Mechanistic Insight into the Formation of Cationic Naked Nanocrystals
Generated under Equilibrium Control

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1. Introduction

• Ligand coated neutral nanocrystals (NCs) dispersions combined with templating polymers are used for preparation of mesoporous films.\(^1\)

• PbSe thin films are used for active layers in energy conversion materials such as Schottky-type solar cells, field effect transistors, NIR photodetectors, and thermoelectrics.

• Cationic naked NCs dispersions are more promising than ligand coated neutral NCs for preparation of mesoporous film because of their (1) energy propagating ability due to close NC-NC distance, (2) strong electrostatic interaction between NC and polar polymer enables ordered mesostructure and (3) generality of NC composition (Scheme 1).

• Cationic naked NCs are usually prepared by treating ligand protected NCs with strong electrophilic reagents that irreversibly cleave bonds between native organic ligands and the NC surface (Scheme 2a).\(^2\)

• If ordered cationic naked PbSe NC film is obtained, improvement as energy conversion material is expected.

Problem: for some materials (including PbSe), irreversible cleaving of NC-ligand bonds cause desorption of excess metal cations which stabilize the NC colloids, making the NCs poor dispersive as building units for mesoporous films (Scheme 2a).

This Work: use of relatively weak neutral Lewis acid for NC-ligand cleavage to generate reversibly physisorbing anionic species that stabilizes the NC surface until coordinating solvent is able to repassivate the surface (Scheme 2b).

Scheme 1. Assembly of cationic naked NC and BCP into mesoporous structure. The SEM image is TiO\(_2\) NC/BCP on Si.

Scheme 2. Ligand stripping by (a) positive electrophile and (b) neutral Lewis acid.
2. Results and Discussion

2.1 Synthesis and Characterization of Stable Cationic NC Dispersion

• Ligand stripping of oleate coated PbSe NC in DMF was attempted with three kinds of electrophiles (Fig. 1a).
  i) NOBF₄ (oxidant): precipitation ✗
  ii) Me₃OBF₄ (methylation reagent): poor dispersibility ✗
  iii) Et₂OBF₃ (Lewis acid): stable dispersion ✓

• EDX and IR analyses of PbSe-OA NC treated with Et₂OBF₃ shows large decrease in carbon signals at 0.3 keV and 2900 cm⁻¹, respectively (Fig. 1b,c). => PbSe-OA treated with Et₂OBF₃ is naked.

• Hydrodynamic diameter (calculated from DOSY signal of OA on the NC) of PbSe-OA NC is 10.0±0.5 nm. After treatment by Et₂OBF₃, it decreased to 6.3±0.3 nm. It is comparable to the core diameter in TEM 6.8±0.5 nm. Et₂OBF₃ treated PbSe NC is not only naked but also well dispersed.

• ICP-AES (Inductively coupled Plasma Emission Spectrometry) was used for quantifying Pb and Se in isolated PbSe NCs (Fig. 1d,e).

⇒ Et₂OBF₃ treated PbSe NC avoided desorption of cation (Pb²⁺) from the surface.

• Stable cationic naked NC dispersions of ZnO, Mn₂O₃, Ti₂O₃, and Ni also could be prepared by treatment with Et₂OBF₃.

**Figure 1.** Ligand stripping of PbSe-OA NC by electrophiles i-iii. (a) Treatment of PbSe-OA NC and dispersiveness of the product. (b) EDX and (c) IR spectra of NCs before (red line) and after (purple line) treatment with EtO₂BF₃. (d) Pb/Se ratio of NCs determined by ICP-AES analysis. (e) Model composition and structure of NC (ii) and (iii) calculated from Pb/Se ratio in (d).
2.3. Mechanism of formation of cationic naked PbSe NC

- To elucidate the stripping mechanism, titration of PbSe-OA NC by Et₂O·BF₃ measured by ¹H NMR was conducted (Fig. 2a).
  => OA·BF₃⁻ was formed by addition of Et₂O·BF₃.

- Titration of PbSe-OA by Et₂O·BF₃ measured by ¹H DOSY shows time averaged diffusion constant (D) of OA moieties. At 0.2 equiv., both of OA and OA·BF₃⁻ slowly diffuse with NC core (D = 1×10⁻¹⁰ m²s⁻¹, Fig. 2b). At 0.5 equiv., OA⁻ stayed same diffusivity (Fig. 2c). This means OA⁻ is always on the NC surface regardless of Et₂O·BF₃ addition. On the contrary, D of OA·BF₃⁻ increased to 2.4×10⁻¹⁰ m²s⁻¹. It is intermediate value between NC and free OA moiety. That means OA·BF₃⁻ stabilized cationic NC surface until coordination solvent is able to repassivate the surface.

2.4. Formation of Counter Ion BF₄⁻

- ¹⁹F NMR and FT-IR of isolated cationic naked NC shows its counter ion is BF₄⁻ (Fig. 3). How is it formed?

- ¹⁹F NMR of Et₂OBF₃ in DMF revealed DMF facilitated disproportionation reaction to yield BF₄⁻ (Fig. 4a,b).

- Negative-ion mode ESI-MS of Pb(OA)₂⁺ Et₂OBF₃ in benzene was conducted to find the another source of BF₄⁻. Anionic species shown in green were detected and reaction mechanism of BF₄⁻ generation was predicted (Fig. 5a,b).

- Anionic OA-B species other than OABF₃⁻ generated by both mechanisms may contribute to NC stabilization.

- D of BF₄⁻ on the NC is comparable to D in free (Fig. 3). =>BF₄⁻ don't interact with the NC in solution.

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**Figure 2.** ¹H NMR titration study of PbSe-OA by Et₂O·BF₃ (vs OA moiety) in DMF. (a) Generation of OA·BF₃⁻ (b) Dependence of diffusion coefficient of OA⁻ and OA·BF₃⁻ on equivalent of Et₂O·BF₃ (c) ¹H DOSY spectrum at 0.5 equiv. of Et₂O·BF₃.

**Figure 3.** Elucidation of counter ion on cationic naked PbSe NC by ¹⁹F NMR (DOSY). (a) NaBF₄ as a reference of BF₄⁻. (b) Redispersed cationic naked PbSe NC.

**Figure 4.** Reaction mechanism investigation of BF₄⁻ origin by ¹⁹F NMR. (a) ¹⁹F NMR spectrum of Et₂OBF₃ in DMF (b) Found species and supposed mechanism of BF₄⁻ generation.

**Figure 5.** Reaction mechanism investigation of BF₄⁻ origin by ESI-MS (a) ESI-MS spectrum of Et₂OBF₃ + Pb(OA)₂ in benzene. (b) Proposed mechanism of BF₄⁻ generation. Found species are shown in green and numbered.
2.5. In Film Architecture of the Cationic Naked PbSe NC

• Cationic naked PbSe NC films were prepared using two methods.
  1) Spin-coating of PbSe-OA NC dispersion on Si substrate (Fig 5a). Then removing OA ligands (Fig. 5b).
    => disordered structure
  2) Preparing cationic naked PbSe NC dispersion. Then spin-coating on Si substrate (Fig 5c).
    => Newly available method 2 gives ordered structure
• Cationic naked PbSe NC deposited with BCP (Scheme 1) yields highly ordered mesostructure with 45 nm periodicity (Fig. 6).
  => electrostatic interaction enables construction of a novel highly ordered mesostructure, which was unachievable by neutral NCs.

3. Conclusion

• OA ligand was stripped without cation desorption by addition of neutral Lewis acid. Stable naked cationic NC dispersion was obtained.
• $^1$H DOSY study of PbSe-OA NC with Et$_2$O:BF$_3$ shows the surface of the naked cationic NC is mainly stabilized by weak interaction with OA:BF$_3$.
• Unexpectedly, counter anion of the purified naked cationic NC turned out to be BF$_4$$. Mechanistic studies of model reactions revealed its origin.
• Well dispersed cationic naked NC enabled preparation of previously unobtainable (1) ordered PbSe film with small interparticle distance and (2) mesoporous PbSe-polymer composite.

4. References
