}, and repetition rate of 1 Hz) onto an area of 0.25 cm^2. As shown in Fig. 1, the UV wavelength used is at the edge of an absorption peak present only in the nanocomposite samples. Therefore, direct photolysis possibly in combination with indirect thermolysis causes the precursor decomposition:

$$Cd(SC_{12}H_{25})_2 + TOPAS \xrightarrow{UV} CdS + TOPAS + S(C_{12}H_{25})_2. \quad (1)$$

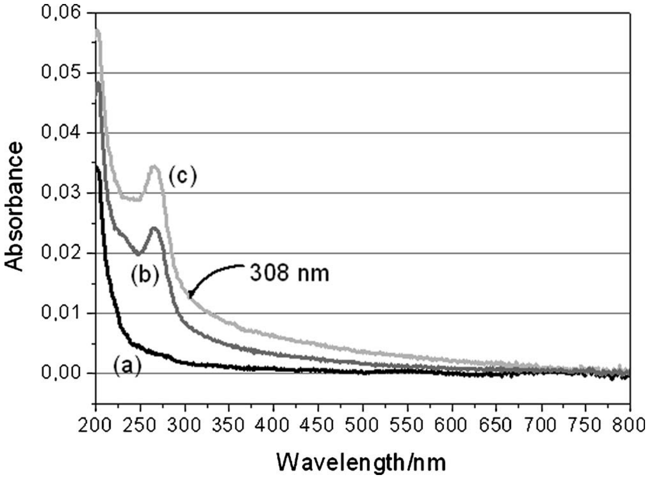

FIG. 1. Absorption spectra of the samples (a) TOPAS, (b) 10% $Cd(SC_{12}H_{25})_2$–90% TOPAS (c) 20% $Cd(SC_{12}H_{25})_2$–80% TOPAS.

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[a] Electronic mail: athanassia.athanassiou@unile.it

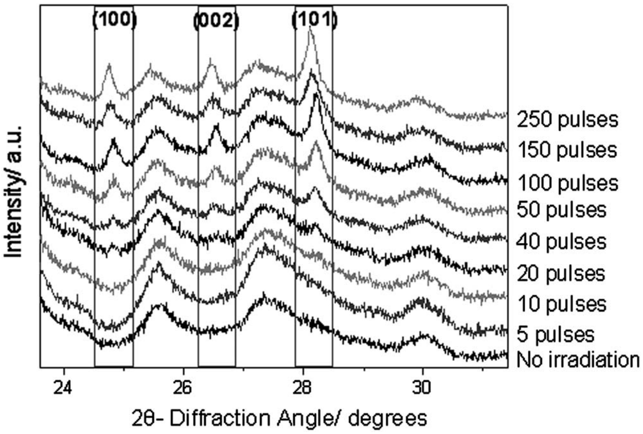

FIG. 2. XRD diffraction patterns before and after laser irradiation of the sample 20% $Cd(SC_{12}H_{25})_2$–80% TOPAS. The number of laser pulses is shown.

The irradiated area exhibits a color change from transparent to light yellow, exclusively attributed to the formation of the nanocrystals, since it does not occur in the polymer samples without precursors, even at higher laser energies.

x-ray diffraction (XRD) measurements were carried out by using Cu $K\alpha$ radiation (Rigaku, Dmax 2400, 12 kW, Cu target, Bragg-Brentano geometry), before and after irradiation to verify the phase changes of the precursors to nanocrystals. Indeed, with increasing the number of laser pulses, Bragg diffraction peaks are formed, attributed to the hexagonal phase of CdS (crystal symmetry $P6_3mc$ and lattice constants $a=0.4121$ nm and $c=0.6682$ nm) (Fig. 2).[14] In the samples containing 20% by weight precursor (Fig. 2), the peaks of the crystalline structures start being evident after 20 laser pulses (possible evidence at 10 pulses but obscured by the high background noise). After 40 incident pulses, the low background noise allows a safe estimation of the average size of the formed nanocrystals, using the Scherrer formula for spherical particles:[15]

$$D = 0.9\lambda/B\cos\theta, \tag{2}$$

where D is the diameter of the particles, B is the full width at half maximum (FWHM) of a CdS XRD peak, λ is the wavelength of the x-ray, and θ_B is the Bragg angle of diffraction. The width of the formed peaks remains constant above 40 incident pulses, indicating a stable mean diameter of $\sim 46.0 \pm 5.0$ nm. Their intensity saturates above 50 pulses, signifying that the formation of the crystalline structures is concluded. The XRD diffraction patterns of samples containing 10% by weight precursors are very similar to these of the samples with 20% precursors. The mean diameter of the crystals formed after irradiation with more than 50 pulses was calculated around 44.0 ± 5.0 nm. Above 50 pulses, the crystalline peaks saturate in width and intensity, signifying the completion of the crystal growth. In conclusion, after a certain number of pulses (~50) the formed CdS atoms aggregate into no further changeable nanocrystal arrangements.

The fluorescence of the nanocomposites was also collected for different numbers of pulses. After each irradiation pulse, the fluence of the laser was attenuated to 5.0 mJ cm^{-2} for the excitation of the previously irradiated area. The laser induced emission was collected by an optical fiber through a cutoff filter (<340 nm) to a spectrometer with a linear charge coupled device array detector and 1 nm resolution.

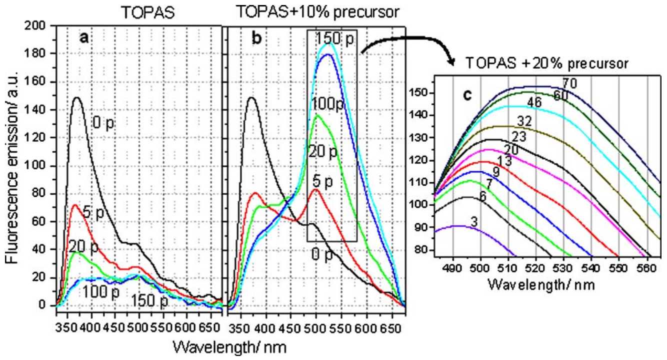

FIG. 3. (Color online) PL emission spectra after different numbers of irradiation pulses from the samples: (a) pure TOPAS, (b) 10% $Cd(SC_{12}H_{25})_2$ 90% TOPAS, (c) 20% $Cd(SC_{12}H_{25})_2$ 80% TOPAS, focusing in the wavelength range 480–580 nm.

The photoluminescence (PL) emission of the pure polymer samples decreases with increasing number of pulses, indicating photochemical modifications [Fig. 3(a)] that do not affect the transparency and the surface quality of the polymer. After irradiation of the nanocomposite samples with few pulses, the PL emission of the polymer (365 nm) decreases and a new peak arises around 490–495 nm [Fig. 3(b)]. This new peak is monitored exclusively in the samples with precursors, and it shifts toward longer wavelength upon increasing the number of incident laser pulses. The redshift in the samples irradiated below about 40 pulses indicates the formation of quantum dots of size smaller or comparable to the exciton Bohr radius of the bulk CdS (7–9 nm).[16–21] The shift saturates above 40 pulses and broadening of the spectra becomes dominant [Fig. 3(c)]. According to the XRD data at these numbers of pulses, the size of the nanocrystals clearly exceeds the exciton Bohr radius, and as a result the nanocomposites emit like bulk CdS crystals.

These observations are analyzed quantitatively after spectral deconvolution of the PL emission spectra using Gaussian functions. Figure 4(a) shows that four Gaussian bands compose the PL spectra of the polymer after irradiation, the relative intensities of which depend on the number of incident pulses, and thus on the degree of photochemical modifications. At insets (b) and (c) of Fig. 4 are shown two extra Gaussian bands contributing to the emission spectra of the samples with the thiolate precursors, attributed to the CdS nanocrystals (light grey shadowed band) and to the oxide of cadmium, CdO in the range of 537–540 nm (dark gray shadowed band). In Fig. 4 is shown the evolution of the energy and of the intensity of the CdS band with the number of pulses. The shift of the emission energy from 2.53–2.47 eV (i.e., 490–501 nm) starts from the very first pulses and reaches a plateau after about 40 pulses. We remind that CdS dots larger than 7–9 nm exhibit bulk properties with absorption edge/emission slightly above 500 nm,[18–20] whereas smaller dots can be tuned toward higher energy by decreasing their size.[21,22] The redshift with increasing number of pulses indicates an increase in the size of the formed crystals from the quantum size to the bulk regime. In particular, the size of the formed nanocrystals starts from 5 nm for 3 pulses according to Henglein's empirical curve,[21] and reaches 45 nm after 40 pulses calculated from the x-ray diffraction patterns. The intensity of the CdS emission peak reaches a plateau after ~50 incident pulses,

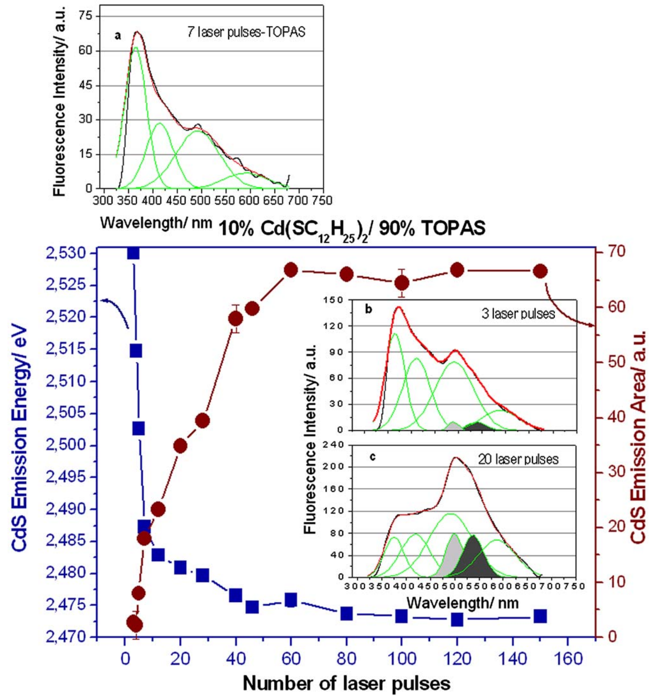

FIG. 4. (Color online) Evolution of the energy and of the intensity of the CdS emission upon increasing number of laser pulses. (Insets) Spectral deconvolution of the PL spectra from (a) pure TOPAS (b)–(c) 10% $Cd(SC_{12}H_{25})_2$–90% TOPAS after different numbers of incident laser pulses using Gaussian functions.

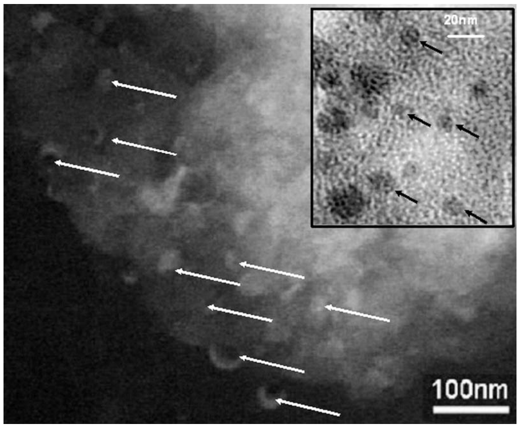

FIG. 5. HAADF-STEM image showing CdS clusters (some are indicated by the arrows) produced after irradiation with 30 laser pulses of the sample 10% $Cd(SC_{12}H_{25})_2$ in 90% TOPAS by weight. The inset shows a high magnification TEM image from the same sample. Black dot contrast corresponds to CdS clusters embedded in an amorphous matrix.

indicating completion of the crystal growth, in total agreement with the XRD finding.

The intensity of the PL emission of the amorphous CdO keeps increasing above 50 pulses, together with the intensity of the emission at longer wavelengths. The latter is attributed to recombination of charge carrier in trap states due to increasing amount of defects in the surface of the nanocrystals. For clean nanocrystal production in the quantization regime, the irradiation should be terminated after 40–50 laser pulses, since additional pulses contribute only to the formation of surface defects and CdO.

The samples after laser irradiation were studied also by transmission electron microscopy (TEM) (TECNAI F30 operating at 300 kV and point-to-point resolution of 0.205 nm). For the examination of the samples, the lightly colored irradiated areas were dissolved in toluene. A few drops of the solution were deposited on the TEM grid. Figure 5 shows a high angle annular dark field (HAADF) scanning TEM (STEM) image of CdS nanocrystals produced after 30 incident pulses on the sample with 10% precursor. According to the PL emission measurements, the average size of the formed nanocrystals after this number of pulses should be close to the border between the quantum confinement regime and the bulk material. Indeed, in the inset, which presents a higher magnification of the TEM image, can be observed nanoparticles with diameter less than 10 nm, while the distribution in the size of the nanoparticles is estimated between <10 and about 20 nm.

In summary, in this work is presented a demonstration of use of photons for the formation of nanocrystal semiconductors in polymer films. This unconventional approach has the advantages that nanocrystals can be selectively fabricated in specific areas of the polymer, controlling their size pulse by pulse. The appropriate selection of polymer and laser characteristics leads to nanocrystal formation without surface defects at the irradiated areas, avoiding any macroscopic damage to the host polymer. The technique can be expanded to other compounds and generalized. Evidence of ZnS quantum dot formation in the TOPAS® matrix containing Zn precursors is already available at NNL. Finally, our technique opens the way to the fabrication of patterns of nanocrystals into the volume of polymers, using two- and three-photon absorption, which might be exploited for new optical devices.

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