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A novel way to synthesize Pb nanotapes in liquid ammonia

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Abstract

Lead nanotapes were synthesized in liquid ammonia solvent in the presence of sodium metal at low temperature. The process was template free. Transmission electron microscopy (TEM) observations and X-ray diffraction (XRD) characterizations revealed that the as-prepared Pb nanotapes have average diameters in the range of 40–50 nm, and lengths up to several hundred nanometers, and exhibit cubic crystal structures.

Keywords: Pb; Nanotapes; Chemical synthesis; Liquid ammonia

The synthesis of one-dimensional metal and semiconductor materials has received much attention recently because of their potential use in fabricating nanoscale electronic, photonic, and sensing devices [1–4]. Up to now, considerable effort has been focused on the fabricating of these one-dimensional materials and some nanowires such as Ag [5,6], Ni [7], Cu [8], InP [9], In_2O_3 [10] and GaN [11]. have been successfully synthesized. Many experimental approaches of fabricating nanotapes have been reported, utilizing a variety of nanofabrication techniques and crystal growth methods, including electrodeposition [7], thermal decomposition [12,13], template synthesis [14], vapor–liquid–solid (VLS) growth [9,11,15], catalytic chemical vapor deposition (CVD) growth [10,16], and so on.

In this paper, we demonstrate a novel method to prepare Pb nanotapes without template. The process was performed in liquid ammonia in the presence of sodium metal. The ability of liquid ammonia dissolving alkali and alkaline earth metals to form blue solutions is one of its most remarkable and useful properties. Such solutions contain stable solvated electrons and have been consequently used in both organic and inorganic chemistry [17,18]. Compared with conventional reduction in aqueous solvent, this method is carried out at very low temperature (below the boiling point of ammonia, -33.4 °C). However, the solvent can be recycled, it is expected that the method could be used in industrial scale as a cheap and convenient way in preparation of chemicals.

Lead(II) iodide and sodium metal were of chemical purity and used as received. Ammonia gas was produced by dropping ammonia liquor onto sodium hydroxide. The synthesis reaction was processed in a DC-4006 low temperature thermostat. The temperature can be adjusted in the range of -40 to 90 °C, and absolute ethanol was used as medium in the bath. The structure of synthesized nanotapes was characterized on a Philips X'per pro X-ray powder diffractometer (XRD), using Cu Kα radiation (λ = 1.5418 Å), the operation voltage and current were 40 kV and 40 mA, respectively. The morphology and selective area electron diffraction (SAED) patterns of nanotapes was

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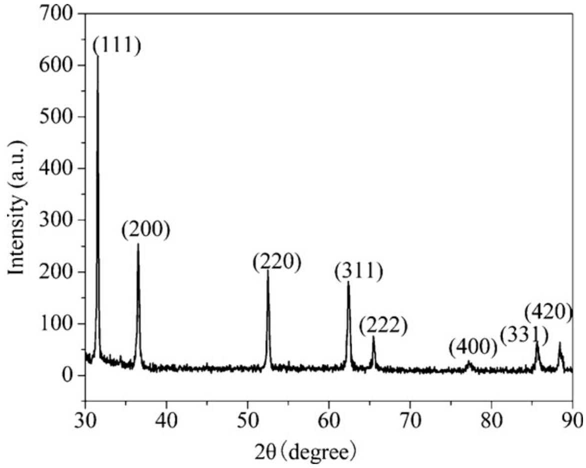

Fig. 1. XRD patterns of Pb nanotapes.

observed on a JEOL TEM-2010 transmission electron microscope (TEM); for the observations, samples were prepared by dropping the product powder ethanol dispersion on carbon-coated Cu grids, and observed under an electric potential of 200 kV. The surface structure charaction of Pb nanotapes was performed on an AVATAR 360 Fourier transform infrared spectroscopy (FT-IR) using KBr pellet. The element analysis of nanotapes was measured on an Oxford Link ISIS energy-dispersive X-ray spectrometer (EDX).

In a typical procedure, a 250 mL three-neck flask was kept in the thermostat bath. The flask was equipped with a drain sleeve, which was connected with outer-cycle of the thermostat so that the ammonia gases can be condensed to liquid ammonia. The temperature of thermostat was set to -40 °C. After the temperature was lower than -34 °C, ammonia gas was produced by dropping ammonia liquor onto a large amount of solid sodium hydroxide, and it was dried through two solid NaOH columns before led into drain sleeve. Ammonia gas was condensed to liquid ammonia in the flask, after about 50 mL liquid ammonia was collected, 0.92 g PbI_2 (2.0 mmol) was added to the flask, under violent stirring. After the dispersion of PbI_2 in liquid ammonia, the colour of suspension was white. Later, 0.69 g (30 mmol) of sodium metal was carefully added to the flask and the colour of solution became dark. After 30 min at -40 °C, 60 mL of absolute ethanol was carefully added to the flask to quench the reaction. The reaction mixture was kept at ambient temperature over night. The ammonia gas from the flask was absorbed by distilled water. The black precipitate was filtered and washed six times with 80 mL absolute ethanol, then dried in vacuum at room temperature for 2 days. The black powder was the expected product, Pb nanotapes.

XRD measurements were made on the bulk samples and to assess the overall crystal structure and phase purity of the product. Fig. 1 shows the XRD patterns of as-prepared Pb nanotapes. The diffraction peaks at $2\theta = 31.2°$, 36.2°, 52.2°, 62.1°, 65.2°, 76.9°, 85.4° and 88.2° correspond to the (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (3 3 1) and (4 2 0) planes, respectively. All the diffraction peaks can be indexed to a cubic structure Pb according to the literature pattern (JCPDS 04-0686). The strong intensities of the Pb diffraction peaks relative to the background signal exhibit that the resulting powder had high purity of the cubic Pb Phase. XRD pattern also indicates that there is no impurity in the product. The results show that PbI_2 was reduced to Pb perfectly. It is supposed the reaction mechanism is that sodium metal dissolved in liquid ammonia, which contains solvate electrons, reduced Pb^{2+} to Pb^0.

Fig. 2 shows TEM images of Pb nanotapes. A typical whole morphology and SAED of Pb nanotapes is shown in Fig. 2a. It can be seen that the most of nanotapes are straight and uniform along their entire length with an average diameter of about 40–50 nm and lengths up to several hundred nanometers. The orientations of Pb nanotapes are in disorder. The spotty diffraction rings in Fig. 2a (inset) show the polycrystalline nature of the Pb nanotapes. Fig. 2b shows a part of individual Pb nanotapes. It can be seen that the surface of nanotapes is smooth, and the diameter is uniform along the length. The formation mechanism of Pb nanotapes is not very clear, but we suppose that it may be as follows: As it is well known that the ammoniate electron is in a cavum surrounded by ammonia molecules, both reduction and nucleation reactions processed in these cavums. The surface of Pb nanocrystals adsorbed a large amount of ammonia molecules, which formed chains through hydrogen bond; this is assisting Pb nanocrystals to growth of nanotapes.