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Hydrothermal fabrication and superconductivity of isotropic Pb hollow microspheres

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ABSTRACT

In this work, we report a facile solvothermal route for synthesis of multi-crystalline isotropic Pb hollow sphere-like samples. In the absence of any template and catalyst, large-scale uniform Pb hollow microspheres with an inside diameter of 400 nm have been produced. The products are detected by electron microscopy, X-ray diffraction/photoelectron energy spectroscopy. Magnetic measurements reveal these as-fabricated specimens are superconducting with an onset T_c 11.05 K, which is 3.86 K above the bulk T_c (7.19 K). Superconducting Pb hollow microspheres with the high T_c may open up new possibilities for the fundamental understanding of the effect of dimensionality and superconducting mechanism.

The study of superconductivity in nanostructures including quasi-zero/one-dimensional nanostructures is driven both by open questions in these systems and by their potential applications in dissi-pationless electronic devices [1–19]. For several decades, low-dimensional Pb nanowires have been extensively studied, including single-crystalline, amorphous and granular nanowires of Pb [2,3,11–19] because it has the third higher superconducting transition temperature (T_c) among the elemental bulk superconductors reported [1,2]. Recently, a number of experiments have studied the properties of single crystal superconducting nanowires [2–19]. For example, our group has systematically reported superconducting MgB_2 and iron-based nanowires [6,10,18] and the transport properties/the photoelectric effects on single crystalline semiconducting [20]. As for low-dimensional anisotropic wire-like superconducting material, it has been generally accepted that when the size/the diameter is reduced toward and below the Ginzburg–Landau phase coherence length and the magnetic penetration depth, and the superconductivity is suppressed via thermally activated phase slip and quantum phase slip processes [1–3]. For isotropic microsphere, however, here it is quite natural to ask whether there exist superconducting bulks that exhibit an enhancement of the superconducting transition temperature T_c [2,3,6–19], particularly for hollow structures. More recently, Lortz's research group has reported on 'Giant' enhancement of the upper critical field and fluctuations above the bulk T_c in superconducting ultrathin lead nanowire arrays [15]. Up to now, however, report of enhancement of the superconducting transition temperature has been limited [6,10,15,18], especially for isotropic microspheres. Toward this end we for the first time describe a single-step route for the synthesis of Pb hollow microspheres using a hydrothermal method. The superconducting state is confirmed by magnetism measurements where Meissner effect is used to expect for a superconductor with transition temperature T_c (11.05 K). This method can continuously be used to synthesize mass area high pure Pb hollow microspheres at friendly environment process and low cost, which is a potential application for the building blocks in Pb-based superconducting nanodevices and as low dissipation interconnects in nanoscale electronics.

Basic synthetic process of the experiment is similar to that of our earlier work [21]. In a typical experiment, 0.5 mol mixtures of lead nitrate and iron powders, PVP (0.3 g), and thylene glycol (EG) solution were dissolved in 15 mL of distilled water with stirring. To this resulting solution, 0.50 mL of aqueous hydrazine solution (80%) and 0.01 mL of nitrate (25%) were dropped quickly in turn, and the mixture was transferred into a Teflon-lined autoclave (25 mL), heated to 80 °C, and maintained at this temperature for 2 h. After the hydrothermal treatment, the precipitate was

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collected and rinsed with distilled water and ethanol, respectively, and then dried in air for further characterization.

Morphology, phase/valent state, and chemical composition were extensively characterized by scanning/transmission electron microscopy (SEM/TEM), X-ray diffraction [XRD (Philips X Pert Prodiffractometer with Cu *K*a (K=1.54056 Å) radiation)]/selected area electron diffraction (SAED)/high-resolution X-ray photoelectron spectroscopy (HRXPS), and energy dispersive X-ray spectroscopy (EDS), respectively. Magnetization measurements from 2 K to 50/13 K were performed with a superconducting quantum interference device (SQUID) magnetometer (MPMS-9, Quantum Design) in H_{dc} (30 Oe) and H_{ac} (30 Oe, frequency 1117 Hz) as well as both zero field cooling (ZFC) and field cooling mode (FC) at an applied field (30 Oe), respectively.

Based on SEM/TEM, SAED, XRD, EDS, and HRXPS, morphology/size, structure, valent state, and microcomposition of the as-obtained specimens are detected in detail. Representative SEM and TEM images are revealed in Fig. 1a and b, in which all Pb samples without any oxidized lead have a similar morphology/size

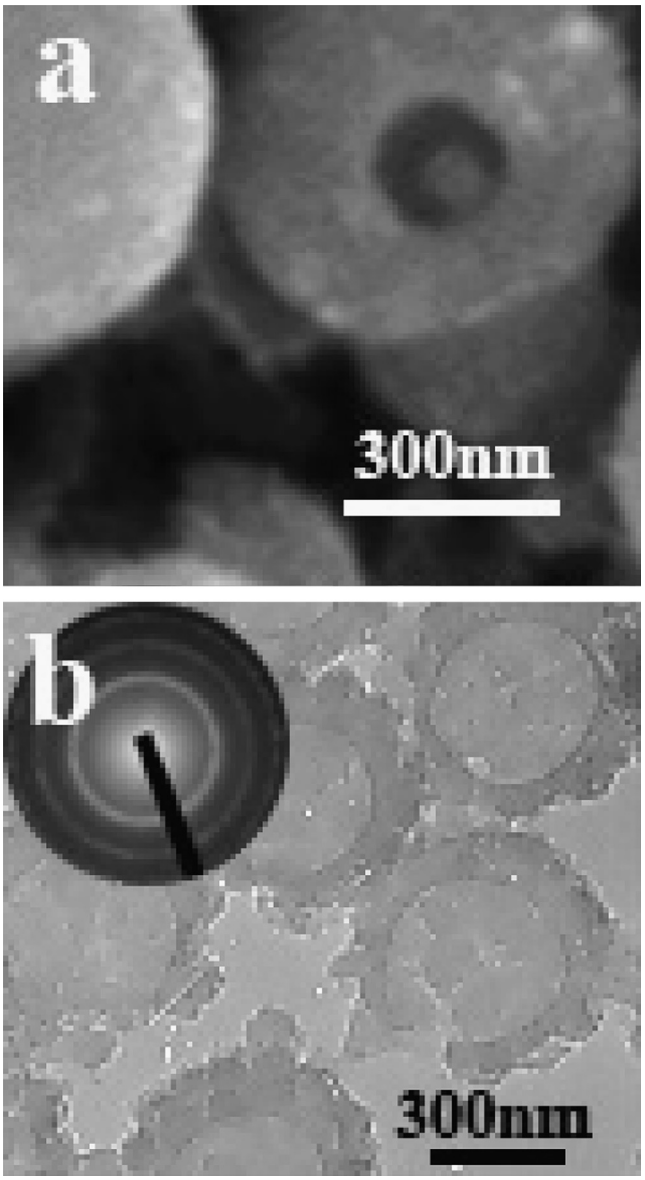

Fig. 1. (a) SEM image of the as-synthesized large-scale Pb microsphere; (b) a typical TEM image (inset for SAED patterns).

(microsphere), and hollow structure can be seen clearly, and the counterpart inner/outer diameter/thickness is about 400/600/100 nm. Corresponding SAED patterns for microstructures (inset in Fig. 1b) are composed of the regular clear diffraction rings (a polycrystalline nature), which are compatible with XRD patterns shown in Fig.2 a. As shown in Fig. 2b and c, microcomposition, composition, and valent state of the as-obtained specimens are further confirmed by EDS, and HRXPS spectra (one of the most sensitive instruments to oxygen), indicating that the sample is a high pure Pb without any oxidation of the Pb mainly because of reductants (iron powders, PVP, and EG) used in synthetic route. However, before the measurements the samples were stored for 24 h in air condition and then covered with 1–3 nm amorphous PbO layer verified by TEM, which is similar to the earlier work [15]. Of course, TEM images exhibited significant fraction of PbO cover layer on the surface of microspheres under the same growth conditions lack of PVP and EG.

As our previous report [21], it can be seen that initially, this Pb hollow microsphere undergoes consequent nucleation obtaining mainly small particles and later these particles grow larger and become numerous microsphere samples in a blank sample (without surfactants). In the subsequent process, driven by the minimization of the total energy of the system, the small primary Pb nanoparticles aggregated together to form 3D spheres (with PVP assisted). It is possible to realize that the nucleation and growth of Pb is controlled by the ions diffusion in viscous solution, which is similar our earlier work [21].

As shown in Fig. 2d and e, a SQUID magnetometer by Quantum Design was used to measure the zero field cool (ZFC) and field cool (FC) DC susceptibility of the as-obtained Pb microsphere over a temperature range of 2–50 K under an applied field of 30 Oe and AC susceptibility over a temperature range of 2–13 K in an AC field of 30 Oe and frequency 1117 Hz. As shown in Fig. 2d, FC/ZFC susceptibility is essentially temperature independent, indicating the sample is a Pauli paramagnet before the onset of superconductivity. A sharp drop indicating the magnetic onset of superconductivity appears at over 11 K, which is the same as the result of measuring AC susceptibility (as shown in Fig. 2e). Considering that the FC susceptibility is flat down to 5.0 K, the superconducting volume fraction will be over 84% under the remnant field of about 30 Oe. Strong diamagnetic signals can be more clearly seen at 11.05 K in both ZFC and FC. The volume fraction of magnetic shielding (ZFC) is about 89%, indicating bulk superconductivity. The mass susceptibility of the shielding measurement at 3 K is $-0.02728\ \mathrm{cm}^3/\mathrm{g}$. From this, one can roughly estimate the superconducting volume fraction by $S=4\pi\chi_g\rho_s$ (where χ_g and ρ_s are magnetic susceptibility and density value of sample, respectively) [1–3,6,10]. Unlike the previous report on anisotropy Pb nanowire arrays [15], this strong T_c enhancement in such an isotropic nanostructured material is something very unusual. Based on isotropic solid and hollow microsphere, in fact, this contribution is from a significant volume fraction of the sample and the modified phonon frequencies of the surface layer of the microspheres, which is similar to the aforementioned report [15]. However, until now, the detailed physical mechanism to explain the origin of the T_c enhancement is still under our further investigation.

In conclusion, we have presented the morphologically controlled growth of isotropic hollow microsphere through an economical and facile solvothermal rout. This approach requires neither a single-crystal surface nor templates of any kind. Characterization of the Pb isotropic microsphere confirms their exceptional crystalline quality and indicates their suitability for numerous wide-ranging applications. Surprisingly, the bulk superconductivity of these Pb isotropic microsphere with such high T_c is confirmed by AC and DC magnetization measurements.