

DOI: 10.1002/sml.200500206

Nanocrystals as Precursors for Flexible Functional Films**

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Near-infrared (NIR) emitting Lead nanocrystals of lead chalcogenides near-infrared (NIR) emitting nanocrystals^[1-3] are considered fundamental functional building blocks for nanotechnological devices involving telecommunications^[3] and biology.^[2] The recent demonstration of highly efficient, multiple-exciton generation in lead chalcogenide nanocrystals^[4] have has dramatically increased the already compelling relevance of this class of materials, especially for solar energy harvesting. The main limit to the application of such nanomaterials is the instability of their luminescence, particularly towards oxidation,^[5] accentuated by the present unavailability of a procedure to efficiently coat them with a shell of a wide-bandgap semiconductor.^[6] Solids composed of nanocrystals^[7] have also attracted attention for the technological potential of their collective behaviour,^[8-10] yet although they inherit the vulnerability of the parent nanocrystals. A densely packed film of luminescent nanocrystals having mechanical, physical, and chemical stability,

along with accessibility to chemical species, is needed for most applications.^[9,11] The strategy for the creation of such composites almost always involve the use of nanocrystals as an additive to a usual standard synthesis of the matrix of choice.^[12] The main drawback of most of these procedures is that they require very careful control of the surface capping of the nanocrystals in order to avoid phase segregation and quenching of the luminescence. We here present here instead a general strategy to obtain tailorable and patternable functional flexible films of densely packed nanocrystals of different kinds by using the as-prepared nanocrystals as precursors in a low-power, room-temperature, O₂ plasma treatment.

The PbS nanocrystals are were synthesized, using by a hot-injection method,^[13] with lead chloride (PbCl₂) and elemental sulphur sulfur as reagents, and oleylamine (OLA) as coordinating solvent.^[14] The lead precursor was has been suggested to be a PbCl₂-OLA complex.^[14] As shown in Supporting Figure S1 in the Supporting Information, the powder X-ray diffraction (PXRD) pattern and high high-resolution transmission electron microscopy (HRTEM) images on of the dried nanocrystals confirm them to be nanocrystalline PbS, while their optical characterization demonstrates their high quality and monodispersity. After treatment with oleic acid to precipitate the PbCl₂-oleylamine OLA complex and several cycles of washing to remove traces of PbCl₂, the nanocrystals still show detectable Cl content (ca. ≈2 at. % against the approx. ≈6 at. % of Pb), as demonstrated by X-ray photoelectron spectroscopy (XPS) (Supporting Figure S1). This observation supports the idea of a lead-rich nanocrystal surface where chloride counterions balance the positive charge on the lead surface ions. This hypothesis is further supported by the PXRD data (Supporting Figure S1), which shows the absence of PbCl₂ peaks. Considering the observed atomic percentage of Cl, even with the errors associated with XPS compositional analysis, a crystalline PbCl₂ phase should have been visible in the PXRD, and amorphous PbCl₂ is usually only obtained by quench deposition.^[15]

These nanocrystals can be readily used as precursors for the one-step formation of flexible photoluminescent films (Figure 1). A Thus, a solution containing PbS nanocrystals and the excess PbCl₂-OLA complex is was repeatedly drop-cast onto a glass slide until a thick film (1–50 μm) is had formed. At this stage the film is composed of densely packed nanocrystals, separated by the OLA capping ligands. The film is was then exposed to a 5-W air plasma for 48 h, and can thenfter which it could be lifted- off the substrate without damage from the substrate. Surprisingly, the resulting material is flexible and can be folded like paper, as shown in Figure 1 c.

The morphology of the films and their nanoscopic organization was probed by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) ; see (Figure 1 and Supporting Figure S2, Supporting Information). The nanocrystals tend to form ordered superstructures,^[7] commonly described as supercrystals, with cubic symmetry. The peak in the small small-angle X-ray scattering (SAXS) curve (Supporting Figure S3) cannot be fitted

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[**] We thank S.Y. Choi and S. Petrov for PXRD measurements, M. Mamak and N. Coombs at the Center for Nanostructure Imaging (CNI) for TEM/SEM characterizations, R. N. S. Sodhi for XPS and TOF-SIMS measurements, M. Hines for valuable suggestions, and K. Landskron for proofreading the manuscript. G.A.O. is the Government of Canada Research Chair in Materials Chemistry. He is deeply indebted to the Natural Sciences and Engineering Research Council of Canada for financial support of this work.

Supporting information for this article is available on the WWW under <http://www.small-journal.com> or from the author.

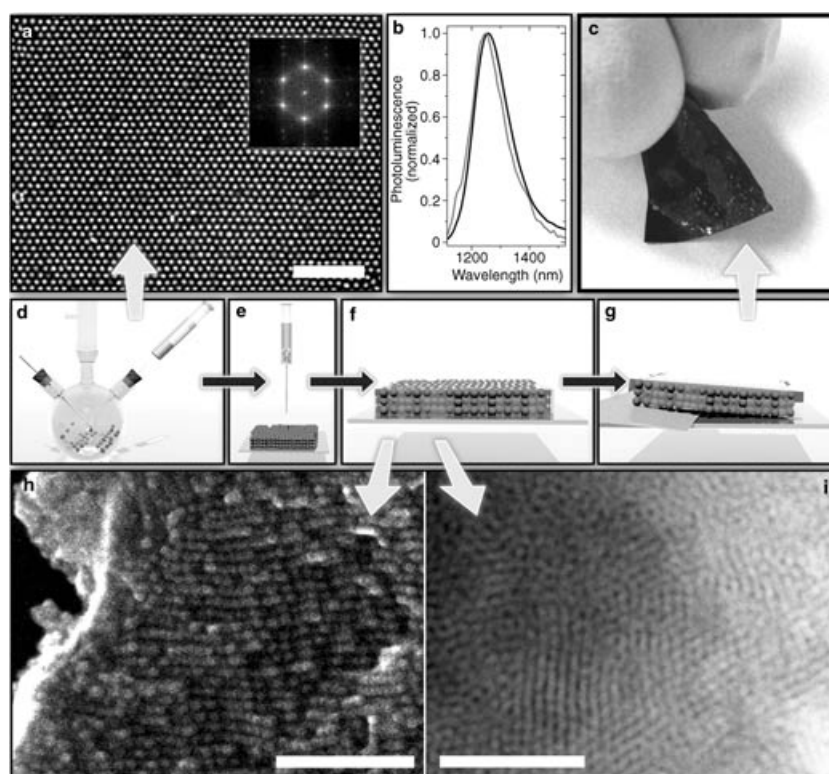


Figure 1. Fabrication, morphology, and optical properties of plasma-treated nanocrystal films. a) TEM characterization of the purified nanocrystals. In the inset, the fast Fourier transform (FFT) of the image demonstrates the periodicity of the close close-packed monolayer; b) Photoluminescence (PL) spectra of a dried film before (black) and after plasma- treatment (gray); c) Photo of a plasma-treated nanocrystal film under flexure; d–g) Fabrication stages of plasma-treated nanocrystal films; h, i) SEM and TEM characterizations of the film, respectively. All scale bars are 80 nm.

by considering randomly- distributed, monodisperse nanocrystals,^[8] and thus which suggests the presence of a residual order in the packing of the nanocrystals even after plasma treatment. The surface-to-surface distance between nanocrystals is was found to be ranging between 1 and 3 nm from (by TEM analysis), which is close to the nanocrystal spacing in the drop-cast films determined by interdigitated OLA chains (ca. ≈ 2 nm).^[3]

The nature of the generated matrix was determined with by several analytical techniques. PXRD characterization (Figure 2a) shows showed that the only discernible peaks are associated with the PbS crystalline phase, thus suggesting the amorphous nature of the matrix. An XPS-characterization survey scan (Figure 2b) shows showed that the plasma treatment heavily decreases the amount of carbon content of carbon (C:Pb drops from 13.7 ± 0.9 to 0.1 ± 0.2), and nitrogen (undetectable after treatment), and also seems to decrease the chlorine content (Cl:Pb from 0.4 ± 0.9 to 0.1 ± 0.2). The deconvolution of the O 1s peak (Figure 2c) shows the presence of PbO_x species resulting from oxidation of the PbCl₂-OLA complex and PbSO₄ due to oxidation of the PbS nanocrystal surface (peaks at 529.30 and 531.31 eV, respectively, with a 1:2 area ratio). The high-resolution spectrum of the S 2p peak (Figure 2d) shows contributions from PbS nanocrystals, sulphite sulfite, and sulphate sulfate spe-

cies (peaks at 161.42, 166.64, 168.51 eV, respectively, with 1:3:6.5 area ratios).

The films showed to readily adsorb carbon upon exposure to the atmosphere, presumably due to the recombination of the radicals formed into the plasma chamber. The carbon concentration in the flexible films is also increasing increases with the increasing thickness of the precursor nanocrystal film. This is consistently with the accepted model of plasma- polymerization,^[16] in which ablation and polymerization of the organic components are occurring simultaneously. Here, an increase in film thickness hampers the ablation of the ligands from the bulk, thus favourfavoring the formation of a 3D polymer network. A high carbon content (> 5% from XPS) was found not to be necessary to obtain a flexible film, differently from as opposed to the situation

with the PbCl₂-OLA complex. XPS analysis of plasma-treated nanocrystal films obtained from PbCl₂-OLA-free nanocrystals (see Supporting Information) confirmed the absence of PbO_x PbO_x, thus suggesting it to be responsible for the flexibility of our films.

Preliminary investigations encourage the belief that this nanocrystal plasma “polymerization” can be extended to different nanocrystals. Analogously synthesized CdS nanocrystals (using from CdCl₂) are able to form films having with a similar structure when subjected to plasma treatment (Supporting Figure S4). Tuning of the matrix properties and composition by using core-shell nanocrystals and different solubilized chlorides or alkoxides should also be possible. In this context, preliminary results indicate that densely-packed PbS quantum dots can be prepared in an SiO₂ matrix can be prepared by exposing the nanocrystals to air plasma in the presence of silicon alkoxides (data not shown).

The photoluminescence (PL) of these plasma-treated nanocrystal films (Figure 1i) is strikingly intense. The difference in absolute photoluminescence of the films before and after the treatment is less than 10%, thus demonstrating that the process does not create non-radiative recombination pathways. N, and no trap trap-state emission was is seen at higher wavelengths. While the

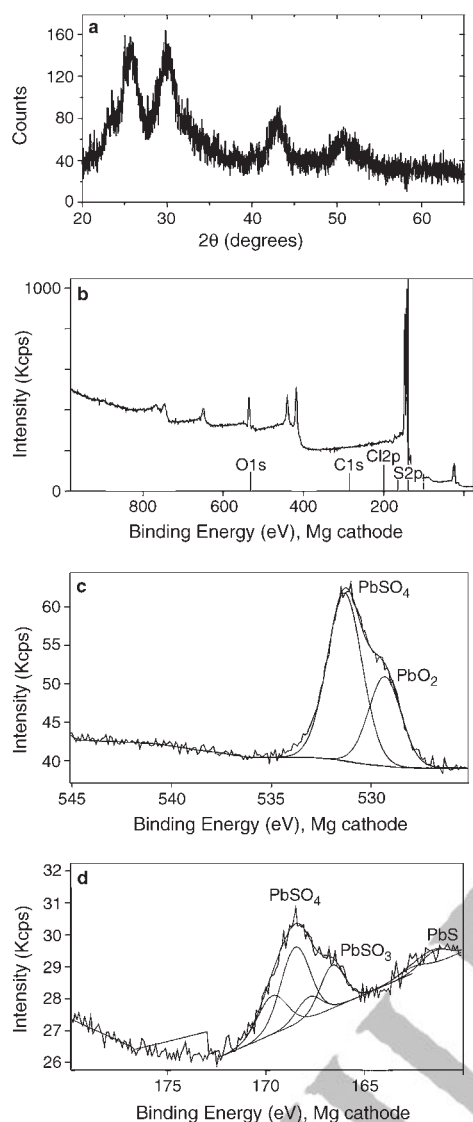


Figure 2. Characterization of plasma-treated flexible nanocrystal films. a) PXRD pattern showing the presence of the nanocrystalline PbS phase. b) XPS survey spectrum after Argon argon ion sputtering. c) XPS spectrum of the O1s peak. d) XPS spectrum of the S peak.

plasma treatment does not significantly affect the photoluminescence full width at half maximum (FWHM), a blue shift in the peak position is often observed (see Figure 1b), which indicating indicates that the physico-chemical nature of the surface of the nanocrystals and/or their average size is modified by the plasma, consistent with the results of photo-oxidation experiments on CdSe nanocrystals.^[17]

The film obtained by plasma- treating treatment of the purified-amine-capped nanocrystals (PbCl₂-OLA-free) is luminescent but brittle, while oleic- acid-capped nanocrystals produce films that are both non-luminescent and brittle. The presence of chloride ions on the surface of the nanocrystals confers oxidation stability, while dissolved PbCl₂ is required for the formation of the flexible matrix.

The plasma-treated films were exposed to a 10% H₂SO₄ solution, hot toluene, 100 °C annealing, and extended UV radiation. None of these treatments was found to substan-

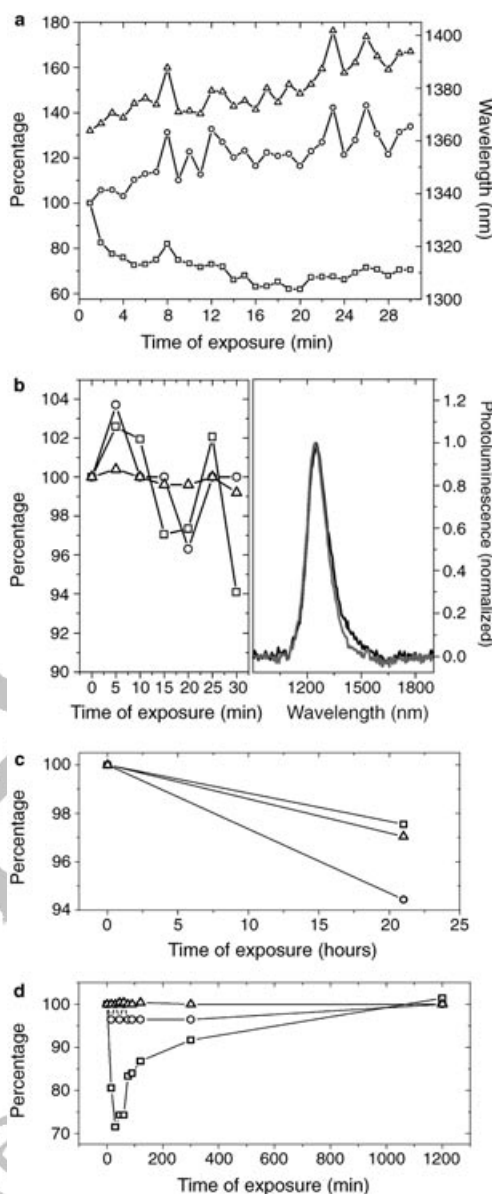


Figure 3. Stability of plasma-treated flexible nanocrystal films. T, showing total photoluminescence (%; squares), FWHM peak width (%; circles), and peak position (nm; triangles) as a function of the time of exposure to a 10% H₂SO₄ solution (a), a toluene solution at 80 °C toluene solution (b, left panel), heating to 100 °C in air (c), and irradiation with a UV lamp (d). The lines in each panel serve as guides to the eye. The PL spectra of the sample before (black) and after (gray) 10 h of exposure to a toluene solution at 80 °C toluene solution are shown in the right panel of ((b, right panel).

tially reduce the PL of the films, as shown in Figure 3. We further found concentrated HCl to be an appropriate etchant, thus allowing us to selectively dissolve the PbS nanocrystals without damaging the PbSO₄ and PbO_x matrix^[18] (Figure 4). HCl solution was flowed passed through the 20- μ m channels of a polydimethylsiloxane (PDMS) elastomeric stamp pressed conformally on the surface of the plasma-treated film. The solution was forced to flow along the channels by capillary forces, and its action was then rapidly quenched with distilled water. In Figure 4 an An optical

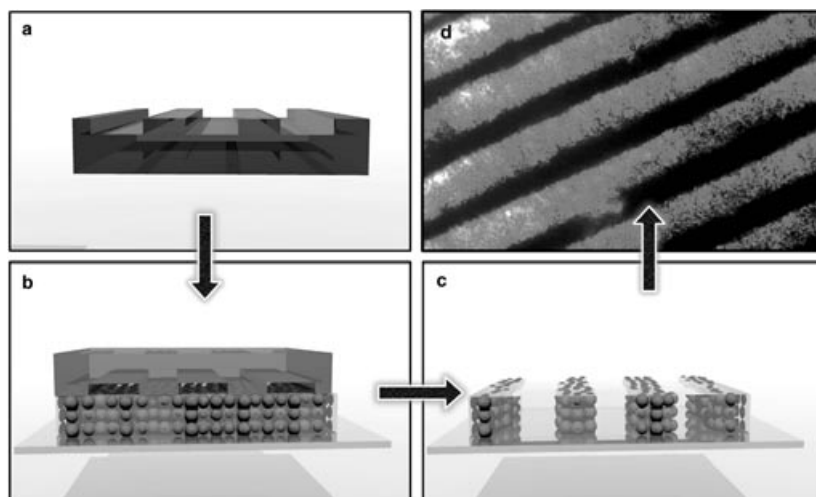


Figure 4. Fabrication of patterns in plasma-treated flexible nanocrystal films. a-, b) A PDMS stamp bearing 20- μm -wide channels is pressed onto the plasma-treated film. c) A concentrated HCl solution is flowed passed through the channels by placing a drop at one of their ends, and, and exposed nanocrystals are selectively dissolved. d) Transmission optical micrograph of the patterned film. The black stripes are where nanocrystals have not been dissolved, while gray stripes are where nanocrystals have been dissolved.

transmission micrograph is displayed of the patterned film, which showing shows black stripes of for the nanocrystal-filled matrix and gray stripes where the nanocrystals have been dissolved, is displayed in Figure 4. The soft lithographically patterned film is still flexible, free-standing, and luminescent. This experiment demonstrates that the nanocrystals inside the matrix are accessible to chemicals.

We In conclusion, we have introduced developed a method for producing functional films with a new and unique combination of properties that enabling enables the use of nanocrystals as precursors. Such films are easy to make and pattern, and have strong and narrow NIR photoluminescence, flexibility, and compositional tunability, making worthwhile it worthwhile to investigate their applicability in flexible displays, sensors,^[11] solar cells,^[4,19] active photonic crystals, optically responsive “smart” clothing and packaging, and multilayer laser cavities, whose frequency can be tuned by compression or stretching.

Keywords:

films • lead sulphidelead sulfides • nanocrystalsnanocrystalline materials • plasma chemistry • quantum dots • thin filmsquantum dots

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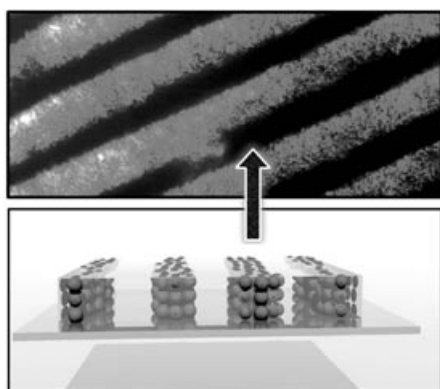
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Received: June 22, 2005

Published online on ■■■, 2005



Nanocrystals—your flexible friends! The use of nanocrystals as precursors for the one-step formation of flexible functional films by using an air plasma is here demonstrated. This treatment does not harm the photoluminescence of the individual nanocrystal building blocks

but confers it resilience to bending as well as acidic environments, hot solvents, annealing, and UV irradiation. Chemical The chemical accessibility and selective etching of the nanocrystals allows for micron micrometer-scale patterning of the film (see Figure).

■ Thin films ■

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Nanocrystals as Precursors for Flexible Functional Films



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