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Synthesis of size-controlled and discrete core–shell aluminum nanoparticles with a wet chemical process

Yue Cui [a,b], Suling Zhao [a,b,*], Dongliang Tao [c], Zhiqin Liang [a,b], Di Huang [a,b], Zheng Xu [a,b]

[a] *Key Laboratory of Luminescence and Optical Information, Beijing Jiaotong University, Ministry of Education, Beijing 100044, PR China*
[b] *Institute of Optoelectronic Technology, Beijing Jiaotong University, Beijing 100044, PR China*
[c] *College of Chemistry and Chemical Engineering, Fuyang Normal College, Anhui 236000, PR China*

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ABSTRACT

We report a facile strategy for preparing aluminum nanoparticles (Al NPs) with a triphenylphosphine (PPh_3) shell by a wet chemical process and the effects of the organic-ligand/Al ratio on the resultant stability and particle size. X-ray diffraction (XRD) analysis confirmed the face-centered-cubic (fcc) Al NPs, and the surface structure was observed by scanning electron microscopy (SEM). Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and Fourier transform infrared spectrometry (FT-IR) showed that the particle sizes range from 50 to 120 nm with a discrete 3 nm PPh_3 shell. Differential scanning calorimetric–thermal gravimetric analysis (DSC–TG) of Al@PPh_3 core–shell nanoparticles indicated that the melting point of prepared Al NPs is 620 °C, which is much lower than that of the bulk materials.

1. Introduction

Al NPs, which have high combustion enthalpy and release an extremely large amount of energy per volume of reactants over conventional energetic materials, are widely used in various applications due to their special chemical and physical characteristics. Because of their potential to enhance the energy content of energetic materials and reactive nature, Al NPs have prompted interest in their application as fuels, explosives, and energy stores [1,2].

Despite apparent benefits, there are still some undesirable characteristics impairing their performance and applications. Al NPs are prone to attack by air and water during storage [3], and their pyrophoric nature requires passivation by an oxide layer at the particles' surface to act as a barrier for further oxidation [1,4,5]. The oxide layer results in a reduction of energy density and an elevated temperature for ignition, which may cause thermal defects [6,7].

To avoid the loss of active constituents, some chemical methods with protective coatings around the surface have been developed to overcome this obstacle [8–12]. However, these capping schemes have demonstrated limited air stability, broad size distribution and a high degree of aggregation. Herein, we report the first successful example of the synthesis of Al NPs coated with a small organic molecule by a wet chemical process, and the morphological control and reaction mechanism have been discussed.

2. Experimental

$AlCl_3$ (2 mmol) and PPh_3 (20 mmol) were mixed with 40 mL of trimethylbenzene in a bottom flask, and stirred for 0.5 h. 10 ml of trimethylbenzene containing $LiAlH_4$ (6 mmol) was slowly added to the flask. Subsequently, the solution was heated to 164 °C and maintained for 1 h. All reactions were under argon protection. The prepared Al NPs were extracted by a centrifugation process, and washed with 0 °C methyl alcohol and tetrahydrofuran (THF) several times.

Size and structure were determined by XRD, SEM (Hitachi, S-4300), HRTEM (JEM-2100F), and FT-IR (Nicolet-6700) spectroscopy. DSC–TG (DSC200F3) analysis was conducted from room temperature to 800 °C under a dynamic argon atmosphere.

3. Results and discussion

The reaction is explained by the following equation: 1

$$AlCl_3 + LiAlH_4 + PPh_3 \rightarrow Al@PPh_3 + LiCl + H_2 \qquad (1)$$

Fig. 1(a) shows the XRD patterns of Al NPs, which agrees with the JCPDS (no.: 04–0787), and no peak is related to Al_2O_3. If Al_2O_3 was formed during the reaction process, it's peaks have been obtained [13].

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[*] Corresponding author at: Institute of Optoelectronics Technology, Beijing Jiaotong University, Beijing 100044, PR China. Tel.: +86 10 51684462.
E-mail address: slzhao@bjtu.edu.cn (S. Zhao).

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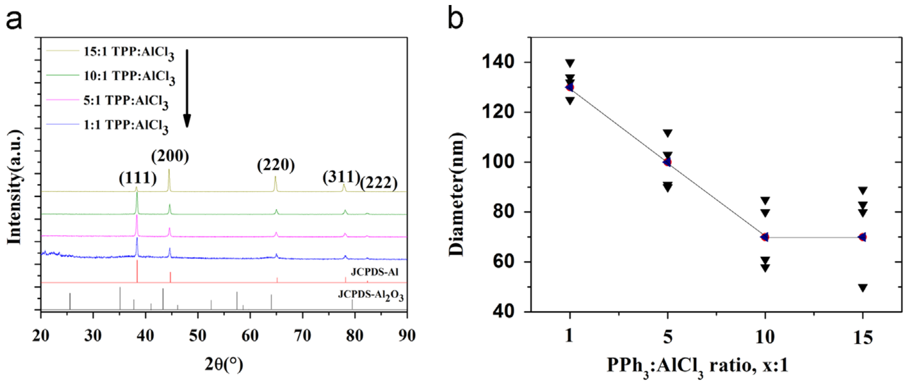

Fig. 1. (a) XRD patterns of prepared Al NCs in the range of TPP:$AlCl_3$ ratios. (b) The size of Al@PPh_3 NPs at 1:1, 5:1, 10:1, and 15:1 PPh_3:$AlCl_3$ molar ratios. Data points were calculated using the Scherrer equation on the half-height peak-width measurements from up to four separately measured XRD patterns. The blue-circled data points linked by a dotted line represent the mean size for the calculated diameter values from each set of XRD peaks. (For interpretation of the reference to color in this figure, the reader is referred to the web version of this article).

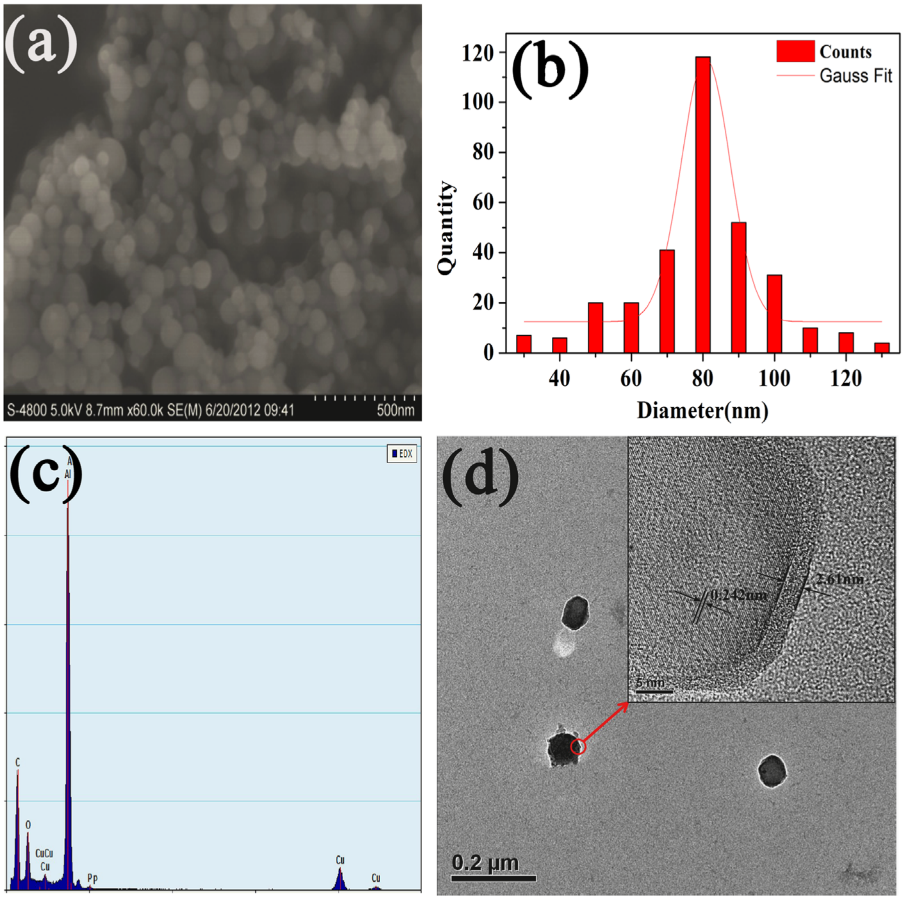

Fig. 2. (a) The SEM image of prepared Al NPs. (b) Size distributions of the Al particles prepared at 164 °C with the PPh_3:$AlCl_3$ at 1:10. (c) EDS analysis on the PPh_3/Al NPs. (d) TEM and HRTEM images of Al@PPh_3 NPs.

The dependence of particle size on the PPh_3/$AlCl_3$ ratio is shown in Fig. 1(b). As the ratio increases, the median particle size decreases, but the distribution broadens. The higher the PPh_3:$AlCl_3$ ratio, the higher the capping agent concentration. This size variation may be due to the increasing solution viscosity. The higher viscosity may lead to less effective reagent mixing, which results in greater embryo and nuclei non-uniformities in size and in the local reaction environment. Therefore, a wider range of Al nanoparticle core sizes before PPh_3 capping will be produced. Once capping begins, the growth of Al NPs ceases.

The microscopic investigation is demonstrated in Fig. 2. SEM images (Fig. 2(a)) and size distributions (Fig. 2(b)) show that the size distribution is uniform. The energy dispersive X-ray spectrometer (EDS) analysis (Fig. 2(c)) indicates a strong peak corresponding to the Al element. Carbon and phosphorus peaks could be attributed to elements of PPh_3. It is concluded that the main element of the prepared sample is Al.

TEM and HRTEM images (Fig. 2(d)) confirm the core–shell structure. The lattice fringe is 0.23 nm, which corresponds to the (111) plane of the Al crystal. The outer shell is composed of an