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A simple route to alkylamine capped antimony nanoparticles

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ABSTRACT

We report the synthesis of antimony (Sb) nanoparticles using a simple solution based thermolysis route. The Sb nanoparticles were capped by the alkylamines, oleylamine (OAm), hexadecylamine (HDA) and dodecylamine (DDA). The electron microscopy results show that well-ordered, monodispersed particles are formed when Sb is capped with OAm and HDA. The X-ray diffraction patterns show peaks indexed to orthorhombic Sb.

1. Introduction

Antimony (Sb) is a semimetal with interesting features such as low conduction band, effective mass, high electron mobility and highly anisotropic behavior [1]. The small overlap of the valence and conduction band of antimony (180 meV at 4.2 K) is typical of semimetals such as bismuth [2]. This material finds usage in electronics such as an anode in Li-ion battery due to its high Li-storage capacity [3]. The use of Sb for the electroanalytical determination of Pb^{2+} and Cd^{2+} by linear sweep anodic stripping voltammetry (LSASV) using modified boron doped diamond electrodes was reported [4]. It has been a challenge to synthesize monodisperse colloidal nanoparticles of Sb. Synthetic methods to Sb, such as solution phase methods, solvothermal synthesis, electrodeposition, mechanochemical reduction have been reported [3,5–8]. Kovachenko et al. [9] reported the colloidal synthesis of Sb by injecting a Sb precursor (tris(dimethylamino)antimony(III) [$Sb(NMe_2)_3$]) or (antimony(III) chloride) into a hot (150–200 °C) solution containing a mixture of trioctylphosphine (TOP), lithium diisopropylamide ($LiN(iPr)_2$) and oleylamine (OAm). Sb particles with sizes in the 10–20 nm range were obtained. Another convenient route to Sb nanoparticles is the reduction of $SbCl_5$ with an alkoxide-activated hydride [1].

We report a simple route to high quality Sb nanoparticles stabilized by oleylamine (OAm), hexadecylamine (HDA) and dodeylamine (DDA). The synthesis method is similar to our previous work on bismuth nanoparticles [10].

2. Experimental

Chemicals: Antimony chloride ($SbCl_3$), sodium borohydride ($NaBH_4$), deionized water, methanol, tri-n-octylphosphine (TOP), hexadecylamine (HDA), tri-n-octylphosphine oxide (TOPO), oleylamine (OAm), dodecylamine (DDA), and toluene were purchased from Aldrich. All chemicals were of analytical grade and used directly as purchased without further purification.

Synthesis of antimony nanoparticles: In a typical room temperature reaction, antimony chloride (0.080 g and 0.32 mmol) was mixed with deionized water (10.0 mL) in a three-necked flask. The solution of 10 mL of sodium borohydride (0.031 g and 0.79 mmol) was carefully added to this mixture and the flask was immediately purged with nitrogen gas to create an inert atmosphere. The mixture was stirred for 2 h followed by the addition of excess methanol. The resultant solution was then centrifuged. The black particles produced were dispersed in tri-n-octylphosphine, TOP (6.0 mL) and stirred continuously to form a TOP–Sb solution, which was then injected into hot oleylamine (6.0 g) at 230 °C. A sudden decrease in temperature was observed. The temperature was kept constant at 230 °C for 2 h after the reaction was removed. An immediate addition of methanol resulted in the reversible flocculation of the nanoparticles. After centrifugation the particles were dissolved in toluene to give a solution of nanocrystallites for characterization.

The above reaction procedure was repeated using oleylamine (OAm) and dodecylamine (DDA) keeping all reaction parameters unchanged.

Characterization: The crystallinity of the dried colloids was determined by powder X-ray diffractometry (XRD). Powder diffraction patterns were recorded in the high angle 2θ range of 5–80° using a Bruker AXS D8 Advance X-ray diffractometer, equipped with

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nickel filtered Co Kα radiation = 1.5418 Å at 40 kV, 40 mA at room temperature. The scan speed and step sizes were 0.05° min^{-1} and 0.00657 respectively. For transmission electron microscopy (TEM) samples were prepared by placing a drop of dilute solution of nanoparticles on Formvar-coated grids (150 mesh). Holey carbon grids were used for high resolution TEM. The samples were allowed to dry completely at room temperature and viewed using a JEOL 1010 TEM and JEOL 2100 HRTEM. Viewing was done at an accelerating voltage of 100 kV (TEM) and 200 kV (HRTEM), and images were captured digitally using a Megaview III camera, stored and measured using Soft Imaging Systems iTEM software. The surface morphology of the nanoparticles was observed by a Zeiss Ultra Plus FEG SEM at 10 kV, equipped with an Oxford detector EDX at 30 kV which uses Aztec software for elemental analysis. The samples were coated with gold using Polaron SC 500 sputter coater.

3. Results and discussion

In this work the bismuth chloride was replaced by antimony chloride. The injection of precursors into a hot coordinating solvent is a well established route to good quality capped nanoparticles. This so called 'hot injection' route makes use of various types of capping groups such as phosphines, alkylamines or thiols. Amongst the alkylamines, hexadecylamine (HDA) has proven to be effective in passivating nanoparticles allowing some degree of shape manipulation [11]. Recently there have been many reports of the use of oleylamine (OAm), another long chain primary amine which acts as an electron donor at high temperature, as a capping group. OAm is especially effective as a capping group for the synthesis of nanomaterials comprising of one magnetic element [12]. There have been very few reports of uniform size and shape of Sb nanoparticles. Methods that use precursors in hot solvents employ Sb alkylamide precursors because these lead to fast and controlled nucleation [9]. In our work we have used readily available antimony chloride as the starting material with sodium borohydride as the reducing agent. The initial reduction is carried out for 2 h. The isolated Sb particles are then dispersed in tri-n-octylphosphine (TOP). The TOP/alkylamine co-surfactant combination results in the formation of stable, uniform particles grown at moderate temperature. We chose hexadecylamine, oleylamine and decylamine as the capping groups for Sb nanoparticles to compare any changes in

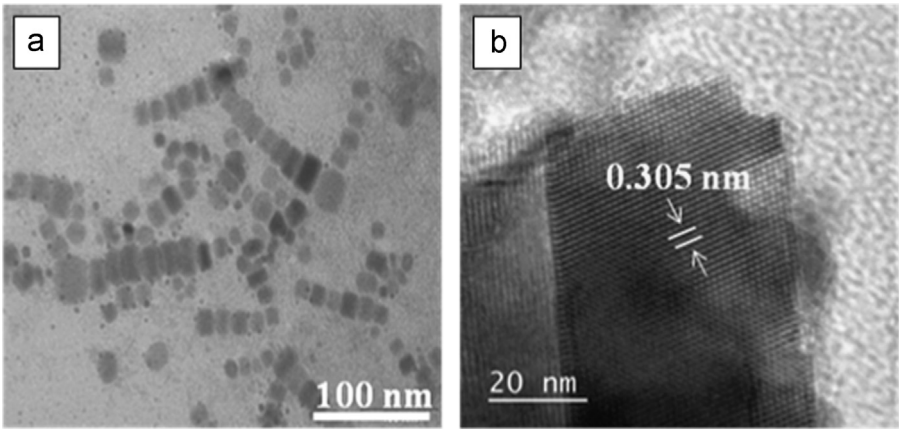

Fig. 1. (a) TEM and (b) HRTEM images of OAm capped Sb nanoparticles synthesized.

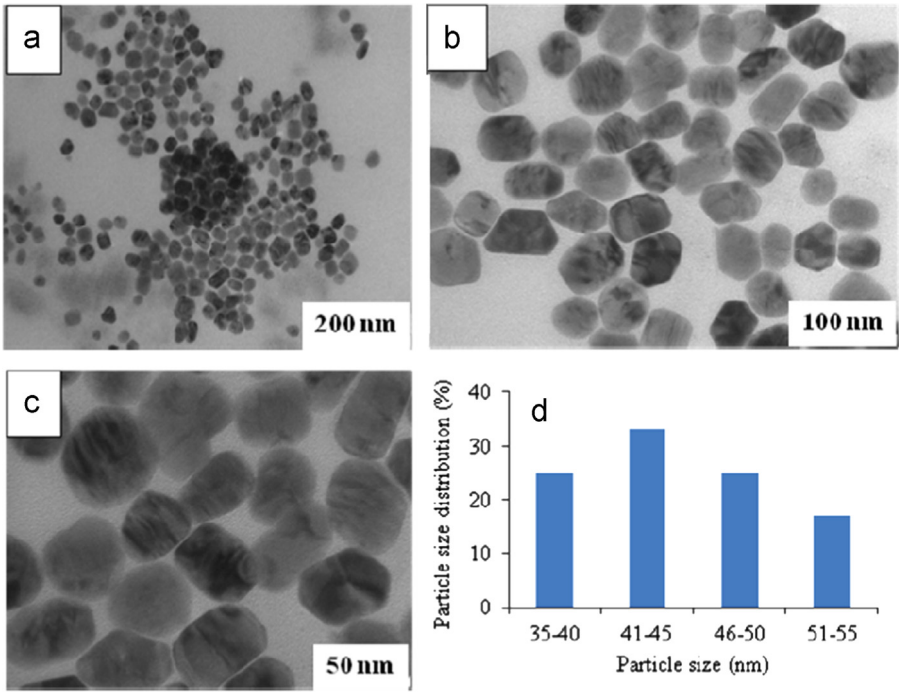

Fig. 2. (a,b) TEM, (c) HRTEM images and (d) particle size distribution histogram of HDA capped Sb nanoparticles.