

Ligands in PbSe Nanocrystals: Characterizations and Plasmonic Interactions

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Ligands on semiconductor nanocrystals such as PbSe have a critical role in controlling electrical and optical properties of an individual nanocrystal and their assembly. Standard synthesis of PbSe nanocrystals usually leaves oleic acid ligands on the nanocrystal surfaces as size stabilizers. Considered insulating (long chains of carbons), oleic acid is typically replaced with short ligands such as hydrazines to decrease the inter-nanocrystal distances and improve electronic coupling among the neighboring nanocrystals [1]. As a consequence, enhanced electrical conduction was obtained in PbSe nanocrystal films with short conducting hydrazine ligands [2]. Despite their importance, detailed microscopy and spectroscopy (EELS) analysis of the ligands are absent.

Here, oleic acid ligand present on colloiddally synthesized PbSe nanocrystals was studied using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) operated at 200 kV [3]. The geometrical orientation inferred from the images was compared to molecular dynamics simulation [4] for 6 nm PbSe nanocrystals. The electronic coupling effects arising from ligand exchange were also studied using localized surface plasmon resonance (LSPR) modes in low loss EELS. More importantly, we observed that the insulating oleic acid ligands act as conducting channels by increasing plasmon lifetime under partial oxidation condition.

Figure 1(a) shows the HAADF-STEM image of as-synthesized PbSe nanocrystals capped with oleic acid ligands occupying radial regions of about 1 nm from the surface of the nanocrystals, which is shorter than the length of oleic acid molecules (1.97 nm). This is indicative of the tendency of the oleic acid ligands to wrap around instead of standing out given the size of the nanocrystals (6 nm) and ligand surface density. Such wrapping conformation is adopted to minimize inter-ligand interaction on the same nanocrystals. With high density of surface ligands, straight ligand arrangement could be achieved as was suggested by molecular dynamics simulation [4].

Under air exposure, PbSe nanocrystals easily oxidize to form oxide shells that are responsible for p-type doping by introducing surface acceptor states. Figure 1(c) shows the completely oxidized PbSe nanocrystals depicting the decreased sizes and blurred images due to the oxide layers on the surface. At early oxidation stage (partial oxidation), prior to the formation of uniform oxide shells, the nanocrystals appear to form links between neighbors, as shown in Figure 1(b). Localized EELS analysis shows that these links are made of carbon based materials, most likely from oleic acid ligands.

Low-loss EELS data from as-synthesized oleic acid-capped PbSe nanocrystals is shown in Figure 2(a) (red curve). The weak peak at 6.5 eV corresponds to the LSPR signals, which becomes narrower and enhanced after undergoing short hydrazine ligand exchange (blue curve). This effect can be explained by an increased plasmon lifetime accommodated by the conducting states in between nanocrystals available after ligand exchange. This peak becomes weaker once the nanocrystals are oxidized (orange curve) indicating a shortening of plasmon lifetime due to the introduction of insulating states from the oxide shells. Similar narrowing and enhancement of the peak were observed when the nanocrystals are

at early oxidation stage (black curve). This leads to the possibility that the linking materials are not only made of oleic acid ligands but also modified to contain conjugate carbon double bonds to support delocalization of electrons. Such modification can be catalyzed by the oxide materials on the nanocrystals. The presence of conjugate carbon bonds was observed by core-loss EELS measurements show in Figure 2(b) by the increase in π^* signals in C K-edge and a shoulder at 4.5 eV in the low loss EELS due to plasmons from delocalized π bonding (black curve - Figure 2a).

References:

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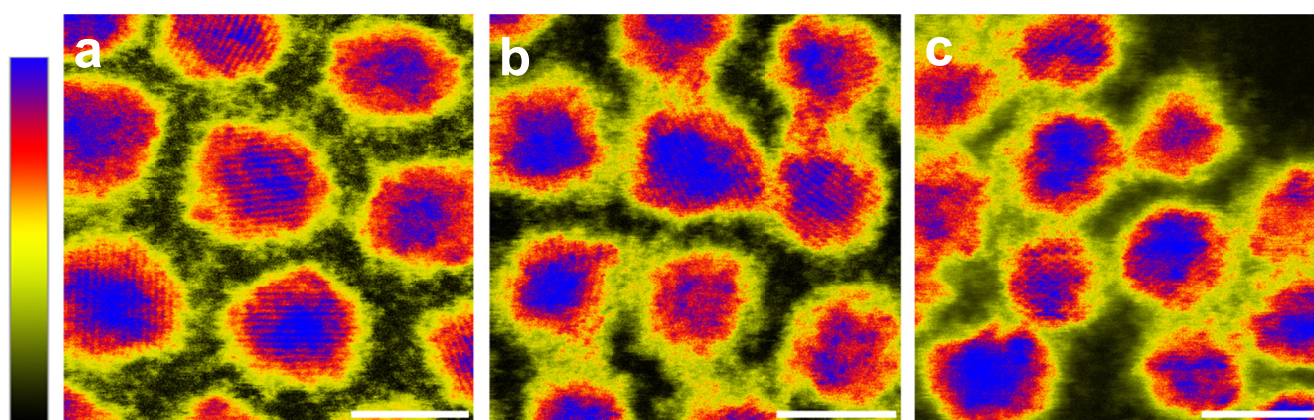


Figure 1. HAADF-STEM images of PbSe nanocrystals (a) capped with oleic acid (as-synthesized), (b) at early oxidation stage, and (c) after extensive oxidation. All scale bars are 5 nm.

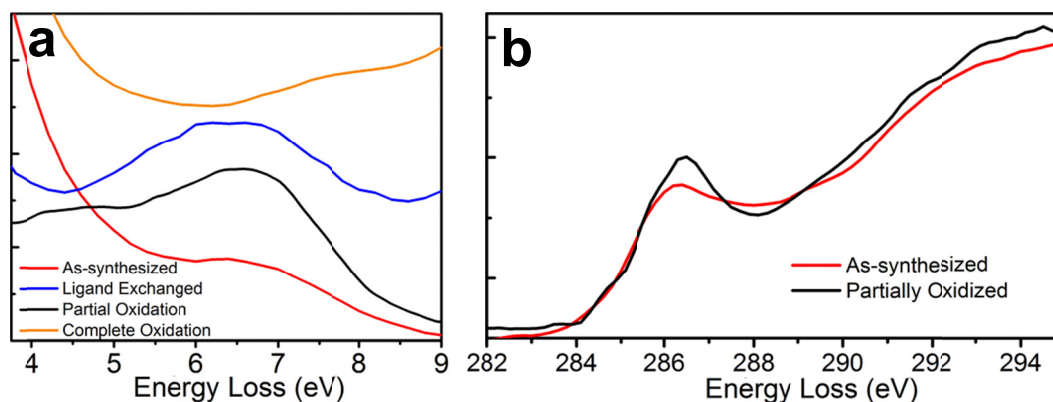


Figure 2. (a) Low-loss EELS data for the samples in Figure 1 and additional ligand exchanged hydrazine capped PbSe nanocrystals. (b) C K-edge EELS data from as-synthesized and partially oxidized (early oxidation) PbSe nanocrystals.