Faceted-charge patchy LnF_3 nanocrystals with a selective solvent interaction

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Abstract

A fast and single-step preparation of patchy LnF_3 faceted-charge nanocrystals are described. These hexagonal faceted nanocrystals allow the spontaneous selective adsorption of cations or anions in the different faces, producing stable and well-defined patches of different charge. The mechanism for the formation of the patches and the properties of the obtained nanocrystals are characterized by a combination of experimental techniques and all-atomic molecular dynamics simulations. The spontaneous dual-charged surface, as well as, the luminescence effects that can be achieved doping host- LaF_3 systems make these new nanocrystals interesting both from a fundamental point of view and for a wide range of applications.

Patchy nanocrystals (NCs) were introduced as a new conceptual model of nanoparticles a few years ago.^[1] They consist of NCs with discrete, well-defined and highly specific attractive interaction sites named patches. Currently, the high interest in self-assembly mechanisms has promoted a deep investigation of patchy NCs of different nature that are able to form bigger tunable structures.^[2–8] Although the concept of patchy nanoparticles seems simple, the synthesis of particles with patches presents many difficulties in practice. The selective creation of discrete patches onto NC surface in a synthetic process is a hard-multistep process with several problems related with the stability on patch creation.^[9] Novel approaches for the formation of patchy NCs propose the adsorption of different ligands onto their surface which may thermodynamically segregate into domains.^[10,11] Other approaches propose linking together different kinds of NCs by organic linkers.^[12]

Our aim here is to achieve shape-faceted binary systems (MX_n) with stable patches that are formed spontaneously during the synthesis. Our approach is based on the concept that the faceted NCs should possess different exposed planes with different properties (for example, hydrophilic and hydrophobic facets) which depend on the exposed atoms in each plane (for example, metal and non-metal atoms), as shown schematically in Figure 1a. When such a NC is obtained, ligands with different functional moieties and different affinities, will be able to absorb specifically and spontaneously on targeted different exposed faces, during the synthetic process (Figure 1b). Carboxylates are excellent candidates to stabilize metallic exposed atoms, due to their direct carboxylic-to-metal coordination while nitrogen-based molecules are well suited to stabilize electrostatically non-metal atoms if they are protonated (in their acidic form).

As a particular realization of this general concept (summarized in Figure 1), we present here new patchy NCs based on metal fluoride NCs. Using LnF_3 faceted-NCs, we achieve the formation of hydrophobic patches (fluorine exposed planes), while the rest of NC is hydrophilic by the exposition of lanthanide cations. The presence of these patches allows the selective stabilization with anionic or cationic ligands depending on the exposed faces. In addition, these NCs are able to adapt to different solvents (e.g. methanol) thanks to the different hydrophilic/hydrophobic role of their exposed planes and due to the role of adsorbed ligands.

Figure 1. Schematic model for the patchy particles proposed in this work. (a) Scheme of faceted hexagonal LnF_3 NCs showing the different atoms in the exposed planes. (b) Scheme of a faceted NC with ions of opposite charge adsorbed onto different facets: carboxylate anions are proposed to adsorb at metal-exposed faces whereas ammonium-based cations are proposed to adsorb at fluoride-exposed faces.

The choice of lanthanide fluoride NCs for the inorganic core is due to the fact that a broad range of LnF_3 NCs has been synthesized and studied in detail in the last years^[13,14]. Our recent studies^[15,16] of LnF_3 NCs with several of the smallest lanthanides show strong interaction of the NCs with ions, which induces tunable self-assembly. Previous studies show that certain LnF_3 NCs have the appropriate faceting required in the mechanism shown in Figure 1. For example, LaF_3 NCs show a typical hexagonal crystalline structure and they have been obtained as triangular faceted nanoplatelets.^[17] In addition, LnF_3 NCs also show interesting properties for luminescent^[18] and biomedical applications,^[19,20] which makes these NCs especially interesting.

We first describe our results for LaF_3 and we will consider other LnF_3 NCs later (CeF_3 and PrF_3). LaF_3 NCs were synthesized according to established procedure in aqueous solution^[21] with some modifications adapted to our proposed model. All anionic precursors were selected to contain carboxylic moieties (citrate and acetate) and for the cationic species, we chose nitrogen-based molecules (ammonium and tetramethylammonium) to favor the electrostatic interaction with the non-

metal atoms of the NC surface. LaF_3 particles were obtained (Figure 2) with a size of ~ 8 nm according to transmission electron microscopy (TEM), in a dispersion which was homogeneous and stable during months. Powder X-ray Diffraction (XRD) shows a pure-hexagonal crystalline structure (see Figure S2). Further analysis by HRTEM (Figures S3 and S4) shows NC faceting compatible with two exposed families of planes: (i) hexagonal $\{0001\}$ and (ii) rectangular $\{1-100\}$ as shown. In consequence, we conclude that we obtained a faceted NC with a platelet shape.

Figure 2. LaF_3 particles size by DLS measurement (% in volume) with the corresponding TEM and HRTEM micrographs of as-synthesized nanocrystals at 100 °C.

Electrokinetic measurements showed that these LaF_3 NCs are negatively charged with a ξ -potential ≈ -60 mV (see SI and Table S1), which is high enough to guarantee their stability in water. ^1H NMR shows clearly the presence of citrate and acetate anions and tetramethylammonium cation onto the NCs washed-surface (Figure S5a). The IR spectrum shown in Figure S5b confirms the ionic adsorption at the NC surface. Considering that the carboxylic bands of acetate and citrate are located at the same wavenumber, stretching bands at 1397 and 1569 cm^{-1} were assigned to be produced from both anions. In addition, in IR we could observe the bending mode of ammonium cation ($\text{N}^+\text{-H}$) at 1488 cm^{-1} and the broad band at $\sim 3258\text{ cm}^{-1}$ has been assigned to include $\nu(\text{N}^+\text{-H})$ and $\nu(\text{O-H})$.

Combining ^1H NMR and IR characterization, we can conclude that the NC surface contains citrate and acetate as adsorbed anions. In the case of cations, we interpret our results by considering that

ammonium (the most hydrophilic cation) is adsorbed onto the NC surface while tetramethylammonium should be playing the counter ion role in the diffusing double layer (see details in SI, Table S2). For electrostatic reasons, it is reasonable to expect that anions adsorb onto La atoms of the NC surface and cations adsorb onto F, thus we expect that ions of different nature will be adsorbed onto different NC facets. However, experimental techniques are not able to discriminate directly if the different ions are selectively distributed onto the different faceted faces.

In order to obtain further information on the organization of the ligands at the NC, we have employed all-atomic MD simulations. Our simulation box contained one LaF_3 NC in a water box with all involved ions in the synthesis (acetate, citrate, ammonium and tetramethylammonium) in excess, to ensure the saturation of the surface (see details in SI). Detailed analysis of the simulation results reveals selective adsorption of the ions (see Figure S8 and Table S4), following the model proposed in Figure 1. Acetate and citrate ions are adsorbed onto surface-exposed La atoms and ammonium ions are adsorbed onto surface-exposed F atoms (see Figure S8). Tetramethylammonium is found only in the diffuse ionic layer surrounding the NC. The equilibrium organization of the ions at the NC obtained from our simulations is shown in Figure 3 (see also Movie S1). In our simulation, we found that in hexagonal faces ($\{0001\}$ planes), we have adsorbed anions (acetate and citrate) with a direct carboxylic-to-metal interaction (see Figure S8). We obtain an adsorbed amount of 13 trivalent citrates and 10 acetates (see Table S4), corresponding to a charge density of -3.4 e/nm^2 approximately for these faces. At the rectangular faces ($\{1-100\}$ planes) of the simulated NC we found a total of 37 adsorbed ammonium cations (see Table S4), corresponding to $+3.4 \text{ e/nm}^2$ which interact electrostatically with exposed fluorine atoms (see Figure S8). It is interesting to note that both hexagonal and rectangular faces acquire the same charge density but with opposite sign. But note that the hexagonal faces have larger area (see SI), so in our simulation the neutral LaF_3 NC acquires a global negative charge due to the ionic adsorption (a total of $(-13 \cdot 3) - 10 + 37 = -12e$ which corresponds to -0.47 e/nm^2). We recall that this result agrees with the high-negative value measured experimentally for the ξ -potential (see SI).

Figure 3. Snapshots (made with VMD)^[22] from MD simulation at 100 °C of LaF₃ NC in ionic solution in water, showing the surface composition of the NCs. LaF₃ atoms and adsorbed ligands are shown as spheres with their Van der Waals radius (green corresponds to La, orange to F, black to C, red to O, blue to N and white to H). We show adsorbed acetate and citrate ions (found only at the hexagonal facet) and adsorbed ammonium ions (found only at the rectangular facet). Water molecules adsorbed to the NC surface are shown in blue as a molecular contour surface (calculated using the surface algorithm implemented in VMD). Free water molecules are not shown for clarity. Tetramethylammonium cations found in the diffuse layer near the NC are also shown.

Additionally, our results also show the presence of strongly adsorbed hydration water molecules on the LaF₃ surface. Previous simulations^[15] of ionic adsorption in metal fluoride NCs using different models for water (implicit and explicit water molecules) concluded that adsorbed water molecules have a substantial role in stabilizing charged surfaces of NCs, avoiding a massive ionic condensation onto the surface. We suspect here that also adsorbed water plays a similar role in LnF₃ NCs preventing a massive ionic condensation onto NC surface.

Overall, our experimental and simulation results indicate that we have successfully obtained the NC model proposed in Figure 1, obtaining faceted NCs with different exposed faces in the core due to the faceting shape. Lanthanum atoms are more exposed in {0001} planes, showing a hydrophilic behavior and fluorine atoms are exposed in {1-100} planes with a more hydrophobic/less hydrophilic behavior. In consequence, each face is stabilized selectively with cations or anions, resulting in charged-face patchy NCs.

Now we consider the influence of two major changes in the proposed NC: (i) the effect of changing the crystal structure (and thus the faceting of the NC) by changing the metal by another lanthanide with different radius and (ii) the behavior of faceted-charge patchy NC in other polar solvents. It has been postulated that the presence of patches with different behavior allows the NC stabilization because of the selective interaction of solvents in the patches.^[23] To this end, we have synthesized CeF_3 and PrF_3 NCs (see SI). Obtained LaF_3 , CeF_3 and PrF_3 NCs (Figure S1) were re-dispersed in water and methanol. Cryo-TEM images for all particles as dispersed in both solvents (water and methanol) are shown in Figure 4.

First of all, we recall that the faceting of the NCs strongly depends on the metal cation radii.^[16] If the metal radius decreases, NC shape becomes more spherical or less faceted avoiding the spontaneous formation of patches by the hexagonal-faceted shape. In this case, faceted NCs are obtained for LaF_3 and CeF_3 but the particles obtained with PrF_3 NCs start to form self-assembly in supraparticles containing some NCs (Figure 4c). This behavior was observed previously in similar particles made by YF_3 and in this case the formation of the supraparticles was driven by ionic bridges^[15] mediated by the citrate ligand.

Focusing on the effect of the solvent, we emphasize here that we do not observe significant difference between the cryo-TEM images obtained in water and methanol (Figure 4). In other words, in spite of the essential role of ionic ligands in our system, we do not observe any significant effect in moving from water to methanol due to the decreasing in the polarity of the solvent. In order to obtain a molecular insight on this behavior, we performed all-atomic MD simulations in which free water solvent was replaced by methanol. The simulations were performed by starting from an equilibrium configuration of the previous MD simulations performed in water. The experimental process was modelled in the following way. We removed all free molecules of the system (both water and ions), maintaining only the adsorbed ions and the water molecules adsorbed onto the NC surface. Then, we added free tetramethylammonium cations as counter ions (in order to neutralize the system) in the diffusion layer and we added methanol as solvent (see SI for full details).

Figure 4. Cryo-TEM images obtained of colloidal solutions in water (left) and methanol (right) of (a) LaF₃ NCs, (b) CeF₃ NCs and (c) PrF₃ NCs. All of them obtained in holly-carbon grids at ~30 mM concentrations.

The results of our MD simulation show an exchange of water for methanol in rectangular {1-100} planes while water molecules adsorbed onto hexagonal {0001} planes remain directly attached during all simulation time (Figure 5a and Movie S2). Remarkably, in our system, adsorbed water is maintained in certain preferential faces while it is exchanged by the new solvent (methanol) in other faces (see Figure S10). Patches formed by fluoride atoms in {1-100} planes show a more hydrophobic/less hydrophilic behavior which allows the fast exchange between both solvents, so solvation water is replaced by methanol over these planes. However, {0001} exposed planes, those stabilized by citrates and acetates, present a more hydrophilic/less hydrophobic role and they maintain their adsorbed water in the presence of the new solvent (methanol). We propose here that this dual water/methanol solvation promoted by the patches of these NCs is the key factor to explain the same role of cryo-TEMs in water

and methanol. These patchy NCs are able to interact selectively with the added solvent modifying their surface chemistry in order to remain stable in less polar solvents.

In order to investigate the mechanism of the water/methanol swapping, we performed ^1H MAS NMR of both samples, as-synthesized LaF_3 NCs and after being stabilized in methanol (Figure S11). The results show significant differences between both spectra compatible with one system stabilized by adsorbed water and the other one with a mixture of water and methanol. A detailed analysis of our simulation results (see Figures S13 and S14) reveals that the molecular mechanism of replacement of water adsorbed in $\{1-100\}$ planes by methanol is always mediated by a free water molecule from solution. First, an incoming methanol molecule attaches to an adsorbed water molecule via hydrogen bonding. An incoming free water molecule destabilizes this configuration and induces the release of the adsorbed water molecule, being replaced by a methanol molecule (a detailed description of the mechanism is shown in Figure S14).

Combining ^1H MAS NMR and MD simulations, we postulate that these patchy NCs are able to selectively exchange water for methanol in $\{1-100\}$ facets whereas this solvent exchange does not occur in $\{0001\}$ faces.

Figure 5. Snapshots (made with VMD)^[22] from a MD simulation of LaF₃ NC in methanol solvent showing adsorbed molecules (ions, water and methanol) over the surface. Adsorbed water (in blue) and adsorbed methanol (purple) are shown as a molecular surface using surface algorithm of VMD. NC atoms and atoms from adsorbed ions are shown in Van der Waals representation. (a) top and lateral views, showing the NC with both hexagonal and rectangular facets with adsorbed molecules, (b) magnified (partial) view of a NC region showing adsorbed ammonium and tetramethylammonium cations and (c) magnified (partial) view of a NC region showing contacts between adsorbed citrate ions (shown as bonds to simplify the image) and adsorbed tetramethylammonium cations. Non-adsorbed molecules are not shown for clarity.

Moreover, solvent exchange is not the unique phenomenon observed when changing the solvent. In methanol solvent simulations, tetramethylammonium cations adsorb onto the NC on {1-100} planes and show substantial correlation with the free carboxylic moieties of citrate ligands adsorbed onto the NC surface (see Figure S9 and Table S5). The resulting NC surface with adsorbed tetramethylammonium cations is shown in Figure 5. This big cation (as compared with ammonium) did not show any significant correlation with the NC surface in our simulations carried out in water (compare the correlation functions shown in Figures S7c and S9c). In the case of simulations with water solvent, the {1-100} planes of the NC surface contained only ammonium cations. However, if methanol is used as solvent, {1-100} exposed planes become more hydrophobic allowing the adsorption of tetramethylammonium to reduce the negative charge of the NC. Concerning the observed electrostatic citrate-tetramethylammonium interactions (Figure 5c), they seem to be induced by an increased counterion condensation by the lower dielectric constant of methanol.

In summary, we present a model of faceted-charge patchy NCs in which cations or anions are selectively adsorbed onto different NC surfaces. A realization of this model using LnF₃ NCs has been investigated experimentally and by MD simulations. NC faceting is promoted by the formation of hexagonal crystalline structure. Each facet has a different behavior, acting as a patch due to the different exposed atoms at the different exposed planes. Consequently, cations and anions from solution are spontaneously anchored in a selective way at different exposed planes creating ionic stabilized patchy NCs. When water solvent is replaced by methanol, the NC surface releases adsorbed water in specific planes, which is replaced by adsorbed methanol, stabilizing NCs in the new medium. In addition, less

hydrophilic cations not adsorbed in water solvent adsorb at the methanol-covered patches reducing the high negative charge of the particles in water, being the new surface chemistry stable in methanol.

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