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Synthesis of Monodisperse Superconducting Lead Nanocrystals

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We report on a new organic-phase synthesis method to produce a large quantity of high-quality monodisperse population of superconducting lead (Pb) nanocrystals. They are obtained from the alcohol reduction of a mixture of lead oleate and lead acetate in the presence of trioctylphosphine in octadecene. We show that the details of lead carboxylate mixture preparation is the key parameter in controlling the nucleation rate of the synthesis. Because mixtures of metal carboxylate have been widely used in synthesizing various high-quality metals or metal−oxide nanocrystals, the results herein should contribute to the understanding of the detailed mechanisms of these syntheses. Because of the large quantities provided by this synthesis, these nanocrystals are particularly well adapted for studies of the effect of quantum confinement on superconductivity.

Introduction

Over the past decade, the development of high-temperature solution-phase synthesis of nanocrystals provided new protocols for the preparation of colloidal solutions of particles with excellent monodispersity. In particular, much attention has been directed to the synthesis of semiconducting quantum dots and magnetic particles.[1−4] Such monodisperse populations of particles can be crystallized into two-dimensional or three-dimensional arrays through solvent evaporation methods,[5,6] and conducting films[7−9] with potential applications in areas of electronics and spintronics have been realized.

Because of the qualitative improvements observed in the preparation of these materials, they are now being considered as model systems for the study of quantum statistical physics of strongly correlated electrons.[10−12] In this context, metal nanocrystals arrays may best be described as quantum electron glasses, whose theoretical understanding remains a challenge. Glassiness has particularly remarkable consequences on superconducting coherence where quantum superconductor−insulator transitions have been observed in amorphous superconductors,[13,14] and a Bosonic insulator with localized Cooper pairs was theoretically predicted.[15] To this end, a synthesis method for producing superconducting nanocrystals is required.

Herein, we report an organic-phase synthesis method for producing large quantities of nearly monodisperse Pb nanocrystals, Figure 1a, as well as the influence of experimental conditions on nanocrystals formation. The nanocrystals of diameter 25 nm are superconducting with a critical temperature $T_c = 7.2$ K, as found in the bulk state.[16] The quality of the nanocrystals provided by this synthesis constitutes a significant improvement over previous attempts to realize superconducting Pb particles.[17−19]

Results and Discussion

The Pb nanocrystals were synthesized by alcohol reduction of lead carboxylates in a solution of octadecene (ODE), oleic acid (OA), and trioctylphosphine (TOP). In a typical synthesis, lead oleate is first prepared from a solution of 15 mmol of lead acetate trihydrate and 30 mmol of oleic acid in ODE (15 mL), kept under vacuum overnight at the temperature of 80 °C. This solution is then aged for several hours under oxygen atmosphere at the temperature of 60 °C. In a second step, a mixture of this lead oleate (1.5mmol) and lead acetate (1.5mmol) in ODE (2.5 mL) is prepared and heated at 80 °C under vacuum for 4 h. The resulting mixture is turbid yellow, containing Pb carboxylate aggregates, as observed by transmission electron microscopy (TEM), inset of Figure 2. Finally, in the third step, 1.5 mL of the resulting mixture is dissolved in ODE (15 mL), 1-octadecanol (0.9 g), and TOP (1 mL). This solution is heated at 125 °C under vacuum for 2 h, where it becomes translucent yellow.

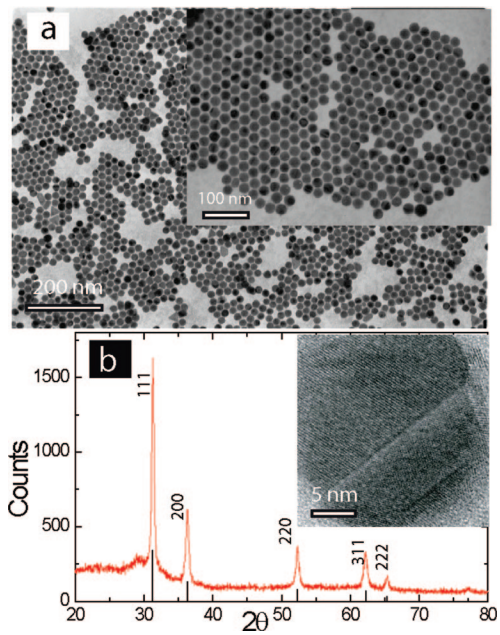


Figure 1. (a) Main panel and inset are TEM images of Pb nanocrystals obtained from two distinct synthesis. (b) Main panel: XRD pattern of the Pb nanocrystals. The standard diffraction peak positions and relative intensities of bulk FCC lead are indicated. The inset shows a HRTEM image (20 nm × 20 nm) of the nanocrystal sample. The ordered distance of 2.7 nm shown in the high-resolution image corresponds to the lattice spacing of the (111) faces of FCC Pb.

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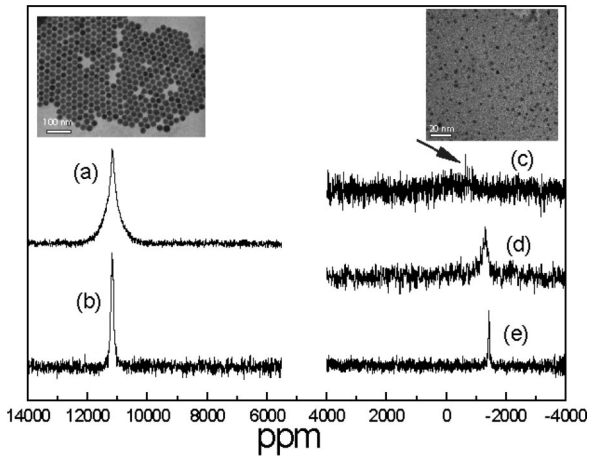


Figure 2. Pb-207 static NMR spectra of (a) metallic Pb0 nanoparticles (left TEM picture), (b) bulk metal Pb, (c) clusters (right TEM picture), (d) lead-oleate aged under oxygen, and (e) pure lead-oleate. All of the spectra are obtained in a 7 T magnetic field at room temperature with a spin echo experiment. The position of the NMR line for lead clusters (indicated by arrow) shows that the clusters responsible for nucleation at the beginning of the synthesis are lead carboxylate aggregates.

Next, under argon, the temperature is quickly raised to 200 °C, followed by a slow increase at a rate of 3.5 °C/min. When the reaction temperature reaches 240 °C, a rapid reaction occurs and the yellow solution becomes brownish black, indicating the formation of Pb^0 nanocrystals. The nanocrystals are grown by ramping the temperature up to about 270 °C, at which point the solution is cooled to room temperature. The nanocrystals are precipitated by centrifugation from the reaction solution by adding an equivalent quantity of isopropanol, and the black nanocrystals that precipitate can be easily redispersed in nonpolar organic solvent, such as chloroform or toluene. The reaction yield is high, providing about 100 mg of materials per synthesis.

The TEM image, Figure 1a, shows that the Pb nanocrystals are nearly monodisperse, spherical particles with a diameter of 25 nm and a typical standard deviation of 15%. X-ray powder diffraction, Figure 1b, and high-resolution TEM, inset Figure 1b, show that the particles are crystalline Pb. This is further confirmed by Pb NMR, indicating that nanocrystals are Pb^0 particles, Figure 2, and by SQUID magnetometry, Figure 3. This last figure shows that the magnetic susceptibility of Pb^0 nanocrystals decreases abruptly below the temperature $T_c = 7.2$ K, as a consequence of the Meissner effect. This effect is one characteristic signature of superconductivity; it is the consequence of the diamagnetic response of dissipation-less superfluid currents to a magnetic field. While the transition temperature $T_c = 7.2$ K found for the nanocrystals is identical to that of bulk Pb,[16] there are several signatures of the small size of the nanocrystals in the magnetization curve. First, the magnitude of the Meissner effect is several orders of magnitudes smaller than expected for bulk Pb. Second, the upper critical field B_c of nanocrystals is much larger ($B_c > 1$ T) than that of bulk Pb, whose value is $B_c = 0.088$ T.[16] Precise measurements of the magnetization data as a function of size of nanocrystals will be reported in a future publication.

The particles are stable and remain dispersed in chloroform for months if properly stored under argon. We find that the monodispersity and the stability of these nanocrystals in organic solvents allow for the realization of self-organized arrays as shown Figure 1.

Key parameters controlling the yield of the reaction, the size, and monodispersity of particles have been identified. The size

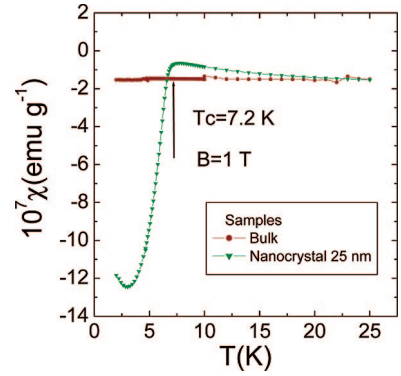


Figure 3. Magnetic susceptibility of Pb nanocysal with diameter 25 nm, as compared to bulk Pb, under a static magnetic field of 1 T. The normal state values of magnetic susceptibility are similar, indicating that nanocrystal sample is mostly composed of metallic Pb with negligeable contribution from oxide or organic ligands. Nanocrystals display the Meissner effect below the critical temperature $T_c = 7.2$ K, as in bulk Pb. Note that the upper critical field of bulk Pb is 0.088 T, smaller than the applied field, which explains the absence of Meissner effect in bulk Pb data.

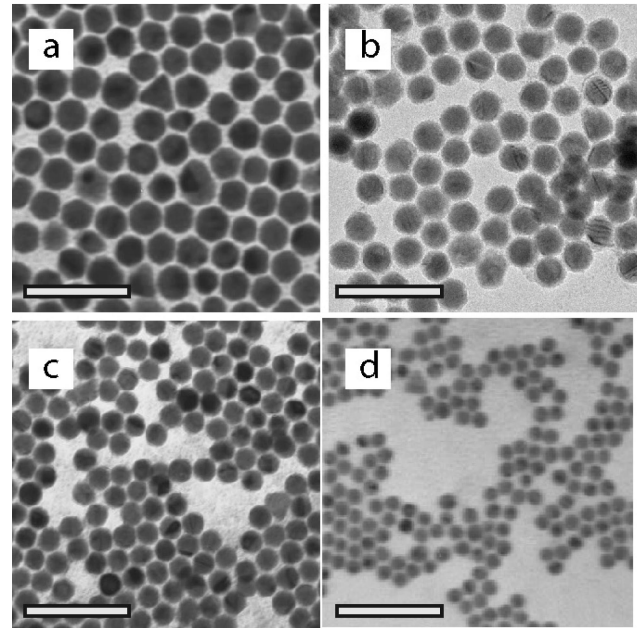


Figure 4. The size of the nanocrystal decreases from (a) to (d) as the final temperature of the solution is decreased from 280 to 240 °C. The scale bar is 100 nm.

of the particles is mostly controlled by the final temperature of the synthesis, as shown in Figure 4, where the particles' diameter increases from 13 to 30 nm as the final temperature is increased from 240 to 280 °C. The nucleation rate depends strongly on the preparation of the lead carboxylate mixture. We found that both aging the lead oleate under oxygen and adding excess lead acetate in the mixture increased the nucleation rate. A large nucleation rate is characterized by an intense yellow color observed at step 3, after 2 h at 125 °C under vacuum. After precipitation by centrifugation, Pb-207 NMR, Figure 2, shows that they consist of lead carboxylate clusters. This is consistent with previous observations of the formation of micelle-like aggregates of lead oleate in organic solvent.[20] Regarding the monodispersity of particles, we found that the presence of the coordinating ligand TOP in solution improved the quality of samples. Note, however, that P NMR does not show the presence of P on particles precipitated from solution reactants,

suggesting that oleic acid is the only capping ligand. Finally, temperature control is important during the growth stage. Samples with narrowest size distribution have been obtained with a rate of 3.5 °C/min.

A fundamental tenet for the synthesis of monodisperse populations of nanocrystal is the separation between nucleation and growth stage. In the "hot-injection" technique introduced by Bawendi and co-workers,[3] the rapid injection of precursor into a hot organic solvent results in a burst nucleation followed by a drop of precursors concentration below the supersaturation level. The nucleuses are then grown to full nanocrystals without additional secondary nucleation. Thus, nucleation and growth are sequentially separated in time. On the other hand, recent progresses have been obtained in the synthesis of monodisperse populations of metal oxides with the "heating up" method,[1] where clearly distinct nucleation and growth stages have not been identified yet. In this method, precursors, reagents, and solvent are mixed at low temperature and heated to initiate both the nucleation and the growth of particles. This last synthesis protocol is very similar to the one presented here for Pb. The major difference is the presence of the long chain alcohol in our synthesis used to reduce Pb^{2+} to Pb^0, to form metallic Pb particles. The use of alcohol or polyol to reduce metal salts to particles is referred to as the "polyol process"[21] and allowed the successful synthesis of monodisperse population of FePt[1]b and Co nanocrystals.[22] Starting from cocarboxylate and hexadecane-diol, we used a protocol similar to the one used for Pb to grow Co nanocrystals, Figure S2. While the precise mechanisms of the "heating up" method, leading to the growth of monodisperse populations of nanocrystals, have yet to be clarified, our observation that the preparation of Pb carboxylate mixture is the key parameter in controlling the yield of the reaction suggests that the formation of clusters in the metal carboxylate precursors may have a significant role in providing the nucleation centers.

Conclusion

In conclusion, we have developed an organic-phase synthesis method for producing a large quantity of high-quality monodisperse population of Pb nanocrystals. This material is particularly well adapted for fundamental studies of the effect of quantum confinement on superconductivity. Furthermore, if enough electronic coupling could be achieved between the nanocrystals, they would allow the first realization of Josephson coupled superconducting arrays on a scale smaller than the zero-temperature superconducting correlation length, which is 80 nm for bulk Pb. We found that the details of lead carboxylate mixture preparation are the key parameter in controlling the nucleation rate of the synthesis. Because mixtures of metal carboxylate have been widely used in synthesizing various high-quality metals or metal−oxide nanocrystals, the results herein should contribute to the understanding of the detailed mechanisms of these syntheses.

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Supporting Information Available: TEM images and NMR figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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