# Simple cubic self-assembly of PbS quantum dots by fine ligand control†

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Colloidal quantum dots (QDs) have attracted substantial attention due to their characteristic optoelectronic properties based on the size confinement effect.[1] They are also known to self-assemble into highly ordered superlattices.[2] The geometry of such self-assembled QDs has been explored to better understand the ensemble effects on their optical and electrical properties.[3] Accordingly, it is essential to prepare two-(2D) and three-dimensional (3D) QD superlattices with different geometry for their solid-state device applications.

Most colloidal quantum dots with a *quasi*-spherical shape readily self-assemble into 3D face-centered cubic (fcc) or body-centered cubic (bcc) superlattices.[4] In contrast, 3D simple cubic (sc) superlattices are difficult to obtain from sphere-like QDs because of their relatively low packing fraction of 0.52 and the low stability by entropy.[5] Therefore, sc superlattices have been expected to have different optical and electronic properties from other packing structures, and the quest has been on to achieve 3D self-assembled sc superlattices. Here, we achieve the selective control of the geometry of the *quasi*-spherical PbS QDs in highly-ordered 2D and 3D superlattices: Disorder, sc, and fcc by selectively removing the ligands from the QD surface through gel permeation chromatography (GPC).

The uniform sphere-like PbS QDs with an average diameter of 7.3 nm were synthesized. The QD sample was purified once by precipitation/redissolution process prior to the GPC process (before-GPC). In the GPC process, the eluted QD solution was collected in 5 consecutive portions (GPC-1 to GPC-5).

The thermogravimetric analysis (TGA) was carried out to evaluate weight ratios of oleic acid (OA) ligands bound to QD surface (Fig. 1a) which gradually increase from GPC-1 to GPC-5. To further determine the ligand density, the atomic Pb/S ratios of GPC-2 and before-GPC were obtained from Rutherford backscattering (RBS) spectrometry in RIKEN Pelletron accelerator facility (Fig. 1b).[6] An average Pb/S ratio (1.27) combined with TGA results was used for estimating the ligand density. The TGA results (Fig. 1c) demonstrate that the ligand density of the PbS QDs gradually increases from GPC-1 (0.6 $nm^{-2}$) to GPC-5 (7.1 $nm^{-2}$) and that the GPC method can precisely and continuously control the ligand density of the PbS QDs. We also estimated the ligand density by nuclear magnetic resonance spectroscopy. The obtained results are consistent with the ligand density obtained from TGA (Fig. 1c).

Based on the difference in their ligand density, the 2D self-assembly of these QDs was achieved by drop-casting dilute solutions onto solid substrates. GPC-1–5 formed 2D superlattices with different and unique geometries.

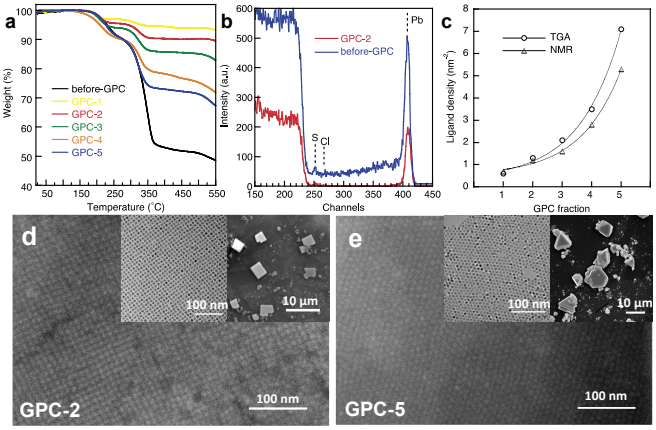


Fig. 1. (a) TGA curves of before-GPC and GPC1-5; (b) RBS spectra of GPC-2 and before-GPC; (c) Ligand density of PbS QDs as a function of the GPC fraction; The scanning electron microscopy (SEM) images of the supercrystal surfaces for GPC-2 (d) and GPC-5 (e); inset: their 2D self-assembled TEM images and SEM images of 3D supercrystals.

GPC-1 QDs showed a random assembly due to insufficient ligands on the QD surface. However, GPC-2 QDs (inset of Fig. 1d) formed a square self-assembled geometry without the fusion between QDs. Also, the GPC-2 QDs in the square superlattice are highly oriented along QD [100] facets. The GPC-3–5 QDs with sufficient ligands formed the hexagonal assemblies with non-oriented facets (inset of Fig. 1e).

Furthermore, the long-range-ordered 3D self-assembled supercrystals for GPC-2 and GPC-5 QDs were prepared by solvent evaporation. GPC-5 QDs can form triangular or hexagonal fcc supercrystals with a hexagonal arrangement on the crystal surface (Fig. 1e). It is noteworthy that GPC-2 QDs self-assembled in cubic supercrystals with sc packing on account of finely controlled ligand removal by GPC, which is usually difficult for quasi-spherical QDs.

In this report, we develop GPC as a method to control the ligand density of the *quasi*-spherical PbS QDs and achieve the selective control of the geometry of QDs in 2D and 3D superlattices: Disorder, sc, and fcc. The precise control of QD self-assembled geometry is expected to greatly improve the performance of next-generation semiconductor devices and photocatalysis.

References
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