

Nanocrystal Plasma Polymerization: From Colloidal Nanocrystals to Inorganic Architectures

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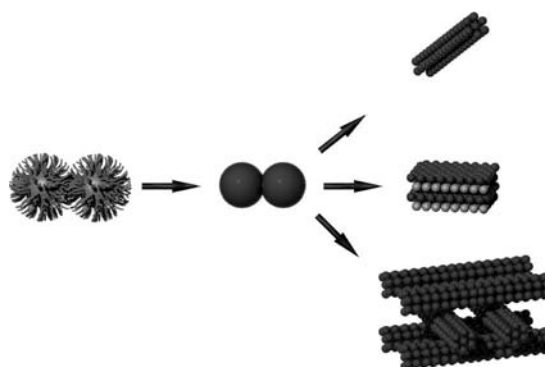
CON SPECTUS

Nanocrystal superstructures are increasingly becoming a subject of intense study. Such materials could constitute a new class of nanocomposites of designed structure, of homogeneous composition, and with unique properties. New phenomena are observed in these materials because of the interaction at such diminutive length scales.

A common problem in the development of devices relying on colloidal nanocrystal assemblies is that the individual nanocrystal building blocks require organic molecules to control their size. These ligands are responsible for the colloidal stability of the individual nanocrystal building blocks and are thus necessary for their solution processibility. Because of the ligands' incompatibility with many solid state applications, it is important to develop post-processing techniques that mildly remove them from these nanocomposites, while maintaining the size-dependent properties of the building blocks.

This Account highlights a new strategy, nanocrystal plasma polymerization (NPP), for processing colloidal nanocrystal assemblies. This technique exposes the nanocomposite to a mild air plasma and allows for the removal of the nanocrystals' capping ligands while preserving their size-dependent and material properties. As a result, the process yields a nearly all-inorganic flexible solid-state material with unprecedented characteristics.

We describe early experiments, in which NPP was used to create arbitrarily complex 1D, 2D, and 3D inorganic free-standing architectures entirely composed of nanocrystals, as well as future directions and challenges. We expect this platform will be useful for the design of new materials and will be a valuable new addition to the nanoscientist's toolbox.



1. Introduction

One of the main causes of diffidence from the physics community toward colloidal nanocrystals is their relatively ill-defined surface, which is, in most cases, coordinated by surfactants of various lengths that have the role of providing colloidal stability, saturating the dangling bonds, and controlling the growth of the nanocrystals. This ligand shell is problematic because it is difficult to model, fragile during physical and chemical processing and, despite recent advances,^{1–3} poorly under-

stood in its influence over the nanocrystals' physical properties. The development of core–shell nanocrystals,^{4–6} for example, has introduced a more familiar inorganic–inorganic interface in the system. The adoption of successive ion layer adsorption and reaction (SILAR) strategies⁷ have then introduced the other familiar concept of epitaxy into the colloidal nanocrystal field. After such breakthroughs, the influence of these ligands still remains nontrivial, especially when solid-state materials based on these colloids have to be developed: nanocrystals' conductivity,⁸ surface

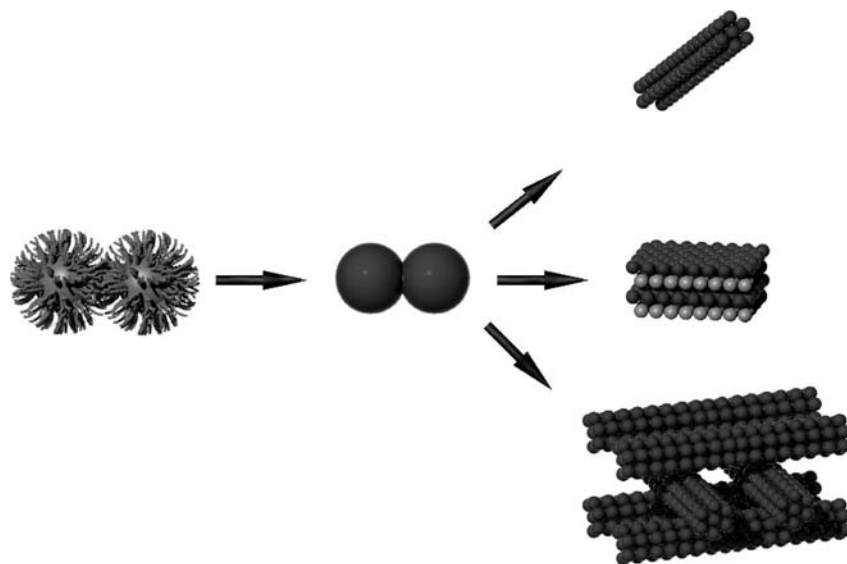


FIGURE 1. Illustration of the nanocrystal plasma polymerization (NPP) process. The assembled colloidal nanocrystals are exposed to controlled plasma treatment, which removes the ligands and connects the nanocrystals through an inorganic matrix. The formation of free-standing 1D, 2D, and 3D architectures entirely composed of nanocrystals is thus possible.

charge,⁹ blinking behavior,¹⁰ and self-assembly⁹ are a few of the characteristics that are affected by the ligand shell. And while the plasticity of this influence to external stimuli might be attractive for sensor applications,^{11,12} it remains undesirable for most solid-state devices. To further complicate the task, with the exception of multidentate ligands,¹³ colloidal nanocrystals need a consistent amount of free ligands in solution in order to maintain their dispersed state and to remain solution processable.^{14–16}

Extensive work has been done to incorporate nanocrystals in a matrix without harming their properties. The main issues are related to the preservation of the properties, especially for quantum dots, where the luminescence has always proved to be sensitive to surface conditions.¹⁷ Other problems arise in achieving a high nanocrystal filling fraction, which is either desirable or necessary for many applications, including amplified spontaneous emission and lasing;^{18,19} for example, the matrix usually becomes very fragile when the nanocrystal volume fraction exceeds a certain value. Nanocrystals are generally created within the matrix by precipitation (as in glasses²⁰), by chemical deposition methods (as for some mesoporous materials²¹), or by ion exchange methods (as for zeolites²²). A review of all incorporation methods is well beyond the scope of this Account, and we will here instead highlight some of the most promising techniques that employed colloidal nanocrystals.

Klimov's group has developed a strategy based on sol–gel processing in which nanocrystals are directly anchored to the

inorganic matrix via a short ligand or using a polymeric intermediate.^{23,24} In the first case, the nanocrystal filling fraction is about 19%, and in the second case, the filling fraction is about 6%. Thin films of these composites can be spin coated on rigid substrates because the films themselves are rigid, after condensation.

Incorporation of nanocrystals in polymers on the other hand is limited by the tendency of nanocrystals to phase segregate,²⁵ which in turn induces fragility in the resulting composite. This tendency is at least partly due to the unfavorable interaction of the nanocrystals' surface ligands with the polymeric matrix. Recent advances in the control of segregation in nanocrystal–polymer composites appear very promising,²⁶ but they are still limited in the filling fraction they can achieve, and they make use of specific polymers.

Much less work has been done on the removal of the ligands from colloidal nanocrystals. This is especially true for nanocrystal quantum dots where it typically results in the loss of photoluminescence; ligand removal creates unsaturated bonds on the surface, which act as carrier traps,¹⁷ reducing the band-edge emission by inducing trap states in the bandgap.^{3,10,27} This mechanism underlies most cases of luminescence instability.¹⁷ Partial removal of the ligands has been used to increase the photoconductive gain in nanocrystal-based photodetectors²⁸ or to develop all-inorganic solar cells based on nanocrystals.²⁹ Such strategies however quench the luminescence and are mostly used to improve the conductivity of the nanocrystal superlattice by increasing exciton wave function overlap between neighboring crystals.

In general, nanocrystals do not need ligands to luminesce, as Stransky–Krastanov self-assembled quantum dots demonstrate; therefore it should be possible to completely remove the ligands from colloidal nanocrystals without altering their luminescence properties. A fascinating strategy used electro-spray organometallic chemical vapor deposition to co-deposit colloidal quantum dots with a higher band gap semiconductor.^{30,31} In this case, the luminescence of the CdSe/ZnSe composite was preserved due to the presence of a ZnSe shell on the initial dots, even when the ligands were removed. However, as in the case of polymer-embedded nanocrystals, the particles often segregated and agglomerated.³²

This Account will focus on an approach developed recently,^{33–35} which we termed nanocrystal plasma polymerization (NPP)^{34,35} (Figure 1). NPP allows the removal of capping ligands and the preservation of the nanocrystals' size-dependent properties through an inexpensive, dry, and low-energy processing step. NPP also consolidates nanocrystals into mechanically stable solids allowing for the replication of arbitrary templates, the formation of multilayer structures, and the dramatic enhancement of their chemical stability. This approach allows for low-temperature fabrication of nearly all-inorganic arbitrary free standing architectures entirely made from self-assembled nanostructures.

In this Account, we describe the array of results and possibilities offered by this processing platform.

2. Nanocrystal Plasma “Polymerization”

2.1. Definition. Nanocrystal plasma polymerization (NPP) can be defined as the plasma treatment of nanostructure assemblies, which preserves their size-dependent properties and individuality while consolidating them within a host matrix. The use of the term “polymerization” is here controversial, since it is sometimes considered misleading. From our knowledge of this process, we can say that it is indeed a plasma polymerization process, which, if brought to completion, leads to the etching of the organic phase and thus to inorganic nanocomposites. This is a characteristic of plasma treatments in which the polymerization, etching, and deposition of organics are simultaneous processes with different and tunable kinetics. Our initial interest was in ligand removal so that the treatment was always brought to completion. Nothing prevents use of this plasma treatment to induce the 3D polymerization of the ligand shell network by halting the process at earlier stages. This would be an interesting way to pro-

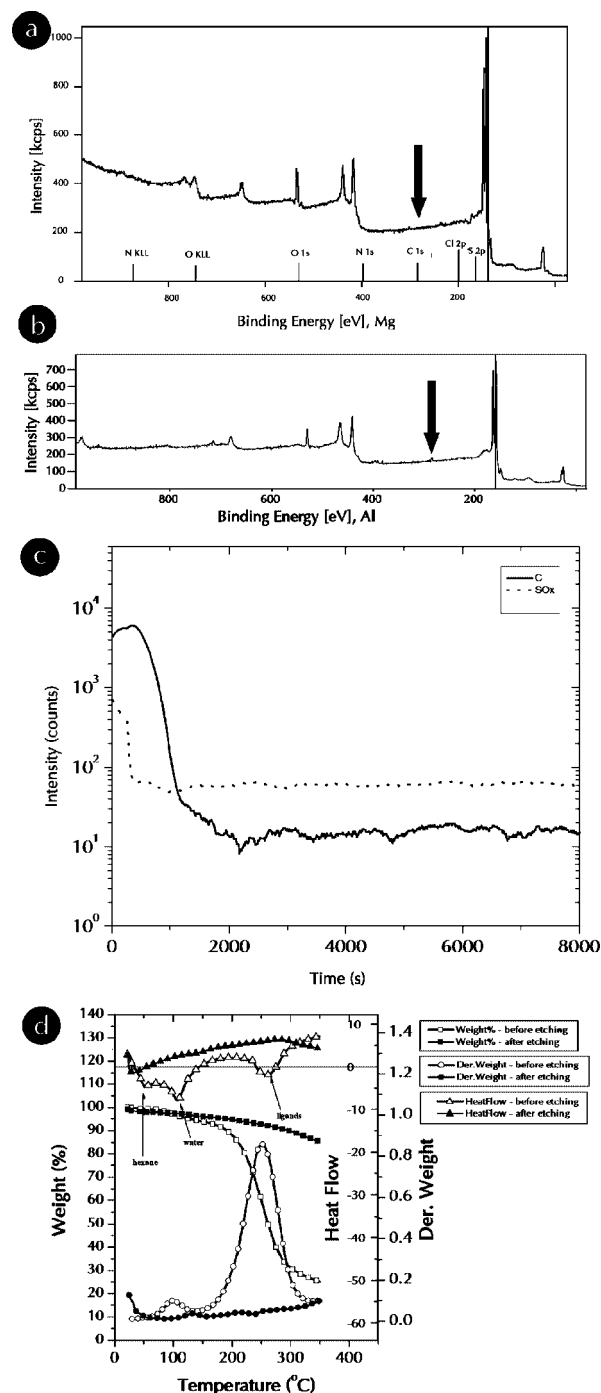


FIGURE 2. Ligand removal.^{34,35} (a) XPS survey spectrum of a PbS nanocrystal film after NPP, the arrow marks the position of the C1s peak; (b) XPS survey spectrum of a Bi₂S₃ nanorod film after NPP, the arrow marks the position of the C1s peak; (c) TOF-SIMS depth profile of C and SO_x anions in an NPP-treated PbS nanocrystal film; (d) TGA and DSC traces obtained from a PbS nanocrystal film before and after NPP (squares indicate sample weight loss, circles indicate the weight loss derivative, triangles indicate heat flow; empty symbols are for the sample before NPP, filled symbols are for the sample after NPP).

duce polymer–nanocrystal composites with large nanocrystal filling fractions.

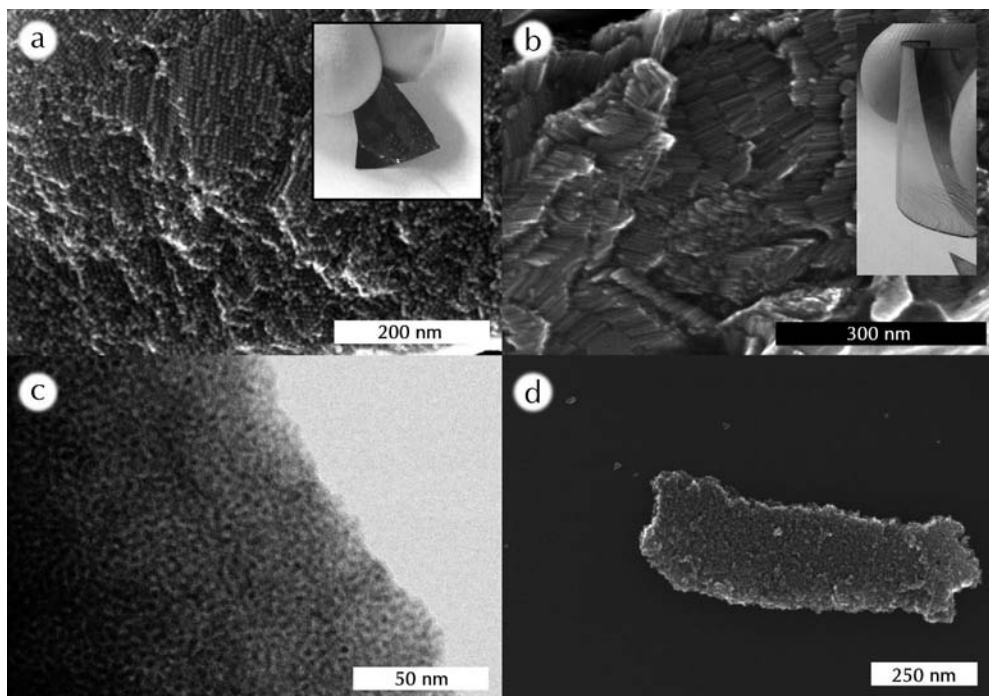


FIGURE 3. Morphology: (a) HR-SEM of a cross-section of a PbS nanocrystal film after NPP, in the inset a photo of a free-standing PbS nanocrystal flexible film; (b) HR-SEM of a cross-section of a Bi_2S_3 nanorod film after NPP, in the inset a photo of the film on a flexible substrate; (c) TEM of a CdS nanocrystal film; (d) HR-SEM of a fragment of a CoFe_2O_4 nanocrystal film.

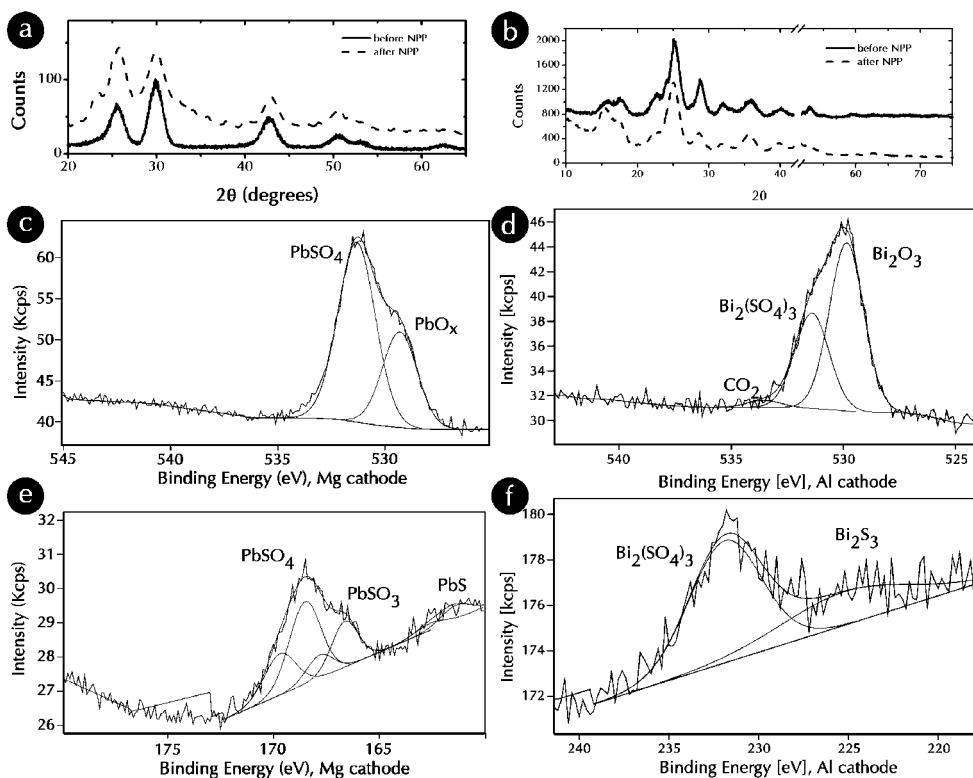


FIGURE 4. Matrix identification after NPP treatment: (a) XRD of PbS nanocrystal films before (—) and after (---) NPP; (b) XRD of Bi_2S_3 nanorod films before (—) and after (---) NPP; (c) high-resolution XPS O1s peak from a PbS nanocrystal film after NPP; (d) high-resolution XPS O1s peak from a Bi_2S_3 nanorod film after NPP; (e) high-resolution XPS S2p peak from a PbS nanocrystal film after NPP; (f) high-resolution XPS S2s peak from a Bi_2S_3 nanorod film after NPP. All assignments are based on the NIST XPS Database.

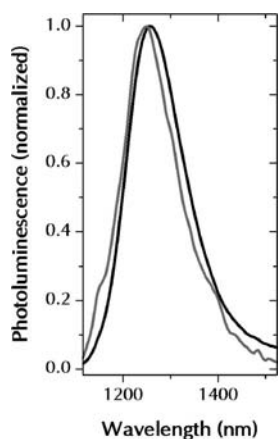


FIGURE 5. The photoluminescence of the film before NPP (black line) is compared with the photoluminescence after NPP (gray line). The two spectra are normalized. The real intensity was measured in several points with the help of an integrating sphere to account for scattering. The quantum yield (QY) was found not to be significantly affected by the NPP treatment.

2.2. The Protocol. Nanocrystals were deposited on a substrate of choice (Si, SiO₂, PET, etc.) using a wide variety of techniques including dip-coating, spin-coating, and drop-casting. Once dried, the film was placed into the plasma chamber and exposed to air plasma.^{33,35,36} The exposure time and the plasma power³⁷ strongly affect the results and must be adjusted for film thickness.

2.3. NPP Removes the Ligands. One of the most attractive aspects of plasma treatment is its ability to selectively remove the organic component of a sample. It has been used for removing surfactants from surfactant-templated mesoporous materials,³⁸ as well as tuning the filling fraction in synthetic opals made of organic colloids.³⁹ In the case of NPP, we found that plasma treatment mainly removes the ligands from the surface of the nanocrystals.

This effect has been demonstrated both on monolayers of nanocrystals^{33,37,40} and on thin nanocrystal superlattices.^{34,35} In Figure 2 are shown the data for PbS and Bi₂S₃ nanocrystal superlattices in which the carbon concentration decreased from around 80% to as low as 3% as demonstrated by XPS (Figure 2a,b). Considering the error of XPS elemental analysis and its tendency to detect carbon adsorbed from the atmosphere, we can consider these films nearly all-inorganic. A time of flight secondary ion mass spectrometry (TOF-SIMS) analysis demonstrates the uniformity of carbon removal throughout the thickness (Figure 2c); carbon has a peak of concentration near the surface but then decreases steeply and remains constant and extremely low throughout the remaining thickness of the sample. Such a surface peak is well-known in plasma-treated surfaces and is attributed to

adsorption of atmospheric CO₂. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed before and after treatment (Figure 2d); the decomposition peak associated with the ligands disappears in the treated sample.

While these results demonstrate that it is possible to remove the ligands from nanocrystal films, milder modifications are also possible with plasmas. Rigorous work has been performed by the groups of Liao and Zharnikov on the influence of different plasmas on self-assembled monolayers (SAM) on different substrates.^{41–45} Downstream plasmas were used in order to focus on the effect of low-energy species, namely, radicals. The processes that they were able to identify were diverse: disordering of the SAM, oxidation of the alkyl matrix, oxidation of the headgroup, cross-linking of the alkyl matrix upon oxidation, and desorption of the SAM upon headgroup oxidation. The kinetics of these processes can be controlled by several parameters including SAM–substrate interaction strength, plasma composition, and alkyl chain length.

This complex set of events tells us about the potential of plasma treatment for the modification of delicate organic surfaces. We refer the reader to some excellent reviews, which deal thoroughly with this topic.^{46–52}

2.4. The Nanostructure's Morphology Is Maintained by NPP. The morphology and microstructure of the multilayer films were probed with high-resolution scanning electron microscopy (HR-SEM) and transmission electron microscopy (TEM). As seen in Figure 3, for all shown compositions the individual nanocrystals are perfectly discernible. Analogous conclusions can be drawn from the results obtained from nanocrystal monolayers.^{33,37,53,40}

Another important morphological feature was the uniformity of the films obtained and their flexibility, as shown in the insets of Figure 3. Very thick films of PbS nanocrystals could be successfully detached from the substrate, yielding a free-standing film that could be folded like paper (see inset in Figure 3a). Flexible thin films could be instead obtained by performing NPP on spin-coated films of nanocrystals on a PET substrate (see Figure 3b).

2.5. The Matrix Is Amorphous and Dependent on the Plasma Composition. The XRD spectra obtained after NPP showed only the original crystalline phase belonging to the starting nanocrystals (see Figure 4a,b).^{34,35} The higher background in the NPP samples is to be attributed to a highly scattering noncrystalline phase.

The matrix consisted of a combination of oxide and sulfide species (also sulfite, in the case of PbS), as shown by the high-resolution XPS spectra in Figure 4c–f. The implantation

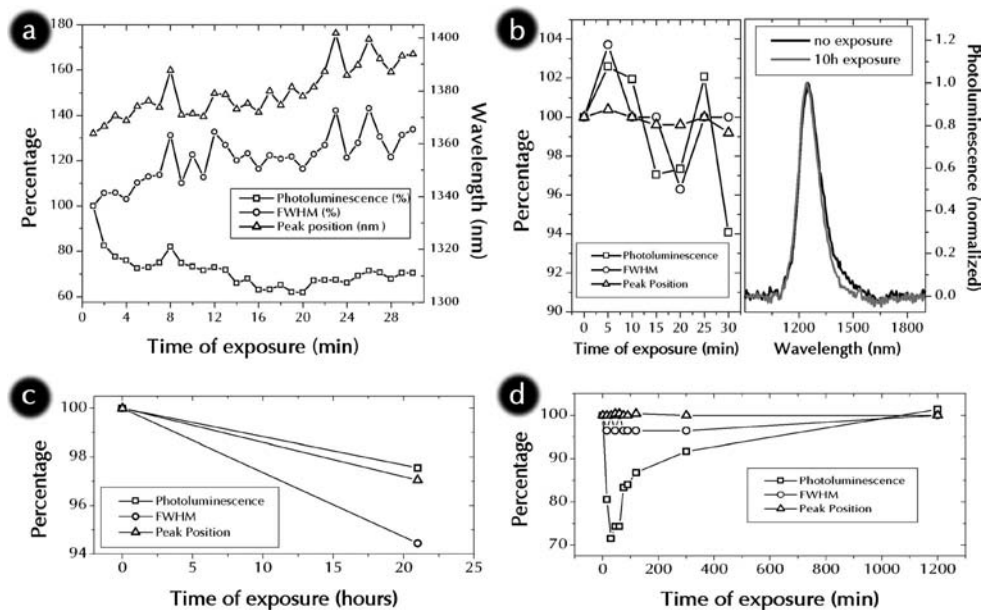


FIGURE 6. Chemical stability of NPP-treated PbS nanocrystal films: (a) photoluminescence time monitoring (peak intensity, fwhm, and peak position) upon exposure to 10% H₂SO₄ solution; (b, left) photoluminescence time monitoring (peak intensity, fwhm, and peak position) upon exposure to 80 °C toluene; (b, right) normalized photoluminescence spectra after 10 h exposure to 80 °C toluene; (c) photoluminescence time monitoring (peak intensity, fwhm, and peak position) upon exposure to 100 °C in air; (d) photoluminescence time monitoring (peak intensity, fwhm, and peak position) upon exposure to UV light.

of oxygen is a characteristic of air and oxygen plasmas, and the surface oxidation of chalcogenide nanocrystals, facilitated by the usually anion-rich nature of their surface,¹⁷ often proceeds via the formation of sulfates, selenates, or tellurates.⁵⁴ The surprising observation was the formation of oxide species. The appearance of these might be attributable to the vacuum facilitating the formation of volatile oxidation byproducts such as SO₂ and to the oxidation of excess cationic precursors present in the film.

These results are consistent with the impressive ones reported by Wiedwald et al. where Co nanocrystals formed by plasma treatment of Co-loaded block-copolymer micelles are also oxidized by oxygen plasma.⁵³ Salient among their findings was the demonstration of the reversibility of nanoparticle oxidation upon exposure of the oxidized nanocrystals to H₂ plasma.⁵³ During this treatment, the particles did not change morphology. This result has been further confirmed by Gehl et al. using CoPt₃ nanocrystals.^{37,40}

2.6. The Properties Are Maintained during NPP. The properties were easily monitored in the case of PbS nanocrystals, due to their strong band-edge emission in the near-infrared (NIR). Our results showed that the plasma has little influence on the emission intensity of PbS nanocrystals. As shown in Figure 5, the width and position of the peak are virtually unchanged. Electrical measurements performed on several nanocrystal systems after NPP showed the films to remain insulating. This is likely to be a consequence of the chemical

nature of the matrix, which is strongly insulating. Changing the composition of the plasma (for example, by using a H₂-H₂S-Ar feed gas) to induce formation of a chalcogenide matrix instead of an oxide matrix might yield a conductive nanocomposite.

2.7. NPP-Treated Films Are More Chemically Stable.

After having characterized the properties of the PbS NPP films, we became curious as to whether the films' luminescence was made more resistant to processing than for the untreated films. Their luminescence was monitored as a function of the time of exposure to different chemical and physical agents.³⁴ In the first case, we exposed the film to a 10 vol % solution of H₂SO₄. As can be seen in Figure 6a, the luminescence decreased rapidly to ~80% of the initial value to then stabilize and remain virtually constant for 30 min. Exposure to toluene at 80 °C (Figure 6b) had no effect on the luminescence for over 30 min. Similar results were obtained when the film was exposed to 100 °C in air (Figure 6c). When instead a film was exposed to UV light, the luminescence intensity decreased rapidly in the first minutes to 70% of the original value to then increase slowly over the course of 20 h (Figure 6d). This behavior is at the moment difficult to explain because the PL upon exposure to UV strongly depends on the chemical environment of the dots. However, these are severe treatments that testify to the chemical inertness of these films, especially when compared with the sensitivity of nanocrystal solids.⁵⁵

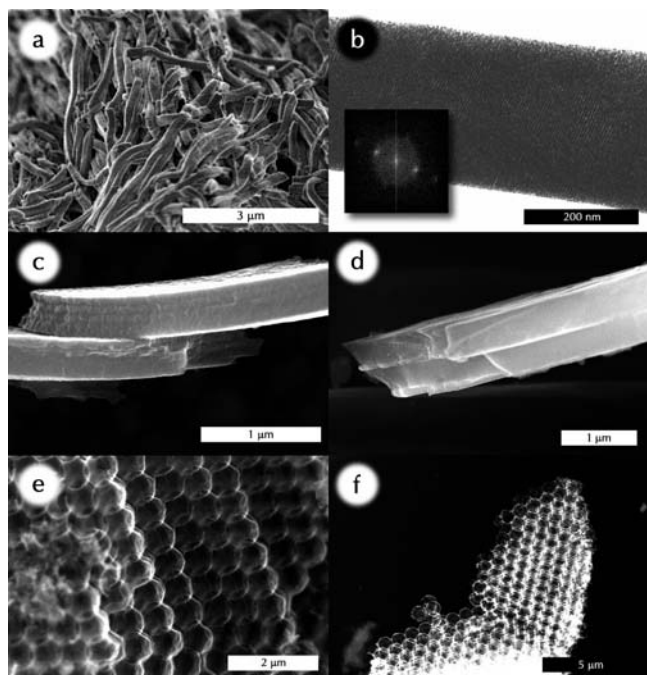


FIGURE 7. Examples of architectures of different dimensionality entirely composed of nanocrystals, which are obtainable via NPP: (a) one-dimensional structures obtained via NPP of PbS nanocrystals in Al_2O_3 membranes; (b) TEM image of a representative microrod showing superlattice formation, in the inset the FFT of the image; (c) two-dimensional structure obtained by depositing alternating layers of PbS and CoFe_2O_4 nanocrystals—the individual layers are visible in the cross-section; (d) two-dimensional architectures obtained by depositing two periods of an ABC multilayer composed of CoFe_2O_4 nanocrystals, PbS nanocrystals, and mesoporous silica; (e) three-dimensional structure obtained by inverting a polystyrene photonic crystal with PbS quantum dots and applying NPP; (f) same material as in panel e but with CoFe_2O_4 nanocrystals.

2.8. Discussion. Nanocrystal plasma polymerization has shown potential in several nanoparticle systems.^{33–35,37} Its action can be understood as an etching process within nanoscale confinement. The ligands between the nanocrystals are etched away leaving behind a minimally oxidized inorganic fraction. From a physics point of view, it is interesting to investigate the behavior of plasma in such tightly confined spaces where the diffusion coefficients of the plasma's components might be significantly modified. From a materials chemistry standpoint, on the other hand, it is fascinating to contemplate the possibility of accessing new flexible nanostructured materials with a dry, scalable, green, and highly tunable method.

It is important to note in fact that NPP is not limited to PbS quantum dots. Although the search for plasma polymerizable nanoparticle species is only in its preliminary stages, many other examples have been demonstrated already including Bi_2S_3 ,³⁵ CoPt_3 ,³⁷ FePt_3 ,³³ CoFe_2O_4 ,⁵⁶ EuS ,⁵⁷ ITO ,⁵⁷ and SnO_2 .⁵⁷ Preliminary data on PbSe nanocrystals or CdSe/CdS/ZnS multishell quantum dots did not show a preservation of

the luminescence after plasma etching. In our opinion, this does not mean that this process is limited to PbS nanocrystals but that surface chemistry plays an important role in this process: differently from most chalcogenide nanocrystals systems, which exhibit a chalcogen-terminated surface, our PbS nanocrystals show what appears to be a PbCl_2 -terminated surface. Also the chemical and physical nature of the produced matrix is likely involved in the preservation of the luminescence. What is important here to understand is that NPP should be seen as a methodology to produce inorganic nanocomposites of nanocrystals separated by a chemically tunable matrix. The final properties will be necessarily affected by the nature of the core–matrix interface.

3. State of the Art

In this section, we will show some preliminary results that demonstrate the potential and flexibility of NPP for nanofabrication. This is intended to encourage further exploration of this technique.

3.1. One-Dimensional Architectures. NPP can be used to fabricate free-standing structures with different dimensionalities (Figure 1). NPP allows the consolidation of nanocrystals infiltrated into a porous template to obtain free-standing replicas upon the selective removal of the template. The improved chemical and mechanical stability conferred by NPP allows removal of the template without substantially harming the nanocomposite. PbS nanocrystals have been infiltrated into anodized Al_2O_3 membranes with pores 200 nm in diameter and 60 μm in length. The nanocrystals were exposed to air plasma, and the membrane was selectively dissolved. The process left NIR luminescent and flexible nanorods that are entirely composed of nanocrystals (see Figure 7a,b).⁵⁸ The same process works for Bi_2S_3 nanorods and CoFe_2O_4 , EuS , ITO , and SnO_2 nanocrystals;⁵⁷ it is also possible to use a mixture of nanocrystals to yield free-standing, multifunctional nanorods.⁵⁸

3.2. Two-Dimensional Architectures. NPP can also be used to form multilayer structures (see Figure 7c,d). Different layers of nanocrystals can be spin-coated on top of each other if every layer is first briefly plasma treated to partially polymerize the nanocrystals together. In this way, it is possible to form multilayers of PbS and CoFe_2O_4 nanocrystals (Figure 7c), which could also include mesoporous layers (Figure 7d).⁵⁹ Plasma exposure can also be used to cure sol–gel precursors to form the final oxide.

In the case of surfactant-templated mesoporous materials,^{60,61} the plasma treatment allows for removal of the sur-

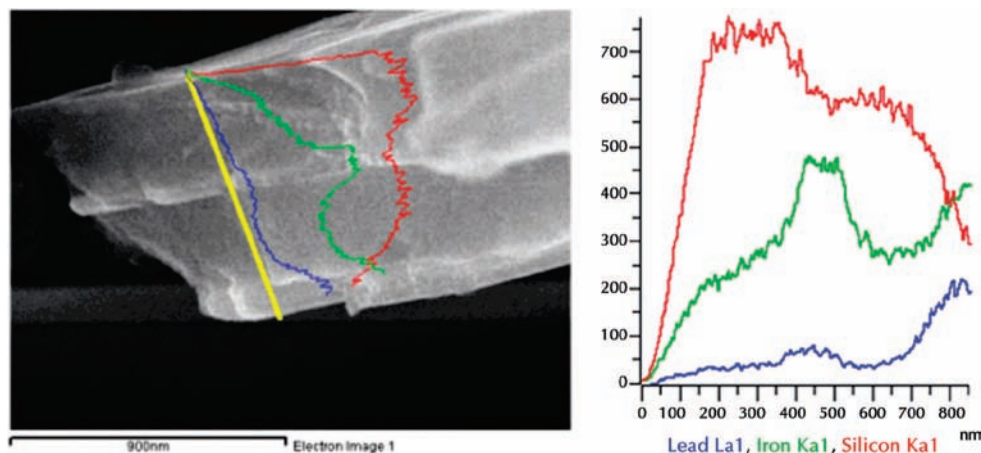


FIGURE 8. EDAX line scan analysis of the multilayer architecture shown in Figure 7d. The high background in the iron spectrum is due to a systematic error in the instrument.

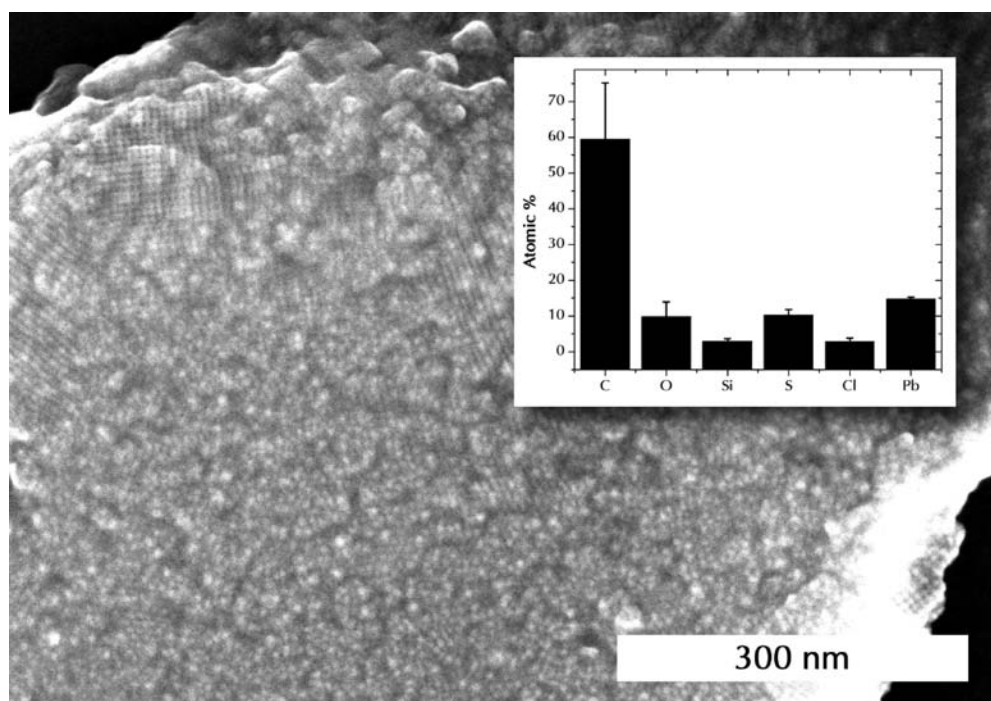


FIGURE 9. HR-SEM characterization of a NPP film obtained from PbS nanocrystals with the addition of tetrabutylorthosilicate (TBOS). In the inset is the EDAX analysis. The carbon content can be attributed to the carbon-coated grid supporting the sample. The relative amounts of Pb, S, and Cl are to be taken with caution, given the superposition of their main peaks.

factants from the pores during the consolidation of the framework.³⁸ As shown in Figure 8, the composition line-scan obtained from energy-dispersive analysis of X-rays (EDAX) confirms the nature of the layers.⁵⁹

3.3. Three-Dimensional Architectures. As an example, we replicated an artificial opal made of polystyrene colloids. The nanocrystals were first infiltrated in the opal following an established method.⁶² The composite structure was then placed in the plasma chamber. The results are shown in Figure 7e,f for PbS and CoFe_2O_4 nanocrystals, respectively.⁵⁸ The interesting aspect of this process is that the consolidation of

the nanocrystals and the removal of the template occur in the same step, allowing for a one-step inversion procedure.

Photonic structures such as opals can now be engineered with desired functionalities, high refractive index, and possibly flexibility.⁶³ Such characteristics can potentially be coupled with active planar defects,⁶⁴ also obtained via NPP. In contrast to other clever approaches to fabricating nanocrystal inverse opals,⁶⁵ this method does not require heat-activated consolidation and therefore can preserve materials and size-dependent properties of the nanocrystal building blocks. One limitation of this method is the shrinking of the nano-

crystal composite observed upon plasma treatment. In the case of the nanocrystal microrods this leads to a detachment of the rods from the walls of the alumina membrane, while in the case of the inverse opals it leads to a decrease in the air void size, compared with the template.

3.4. Tuning the Composition. The composition of the matrix can be tuned by adding plasma-sensitive precursors to the solution of nanocrystals. In our preliminary experiments, tetrabutylorthosilicate (TBOS) was chosen to create a SiO₂ matrix around the nanocrystals. As shown in Figure 9, the EDAX confirms the presence of Si.⁵⁹ Experiments are underway to optimize the amount of additives and demonstrate the generality of the process with other metal alkoxydes.

3.5. Challenges and Opportunities: The Door is Open. Ahead of these successes lie many challenges and opportunities. The influence of plasma exposure on nanocrystals has to be carefully understood, which requires a detailed knowledge of their surface chemistry.

The roles of specific compositions, geometries, and defects also need to be thoroughly examined. Plasma properties and their influence on the NPP process have to be studied, especially when charged species are removed by electrodes or by distancing the sample from the afterglow. While in many cases such issues could be considered of technological nature, in this instance they assume the shape of scientific questions that would help us understand the surface chemistry of our building blocks as well as the behavior of plasmas in such unconventional spatial geometries.

The influence of plasma on nanostructures is more than ever in need of further examination, especially as it is taking the shape of a tremendous opportunity for the design and large scale fabrication of inorganic materials. One can think, for example, of mesoporous materials of nearly arbitrary composition obtained by selectively dissolving one component from a NPP-treated binary nanocrystal superlattice⁹ or creating nanofibrous membranes by applying NPP to films of colloidal nanowires. One can think of using different plasma compositions to obtain different matrix compositions. The possibilities are tantalizingly vast.

With NPP, a wide variety of nanostructure compositions, shapes, and functionalities can now be combined within inorganic free-standing flexible materials, thereby throwing a bridge between bottom-up synthesis and top-down fabrication.

The degrees of freedom available for design are numerous:

- Composition, size, shape, and functionality of the building blocks can be changed by choosing different colloidal nanocrystals or gas feeds.

- Composition of the matrix can be changed by changing the plasma composition or introducing “polymerizable” organometallic additives.
- Porous templates of arbitrary geometry can be replicated with a resolution only limited by the size of the nanocrystals.
- Patternability is made possible by the chemical accessibility of the final composite.

Among the favorable characteristics of this process that we should mention are the following:

- highly scalable
- amenable to combinatorial studies
- dry
- green because solvents, high temperatures, and high powers are not involved
- low cost (especially in a laboratory setting)
- highly tunable parameters, which directly affect the process

While plasma treatment is typically not considered a bottom-up chemical processing technique, development of nanostructures with very large surface areas has made plasma a valuable tool for their chemical manipulation. Furthermore, despite its historical use as a surface modification technique, nanocrystal plasma polymerization shows that plasma can be successfully used to fabricate bulk materials with hierarchical architectures using nanoscopic building blocks. We therefore consider NPP a valuable new addition to the set of available tools for nanochemists and nanoengineers.

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Supporting Information Available. High-resolution survey XPS spectra and SAXRD of PbS nanocrystal solid before and after NPP. This material is available free of charge via the Internet at <http://pubs.acs.org>.

BIOGRAPHICAL INFORMATION

Ludovico Cademartiri received a Laurea degree *summa cum laude* in Materials Science from the University of Parma (2002) under the supervision of Prof. Gianluca Calestani and a Ph.D. in Interdisciplinary Chemistry at the University of Toronto (2008) under the supervision of Prof. Geoffrey A. Ozin, where he has been a postdoctoral researcher since May 2008. In the fall of 2008, he will start a postdoctoral fellowship in the group of Prof. George M. Whitesides at Harvard University. His research interests include dynamic self-assembly, nanocrystal chemistry, nanowire solution synthesis, quasicrystals, photonic crystals, mesoporous materials, and nanochemistry for developing nations.

Arya Ghadimi received a B.A.Sc. in Engineering Science, Nano Engineering specialization, in 2006 at the University of Toronto. Subsequently he completed his M.Sc. in Materials Chemistry and Nano Chemistry under the supervision of Prof. Geoffrey A. Ozin in the University of Toronto's Department of Chemistry. Arya's research has focused on template-assisted self-assembly of colloidal nanocrystals and their plasma polymerization in confined spaces. His interests include intellectual property protection for and commercialization of nanoscience, and he is currently pursuing a J.D. degree specializing in IP and technology transfer.

Geoffrey A. Ozin received a B.Sc. in chemistry from King's College London in 1965 and a D.Phil. in inorganic chemistry from the University of Oxford in 1967. He was ICI Fellow at the University of Southampton from 1967 to 1969 before joining the University of Toronto in 1969; he became Full Professor in 1977 and University Professor in 2001 and has been named Government of Canada Research Chair in Materials Chemistry. He is Honorary Professorial Fellow at The Royal Institution of Great Britain and University College London and Guest Professor at Karlsruhe Institute of Technology. More details are available at the research group's homepage, <http://www.chem.toronto.edu/staff/GAO/group.html>.

FOOTNOTES

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