Layer-by-layer assembly of freestanding thin films with homogeneously distributed upconversion nanocrystals†

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We report a facile and highly-controlled approach to fabricating freestanding upconversion multilayer thin films containing homogeneously distributed lanthanide-doped nanocrystals. Citrate-coated NaYF₄:17%Yb, 3%Er nanocrystals were synthesized using a single-phase high-boiling-point-solvent method, followed by ligand exchange. These hydrophilic upconversion nanocrystals were dispersed in freestanding multilayer polyelectrolyte thin films by layer-by-layer assembly over a sacrificial layer. We found that the nanocomposite multilayer thin films possess outstanding mechanical stability and exhibit NIR-to-visible upconversion luminescence. The effect of the hydrophilic ligand exchange on the upconversion properties of these nanocrystals was explored by characterizing the time evolution of upconversion emission following pulsed NIR excitation. It is found that the ligand-exchange process modestly reduces the intrinsic upconversion efficiency of the nanocrystals relative to the as-synthesized oleic acid coated product. Thin films with NIR-to-visible upconversion properties may be suitable for a variety of optical-device and sensing applications.

Introduction

Layer-by-Layer (LbL) assembly is recognized as one of the most versatile approaches for fabricating composite nanomaterials with multiple functionalities and controlled nanoscale structures. Multilayer LbL thin films can be mechanically stable and freestanding due to strong internal interactions within the nanomembranes, such as interlayer electrostatic attraction. A variety of interactions between the building-block monolayers has been utilized in LbL assembly, including, but not limited to, electrostatics, covalent bonding, hydrogen bonding, and van der Waals forces. The composite LbL thin films preserve the unique properties of their nanoscale building blocks, thus broadening the applications of LbL thin films to an unprecedented level, ranging from super hydrophobic coatings, to ultra-sensitive detections, to ultra-hard materials, to fuel cells. A variety of functional building blocks, including metallic nanoparticles, semiconductor quantum dots, carbon nanostructures, and biomaterials, has been incorporated into LbL assembly. However, to the best of our knowledge, there are no reports on the assembly of lanthanide-doped upconversion nanocrystals into freestanding nanomembranes.

Lanthanide-doped nanocrystals can exhibit the fascinating optical property of upconversion (UC) luminescence, which has great potential in bioimaging, DNA detection, photodynamic therapy, and photovoltaics. The incorporation of UCNCs in composite thin films has been attempted by the as-synthesized oleic acid coated product. Thin films with NIR-to-visible upconversion properties may be suitable for a variety of optical-device and sensing applications.

† Electronic supplementary information (ESI) available: TEM micrographs of Cit-NCs and their LbL multilayer thin films. See DOI: 10.1039/c0jm01602k
optical properties of these nanocrystals was explored by characterizing the time evolution of upconversion emission following pulsed near-infrared excitation. Our novel approach in assembling hydrophilic UCNCs homogeneously into multilayer thin films with a total thickness below 100 nm suggests new possibilities for the application of these unique nanocrystals in functional nanomembranes.

Experimental

Sodium fluoride and acetic acid were obtained from Fisher Scientific. Yttrium oxide (Y$_2$O$_3$, 99.9%), ytterbium oxide (Yb$_2$O$_3$, 99.9%) and erbium oxide (Er$_2$O$_3$, 99.9%) were purchased from American Potash & Chemical Co. Sodium acetate (CH$_3$COONa), oleic acid, citric acid, 1-octadecene, and the polyelectrolytes, poly(allylamine hydrochloride) (PAH), MW = 56 000, and poly(sodium 4-styrenesulfonate) (PSS), MW = 70 000 were obtained from Aldrich. Nanopure water and a resistivity of 18 MΩ cm was used in all experiments.

Synthesis and surface modification

The synthesis of lanthanide-doped NaYF$_4$:17%Yb,3%Er nanocrystals was conducted using the single-phase, high-boiling-point-solvent method of Lin, et al. Typical ly, 0.467 g Y$_2$O$_3$, 0.168 g Yb$_2$O$_3$ and 0.029 g Er$_2$O$_3$ were refluxed with 100 ml of 50/50 acetate/water solution for 8 h until the initial milky white solution became clear. It was then diluted to 200 ml and kept as a stock solution. 20 ml of this solution, containing 0.4 mmol Y(CH$_3$COO)$_3$, 0.085 mmol Yb(CH$_3$COO)$_3$, and 0.015 mmol Er(CH$_3$COO)$_3$, were dissolved in 6 ml of oleic acid. The mixture was held at 100 °C under a vacuum for 60 min. to purge oxygen and water. Acetic acid, formed in an equilibrium between acetate and oleic acid, was likely removed during this process, thus favoring the formation of the lanthanide oleates.

The fluoride-containing solution was prepared by dissolving 0.084 g CH$_3$COONa and 0.085 g NaF in 2 ml of oleic acid and 10 ml of 1-octadecene. (This represents a larger concentration of CH$_3$COONa than that used in ref. 24, and results in smaller nanocrystals.) The mixture was kept at 100 °C under a vacuum for 30 min. while periodically applying Ar to assist the drying process. The fluoride solution was then heated under Ar to 320 °C within 10–15 min. and maintained at this temperature. This solution became clear and homogeneous at temperatures above 240 °C. The lanthanide acetate solution was injected into the fluoride solution. The homogeneous, single-phase reaction mixture was maintained at 320 °C for 30 min. and then allowed to cool to room temperature. The nanoparticles were then precipitated by the addition of ~100 ml of acetone and centrifuged at 5000 rpm for 8 min. The samples were then washed with acetone at least three times.

Surface modification of as-prepared oleic-acid capped UCNCs (OA-NCs) into citrate-capped UCNCs (Cit-NCs) was conducted as follows. Approximately 200 mg of OA-NCs and 8 ml of 1 M citric acid solution were added to a 20 ml vial. The solution was heated to 70 °C and stirred for a minimum of 5 h, but typically overnight. The UCNCs were then collected via a high-speed centrifugation process. The UCNCs were then redispersed in water and the pH was adjusted to 5–6 using 0.1 M NaOH. The UCNCs were again collected via the centrifugation and then dispersed in 1 ml water. A low-speed (2000 rpm) centrifugation was then used to remove any possible aggregates or insoluble materials. The clear, single-particle Cit-NC dispersion was then carefully separated from any solid at the bottom of the tube, either by decanting or by using a pipette.

LbL assembly of multilayer thin films with UCNCs

Silicon-wafer substrates were cut to a typical size of 10 mm × 20 mm and were cleaned in a piranha solution [3 : 1 (v/v) H$_2$SO$_4$/H$_2$O$_2$]. Attention: Piranha solution is extremely dangerous and should be handled very carefully. After cleaning, the substrates were rinsed with Nanopure water at least three times and then stored in water until use. The multilayer thin films were fabricated by the spin-assisted LbL method. To obtain a freestanding thin film, a sacrificial cellulose acetate (CA) layer was first spun on the prepared silicon substrate. A layer of PAH was then deposited onto the CA layer from a 0.2% PAH solution by spin coating for 20 s at 3000 rpm. The substrate was then rinsed once with Nanopure water and dried while spinning for 30 s at 3000 rpm. In a similar manner, 0.2% PSS solution was deposited. This procedure was repeated until the desired number of polymer bilayers was achieved. To form the central layer of Cit-NCs, a 200 µl droplet of the Cit-NC dispersion was deposited onto the stationary substrate, allowed to sit for 5 min., and rotated for 40 s at 3000 rpm. The substrate was then rinsed with water and spun dry. This deposition process is then repeated in order to obtain a high density (i.e., complete monolayer coverage) of Cit-NCs on the thin film. Freestanding LbL thin films can be obtained by dissolving the sacrificial CA layer in acetone. The freestanding LbL films can be lifted from the solution using a variety of substrates, such as glass slides, silicon wafers, and copper grids, for further characterization and investigation. All of the procedures described above were performed in a class 100 cleanroom.

Instruments and measurements

The optical and structural properties of UCNCs were studied using optical microscopy (polarized microscopy and confocal microscopy), AFM, and TEM. Optical microscopic investigation was conducted on an Aramis confocal microscope (Horiba Jobin Yvon, Edison, NJ) equipped with a diode-pumped solid-state (DPSS) laser (532 nm) for confocal fluorescence measurements. Optical micrographs were obtained using a 50× objective (NA = 0.75) and recorded with a three-megapixel CCD camera. The morphology and thickness of the multilayer thin films were measured on a Nano-R™ AFM (Pacific Nanotechnology Inc. Santa Clara, CA, USA) using tapping mode. The freestanding multilayer nanomembranes were deposited onto copper grids for the TEM investigation. TEM images of the UCNCs and free-standing UCNCs nanomembranes were obtained on a FEI Tecnam TF30 field emission TEM operated at 300 kV. Zeta-potentials of UCNCs were measured on a Beckman Coulter Delsa™ Nano system with a flow cell at 15° scattering angle and a 60 V electric field.

Upconversion luminescence kinetics was obtained by exciting the samples with pulsed 980 nm light from an optical parametric oscillator (Continuum SLOPO) pumped by a frequency tripled...
Nd:YAG laser (Continuum Surelite II). Excitation powers were 2–3 mJ pulse and the excitation beam was focused to ~5 mm in diameter at the sample. Steady-state UC luminescence spectra were acquired using a 980 nm CW diode laser (Thor Labs) operated at 68 mW output (35 W/cm²). Visible and NIR emissions were collected and focused with an F-matching lens into a 1/3 m monochromator (Jobin-Yvon, Triax 320) equipped with a red-sensitive photomultiplier tube (Hamamatsu, R928) on the axial port and a NIR-sensitive photomultiplier tube (Hamamatsu, H10300-75) on the lateral port. Luminescence signal was detected using a time-resolved photon counting by feeding the detector output directly into a multichannel scalar (Stanford Research Systems, SR 430) for visible emission, or by first pre-amplifying the signal (Stanford Research Systems, SR445A) for NIR emission. Emission was monitored at 539 and 654 nm for the green and red upconversion, respectively, and at 1530 nm for NIR emission. The detection system was calibrated for relative wavelength response using a standard Tungsten lamp (Stellar Net, SL1-CAL).

Results and discussion

Oleic acid-stabilized NaYF₄:17%Yb³⁺, 3%Er³⁺ UCNCs were synthesized via a single-phase, high-boiling-point-solvent method, described by Lin, et al., which requires neither metal-trifluoroacetate precursors nor the use of autoclaves. These hydrophobic OA-NCs were stirred in an aqueous citric acid solution to conduct the ligand exchange (see Experimental section for details). The resulting Cit-NCs, after pH adjustment, are easily dispersed in aqueous solution. Fig. 1a and 1b show two cuvettes with a lower water layer and an upper toluene layer. The OA-NCs were dispersed in the left cuvette and UC emission is observed only from the organic layer. The TEM results (Fig. 1c and Supporting Information†), show that the citrate-coated UCNCs are highly crystalline nanomaterials.

Comparing the size of the Cit-NCs with that of the OA-NCs (Fig. 1d), we found that the modification and isolation process for the Cit-NCs results in a slight size-selection for smaller nanocrystals. The mean diameter of the Cit-NCs, as shown in Fig. 1d, is 46.9 ± 23.6 nm, which is a marginally smaller than that of as-prepared OA-NCs (51.6 ± 19.8 nm). The modest decrease in mean diameter could be due to selective precipitation of larger crystals during the centrifugation process used for obtaining stable aqueous suspensions of Cit-NCs. The upconversion luminescence spectrum of the Cit-NCs in a Lbl thin film is shown in Fig. 1e, in which three visible emission peaks at 523, 539, and 656 nm can be observed, corresponding to emissions from ¹H₁₁/₂, ⁴S₃/₂ and ⁴F₉/₂, respectively, to the ⁴I₁₅/₂ ground state.⁶⁶

The kinetics of upconversion emission following pulsed NIR excitation was measured for the OA-NCs and Cit-NCs, because the rate constants describing emission kinetics are sensitive to non-radiative relaxation pathways. Comparing the upconversion emission kinetics enables an assessment of the relative quenching effects in the modified and unmodified nanocrystals. A complete description of the photo-physical kinetics leading to UC following pulsed NIR excitation requires the solution of a relatively complex set of coupled rate equations,⁷ for which the values of many relevant microscopic rate constants are not known. Lin et al., however, have previously shown that the time dependence of green and red upconversion, R(t), could be fit adequately well to the following equation:⁴⁴

\[
R(t) = A \left( e^{-k_2t} - e^{-k_1t} \right)
\]  

where A is a scaling constant, and \(k_1\) and \(k_2\) are rate constants. Eqn (1) is the appropriate expression for describing the time-dependence of emission from a state that is being fed by another ‘long-lived’ state, where \(k_1\) and \(k_2\) are the total relaxation rate constants for the two states. It is not surprising, then, that the time-dependence of UC emission follows the general form of eqn (1), since the red and green emitting states are being fed via energy transfer processes following Yb³⁺ excitation. In the present case, however, eqn (1) is being used in a completely empirical manner, and the rate constants are phenomenological. The important consideration here is that differences in non-radiative quenching efficiencies at any point along the UC mechanistic pathway will be reflected in the fitted values of the empirical rate constants, \(k_1\) and \(k_2\). Therefore, a comparison of fitted \(k_1\) and \(k_2\) values can be used to assess the relative UC quenching in the oleic acid and citrate stabilized UCNCs.

The time evolution of green (top) and red (bottom) upconversion emission, following pulsed NIR excitation, of as-prepared OA-NCs in toluene and Cit-NCs in aqueous solution is shown in Fig. 2. The citrate-stabilized nanoparticles show significantly larger fitted rate constants, \(k_1\) and \(k_2\), compared to the oleic acid stabilized nanoparticles, for both the red and green emission. This strongly indicates that quenching by multiphonon processes is more significant in the aqueous dispersion. Several factors could contribute to the increased quenching. First, citrate
ligands are intrinsically more quenching than oleic acid. Following pH adjustment, the carboxylic acid groups on the citric acid ligands are only partially converted into carboxylate, resulting in a large number of OH oscillators at the surface of Cit-NCs. Second, the water solvent used for the citrate-stabilized particles is also more quenching compared to toluene. Finally, the Cit-NCs are, on average, slightly smaller than the as-prepared OA-NCs, as discussed above, and multiphonon quenching tends to increase as particle size decreases. More work is underway to determine the relative contributions from these three mechanisms, but our preliminary results indicate that the increased quenching is due mainly to the replacement of the oleic acid capping ligands with citrate. We note that the increased quenching is due mainly to the replacement of the oleic acid capping ligands with citrate. We note that the increased quenching is due mainly to the replacement of the oleic acid capping ligands with citrate.

The 1.5 μm (47 nm) in aqueous dispersion and in the LbL film. (See Table 1).

Table 1 Ratios of the integrated intensity of green (Er³⁺: 4S3/2 → 4I13/2) and red (Er³⁺: 4I15/2 → 4I15/2) upconversion emission to the integrated intensity of the 1.5 μm NIR emission (Er³⁺: 4I13/2 → 4I15/2) using 980 nm CW excitation (35 W/cm²) for various UCNC samples. The intensity ratios are in terms of relative photon flux. Ratio values reflect correction for instrument response. The OA-NCs were dispersed in toluene.

<table>
<thead>
<tr>
<th>Sample</th>
<th>NC size (nm)</th>
<th>Igreen/I_NIR</th>
<th>Ired/I_NIR</th>
</tr>
</thead>
<tbody>
<tr>
<td>oleic-acid-capped NC</td>
<td>100</td>
<td>0.91</td>
<td>0.51</td>
</tr>
<tr>
<td>oleic-acid-capped NC</td>
<td>52</td>
<td>0.40</td>
<td>0.19</td>
</tr>
<tr>
<td>citrate-capped NC(aq)</td>
<td>47</td>
<td>0.18</td>
<td>0.11</td>
</tr>
<tr>
<td>citrate-capped NC/LbL film</td>
<td>47</td>
<td>0.20</td>
<td>0.08</td>
</tr>
</tbody>
</table>

The UC efficiency of our NC samples under identical excitation flux. For example, the first two entries in Table 1 compare the green-to-NIR and red-to-NIR intensity ratios for 100 nm-diameter OA-NC to those of the 52 nm-diameter OA-NC used in this study. It is well known that the UC efficiency of these NCs is sensitive to particle size.²³,²⁴ Boyer and van Veggel reported that 30 nm 2%Er, 20%Yb: NaYF₄ NCs exhibit a 3-fold reduction in UC quantum efficiency relative to 100 nm NCs.²⁴ The reduction in UC efficiency in the 52 nm OA-NC relative to the 100 nm OA-NC is reflected in Table 1 by the more than 2-fold reduction in the green-to-NIR and red-to-NIR intensity ratios.

Table 1 shows a reduction in relative UC efficiency of the 47 nm Cit-NC sample in aqueous dispersion, compared to the 52 nm OA-NC sample (which was used to prepare the Cit-NC sample) in toluene. This result is consistent with the UC kinetics analysis presented earlier in this section (See Fig. 2). Note, however, that there is no significant difference in UC efficiency comparing the Cit-NC in aqueous dispersions to the Cit-NCs in LbL films.

As shown in Figure 3a, multilayer thin films with a formula of (PAH/PSS)nPAH/UCNCs/PAH(PSS/PAH)n, (nYn), where n is the number of polyelectrolyte bilayers, can be obtained due to the strong electrostatic interaction between the Cit-NCs and PAH polymer. The three film configurations are nine PAH/PSS bilayers (9), (PAH/PSS)9PAH/UCNCs (noted as 9Y), and 9Y9. Surface roughness and morphology of LbL multilayer of 9, 9Y, and 9Y9 thin films were examined using AFM and the results are shown in Fig. 3b–d. All three AFM images have the same Z scale (100 nm) for an easy comparison. It is clear that the surface of pure polyelectrolyte is very smooth, while the roughness of 9Y is significantly increased due to the height of the individual UCNCs. With further deposition of polyelectrolyte multilayers

![Image](https://example.com/image.png)
onto the 9Y films, the surface roughness decreases. As a result, the surface roughness of 9Y9 film is less than that of 9Y thin film. The morphology and surface roughness of the multilayer films indicate uniform deposition of UCNCs within the polymeric multilayer thin films.

Fig. 3e shows the topography of a 9Y9 thin-film edge on the silicon substrate. A profile scan of the AFM image gives a thickness of 55 ± 12 nm, which matches the theoretical calculation for the multilayer films. AFM profile scans of other nYn thin films demonstrated the ability to precisely control the microstructures in the LbL process. Film thickness profiles for three different thin-film compositions are demonstrated in Fig. 3f. We observed that the thicknesses of the 9Y9, 9Y, 9Y9 thin films are 19 ± 2 nm, 40 ± 10 nm, 55 ± 12 nm, respectively. The surface of the 9 film (which contains no UCNC) is extremely smooth, with a surface RMS roughness of 1.7 nm. The incorporation of UCNCs into the film structure introduces significant roughness, as can be seen in the AFM profile curve (Fig. 3f). The average height of UCNCs from AFM measurements is 32.3 nm, which is different from the crystal-size analysis in the TEM experiments, due to the anisotropic, plate-like shape of the UCNCs. From these AFM results, we conclude that individual UCNCs were assembled onto the surface of the polyelectrolyte bilayers. The surface roughness of the 9Y9 films is around 10.4 nm, which is much less than that of 9Y films (13.4 nm). We attribute this to the smoothing effect of the additional polymer assembly onto the rough surface of the nanocomposite thin films.

Fig. 4a shows the optical image of a freestanding 9Y9 film on a TEM copper grid with 50 µm windows. These multilayer nanomembranes, with a total thickness below 100 nm, are extremely mechanically stable and have a shelf life of several months. The nanomembranes can survive a high-vacuum environment and high-energy electron beam, thus enabling detailed characterization via TEM. TEM images of the 9Y9 nanomembrane (Fig. 4b) clearly demonstrate a random and uniform distribution of the UCNCs in the films. From higher resolution TEM images (see Fig. 2f†), isolated UCNCs can be observed, and there are no aggregations or agglomerations. Successful uniform dispersal of UCNCs into the polymeric multilayer thin films is made possible by proper surface modification and unique LbL approach.

The structure and optical properties of 9Y9 films were further studied by a combination of optical microscopy, AFM, and confocal fluorescence microscopy on the same region of a 9Y9 nanomembrane. The UCNCs in the nanomembrane still process strong upconversion emission properties (Fig. 1e). The optical image of the 9Y9 film (Fig. 4c) shows that a portion of the film is folded (dark colored, see arrow). The folding of the 9Y9 film was confirmed by the AFM image (Fig. 4d), in which the film exhibits a thickness of 104 ± 4 nm. Confocal luminescence mapping of the 9Y9 film at the same location is shown in Fig. 4e. Not surprisingly, higher luminescence intensity is observed on the folded section as compared to the single 9Y9 film. On the other hand, the luminescence intensities of 9Y9 thin films are uniform and strong enough to distinguish the edge of the films. The confocal luminescence results are consistent with the observed uniformity of the Cit-NCs in the multilayer nanocomposite membranes.

In addition to mechanical robustness, the LbL multilayer nanomembranes possess reasonable long-term luminescence stability. Fig. 5 shows the integrated intensity of the UC luminescence emission (Green) of a 9Y9 LbL film recorded from the same sample over a period of 12 days (26–29 °C, ~60% relative humidity). A modest decrease in UC luminescence was observed during the first week, after which the intensity stabilized at approximately 68% of the initial measurement. The intensity reduction within the first week may be related to certain structural relaxations of the multilayer thin film after the LbL formation. The long-term stability of UC luminescence indicates great potential in using these UC composite LbL nanomembranes for various applications. It was also observed that the UC luminescence varies somewhat with temperature and humidity. A systematic investigation of the effects of temperature and humidity is planned.

Both surface modification and LbL assembly of UCNCs are important in fabricating nanocomposite thin films with homogeneously distributed UCNCs. The surface of the Cit-NCs is...
negatively charged with a large negative zeta-potential below –50.8 mV, which makes the modified UCNCs stable in aqueous solution and suitable for LbL assembly. Strong interlayer interaction occurs between the UCNCs and PAH during the SA-LbL process. This interaction, as well as the spin process in the SA-

Conclusions

In summary, citrate-coated NaYF₄:17%Yb,3%Er nanocrystals were prepared and incorporated into freestanding nano-

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Notes and references


