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Self-templated synthesis of polycrystalline hollow aluminium nitride nanospheres†

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Polycrystalline hollow AlN nanospheres with diameters ranging from 20 to 200 nm and shell thickness of about 10 nm were successfully synthesized through the reaction of irregular Al nanopowder with a CH_4–NH_3 mixture at around 1000 °C by the self-templated method. The products were well characterized by X-ray diffraction, high-resolution transmission electron microscopy, Raman spectroscopy and photoluminescence measurements. The photoluminescence properties of the hollow AlN nanospheres showed the routine blue emissions for AlN nanoparticles as well as an unusual green emission at around 533 nm, indicating the potential for luminescent devices. The synthesis mechanism was reasonably speculated and further supported by the similar synthesis of hollow AlN nanospheres from regular Al particles.

Introduction

The successful applications in (opto)electronic devices in the past decades make group III nitrides, mainly including GaN, AlN, InN and their alloys, recognized as one of the most important material systems for bandgap engineering.[1] Their superior properties are demonstrated by the light emission covering continuously from the near-IR to the UV region, excellent thermal conductivity and hardness, high resistance to chemicals and high melting point. Their nanoscale quantum confinement geometries, such as nanowires, nanotubes and nanoparticles, are particularly important not only for understanding the fundamental concepts underlying their observed electronic, optical, and mechanical properties, but also for their wide potential applications in future nanodevices such as field effect transistors and nanoscale light-emitting diodes.[2,3] As an important member, hexagonal AlN has a wide bandgap of 6.2 eV and a very small (even negative) electron affinity.[4] Its nanostructures have been attracting increasing attention and much progress has been made in nanoparticles and nanowires.[3,5–9] Very recently, some interesting AlN one-dimensional nanostructures including nanotubes,[10–12] nanobelts[13] as well as nanocones[14] have been discovered. The novel faceted cross-session morphology for h-AlN nanotubes is particularly attractive for extending nanotubular structures from layered compounds to non-layered compounds.[10,15] In addition, it is found that AlN nanowires and nanocones exhibit excellent field emission properties as expected due to the combination of one-dimensional geometry and its small or even negative electron affinity.[8,14a,b] Such advancement in nanostructures and related properties of AlN, especially the existence of AlN nanotubes, stimulates our interest in exploring hollow AlN nanospheres, in reference to the excellent association between nanotubes and fullerenes.[16] Actually, hollow spheres themselves are important morphologies of current intensive interests due to their lower density, higher surface area, and distinct optical, electrical and magnetic properties compared with their bulk materials.[17,18] In this paper, we have developed a self-templated synthesis route, with which polycrystalline hollow AlN nanospheres ranging from 20 to 200 nm in diameter have been obtained and well characterized. The synthesis mechanism was reasonably speculated. The photoluminescence properties of the product indicate the potential for luminescent devices.

Experimental

0.5 g of commercially available Al nanopowder synthesized by laser-induction complex heating evaporation (Shenzhen Junye Nano Material Co., Ltd., China) was placed in an alumina boat and set in the central zone inside a horizontal alumina tube furnace. This Al precursor consisted of irregular nanoparticles, mainly nanospheres and nanowires with diameters of 20–200 nm and 10–100 nm respectively (Fig. 1a). Surface oxidation existed as reflected by a trace of diffraction peaks corresponding to δ-Al_2O_3 species (Fig. 1c). The reaction system was flushed with Ar several times to remove the oxygen and moisture, then heated in Ar at a rate of 5 °C min^{-1} to 700 °C. The Al precursor remained almost unchanged during this stage as learnt from the corresponding transmission electron microscopic (TEM) image (Fig. 1b). As the temperature reached 700 °C, the flow of Ar was replaced by CH_4 and NH_3 of 5 sccm and 500 sccm respectively, and the furnace was subsequently heated to the reaction temperatures of 800, 1000, 1200 or 1300 °C at a rate of 3 °C min^{-1} and kept there for 3 hours. The furnace was then cooled down in NH_3 to room temperature. The products were collected and characterized by

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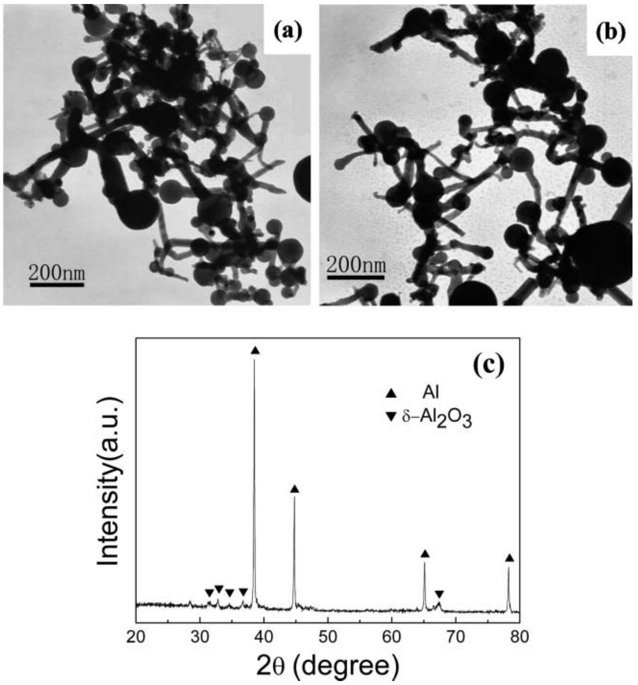

Fig. 1 (a) TEM image of Al nanopowder precursor as-obtained; (b) TEM image of Al nanopowder precursor after progressive annealing to 700 °C in Ar; (c) corresponding XRD curve to (a).

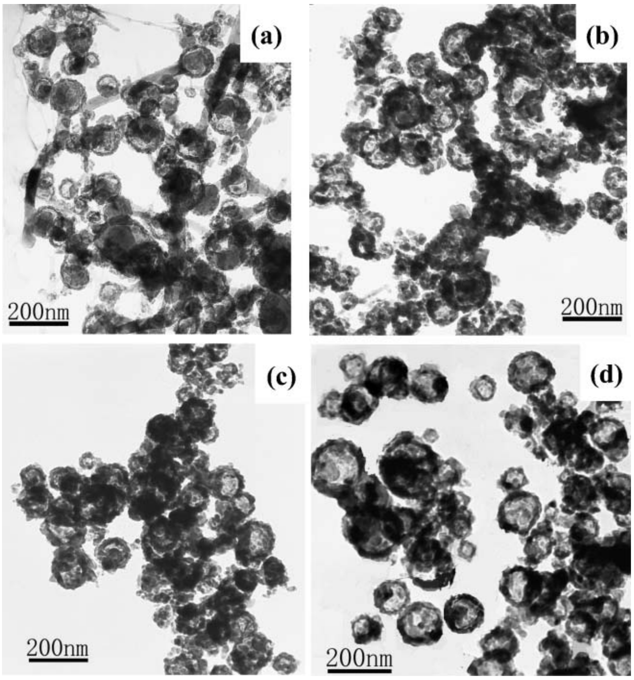

Fig. 2 Typical TEM images of the products obtained at different reaction temperatures. (a) 800 °C; (b) 1000 °C; (c) 1200 °C; (d) 1300 °C.

various methods. X-Ray diffraction (XRD) experiments were carried out on a Philips X'pert Pro X-ray diffractometer with Cu K_α radiation of 1.5418 Å. The morphology and structure of the product were analyzed by TEM (JEOLJEM-1005 at 100 kV), and high-resolution transmission electron microscopy (HRTEM, JEM2010 at 200 kV) equipped with an energy dispersive X-ray spectrometer (EDS, ThermoNORAN). The Raman spectra were recorded on T6400 and JY HR800 laser Raman spectrometers. The room temperature photoluminescence (PL) emission spectrum was measured using an Amino Bowman Series-2 spectrometer with a He–Cd laser with excitation at 325 nm.

Results and discussion

Fig. 2 shows typical TEM images of the as-prepared products for different reaction temperatures. It is seen that a large portion of the Al nanoparticles changed their irregular morphologies to hollow spherical particles of 20 to 200 nm in diameter and 5 to 20 nm in shell thickness, especially when the reaction temperature was higher than 1000 °C. The corresponding evolution of the XRD curves shown in Fig. 3 clearly indicates that these hollow nanospheres are hexagonal AlN (h-AlN), since the XRD curves for pure h-AlN are obtained for the products in Fig. 2c and 2d. Specifically, the product for 800 °C (Fig. 2a) consists of some h-AlN hollow nanospheres and some partially- or un-changed Al precursor mainly in the form of nanospheres or nanowires. Correspondingly, the XRD curve in Fig. 3 for 800 °C is composed of the intensive diffraction peaks for Al and a trace of peaks for h-AlN and δ-Al_2O_3. With increasing reaction temperature, the hollow AlN nanospheres increased accompanied by the consumption of the Al precursor and the δ-Al_2O_3 component, as reflected in Fig. 2 and Fig. 3. This process was completed at around 1200 °C, and correspondingly the XRD curve for the pure h-AlN phase was obtained (Fig. 3, 1200 °C). The XRD curve in Fig. 3 for 1300 °C shows narrower full width at half maximums or sharper peaks than the respective one for 1200 °C, implying that the h-AlN hollow nanospheres obtained at 1300 °C have a higher crystalline degree. Through the preceding correlation of Fig. 2 and Fig. 3,

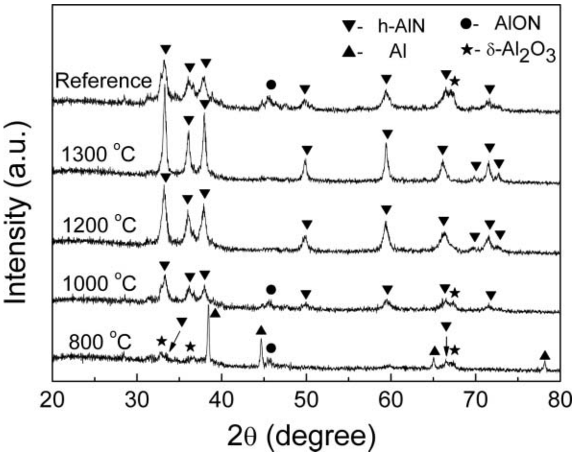

Fig. 3 XRD curves of the products obtained by nitriding the Al nanopowder precursor at the indicated reaction temperatures with CH_4–NH_3. For comparison, the reference curve corresponding to the product by nitriding the Al nanopowder precursor at 1200 °C with NH_3 only (*i.e.* without CH_4) is also presented. It is seen that the oxygen-containing species could not been completely eliminated, indicating the oxygen-scavenger function of CH_4.

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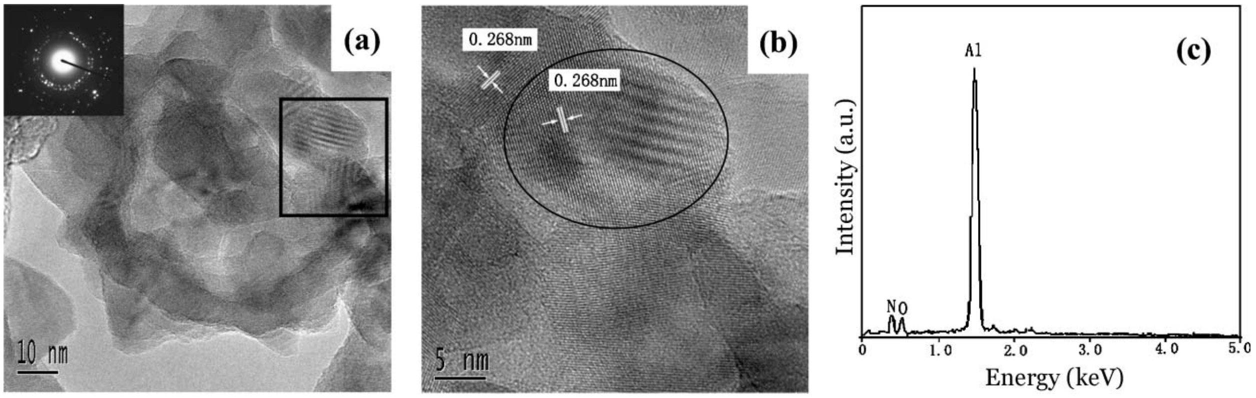

Fig. 4 Typical HRTEM images of a hollow h-AlN nanosphere and the corresponding EDX spectrum. (a) HRTEM image; (b) enlargement of the rectangle part in (a); (c) the corresponding EDX spectrum. Inset in (a) is the SAED pattern.

it is learnt that the formation of h-AlN hollow nanospheres started at around 800 °C and was complete at around 1200 °C.

HRTEM could give a further insight into the microstructure of the AlN hollow nanospheres. The typical HRTEM image in Fig. 4 shows a hollow nanosphere with about 70 and 50 nm in outer and inner diameters respectively, *i.e.*, with the shell thickness of about 10 nm. It is clearly seen that the shell of the AlN hollow nanosphere is composed of many tightly-connected tiny crystallites of a few nanometres, which forms rather rough outer and inner surfaces. This polycrystalline structure is also confirmed by the selected area electron diffraction (SAED) pattern of sharp rings with sparking spots as shown in the inset of Fig. 4a. From the locally enlarged image in Fig. 4b, the spacing between the neighboring parallel fringes is measured to be about 0.268 nm, corresponding to the d_{100} spacing of h-AlN. The EDS spectrum of the sample in Fig. 4c indicates the components of aluminium at 1.5 keV and nitrogen at 0.4 keV, this is consistent with the AlN crystallites. The signal around 0.5 keV comes from the surface contaminant oxygen which is inevitable for h-AlN products.[8,10,14]

The above experimental results indicate that, by a rather simple self-templated synthesis method, hollow h-AlN nanospheres have been successfully produced for the first time from the common Al nanoparticles precursor. Each hollow h-AlN nanosphere consists of many tightly connected tiny crystallites. In comparison with any other reported AlN nanostructures such as nanoparticles,[3,5] nanowires,[6–9] nanotubes,[10–12] nanobelts[13] and nanocones,[14] this novel h-AlN nanostructure has a much higher portion of surface and interfacial atoms, which should be reflected in a microstructure-sensitive detection. Accordingly, Raman spectroscopy was applied to examine the products. Fig. 5 shows the Raman spectra of the hollow h-AlN nanospheres for 1300 °C (Fig. 2d) from two different Raman spectrometers. Both curves show only a singlet around 659 cm^{-1} corresponding to the E_2 (high) mode of h-AlN,[19] which is indeed different from the reported Raman spectra for AlN in literatures where several other modes of A_1(TO), A_1(LO), E_1(TO) and E_1(LO) are usually observable.[13,20] The disappearance of the other modes may result from the increase of defects or disorder degree due to the rather high portion of surface and interfacial atoms. Actually, the weakening or disappearing of some modes with increasing surface atoms, hence defects, could be inferred from the Raman spectrum for AlN nanocrystalline powders where only two modes of A_1(TO) and E_2 (high) were observed.[21] A similar tendency could also have been found for nanostructured GaN.[22] The slight blue-shift of the E_2 (high) mode to high phonon frequency in comparison with the value of about 654 cm^{-1} for an AlN single crystal[19] could be understood by the compressive stress[23] arising from the shrink of the shell on cooling from 1300 °C to ambient in the final stage of the sample preparation.

It is known that nanocrystalline AlN structures are promising for light-emitting applications due to their efficient visible luminescence in the 2–4 eV region.[21,24,25] The room temperature photoluminescence (PL) properties of the hollow AlN nanospheres were also measured for comparison. As shown in Fig. 6, the PL spectrum has a broad emission band ranging from ultraviolet (353 nm, 3.52 eV) to yellow emission (660 nm, 1.88 eV). A dominant blue emission peak is seen at around 468 nm (2.65 eV) which is attributed to oxygen impurities[26] or nitrogen vacancies.[21,27] Actually, the oxygen impurities were detected in the EDS spectrum in Fig. 4c. The emission at around 402 nm could be assigned to the native defects.[25] Notably, a green emission at around 533 nm which is very weak or negligible for AlN nanoparticles[21,25] obviously appeared for the hollow AlN nanospheres. It seems that this

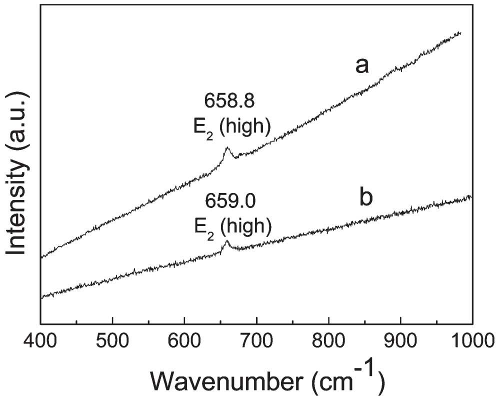

Fig. 5 Raman spectra of the hollow h-AlN nanospheres recorded on T6400 (a) and JY HR800 (b) laser Raman spectrometers, respectively.

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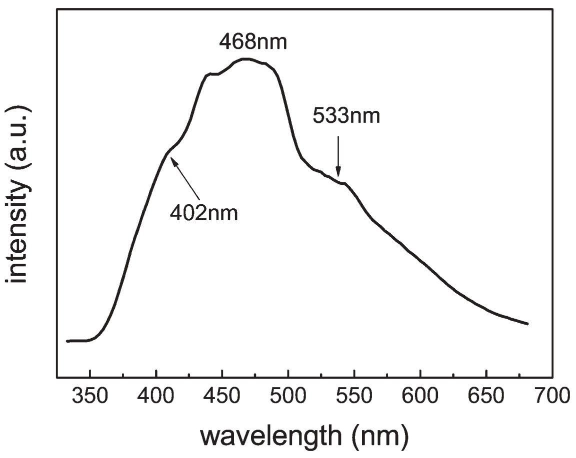

Fig. 6 Photoluminescence spectrum of the hollow h-AlN nanospheres.

emission is morphologically related since similar changing behavior was also observed by comparing the emissions at around 470 nm in PL spectra for GaN particles and hollow spheres.[18] This indicates the potential applications of the hollow AlN nanospheres in luminescent devices.

The synthetic mechanism could be reasonably speculated as illustrated in Fig. 7. When the mixture gases of NH_3 and CH_4 were introduced into the system at a temperature higher than 700 °C, the outer δ-Al_2O_3 layer of the Al powder precursor (Fig. 7a) was reduced to Al, AlON and gaseous Al_2O intermediates through the typical carbothermal reduction by CH_4 and nitridation reactions.[28] Here the trace of CH_4 acted as an oxygen scavenger to clean the Al particle surface, otherwise the oxygen-containing species could not been completely eliminated as reflected in the reference curve in Fig. 3. Accompanied with the consumption of the solid δ-Al_2O_3 shell, the inner Al liquid droplets (the melting point of Al is 660 °C) shrank into spherical balls due to the surface tension. The outer shell of the Al balls were then nitrided by NH_3 to form a core–shell structure composed of Al and AlN respectively (Fig. 7b). The solid AlN shell generated herein functioned as the barrier layer preventing the direct contact of Al and N species, and the further formation of AlN is dominated by the Kirkendall effect.[29] Specifically, the outwardly diffused Al atoms reacted with NH_3 to form the AlN species on the surface of the pre-formed AlN shells since the outward transport rate of Al atoms is much faster than the inward transport rate of N species through the AlN shell.[29] As a result, the inner Al core was gradually evacuated with increasing thickness of the AlN shell (Fig. 7c). Finally, polycrystalline hollow AlN nanospheres were obtained (Fig. 7d). It is seen that, during the reaction process, the Al nanoballs acted not only as the reagent but also as the template just like the roles of MoO_3 nanoparticles in the synthesis of hollow MoS_2 nanospheres,[30] which is a typical self-templated synthesis route. However, different from the cases in which layered compounds such as MoS_2 and WS_2 could form fullerene-like nanostructures,[31] as a non-layered compound, h-AlN formed polycrystalline hollow nanospheres, analogous to the cases in which polycrystalline hollow spheres of GaN and SiO_2 were formed from the corresponding non-layered compounds.[18,32] By replacing the irregular oxygen-containing Al nanopowder with regular oxygen-negligible Al nanoparticles, similar hollow AlN nanospheres could still be synthesized even with only NH_3 as a reaction gas, *i.e.* without the added trace CH_4 (see ESI†), which is in support of the speculated mechanism. This also indicates the oxygen-scavenger function of the trace CH_4 in this study.

Conclusion

In conclusion, a simple self-templated route has been developed by the reaction of Al nanoparticles with a mixture of NH_3–CH_4 gases at a temperature of around 1000 °C and polycrystalline hollow AlN nanospheres have been successfully synthesized for the first time. Despite the irregular morphologies of the Al nanoparticle precursor, the obtained product is fairly spherical with the diameters ranging from 20 to 200 nm and a shell thickness of about 10 nm. Different from the reported Raman spectra for AlN in the literature, the Raman spectrum of the product shows only a singlet at around 659 cm^{-1} corresponding to the E_2 (high) mode of h-AlN, probably resulting from the unique nanostructures. In addition to the routine blue emissions for AlN nanoparticles, the photoluminescence properties of the hollow AlN nanospheres show an unusual green emission at around 533 nm, indicating potential applications in luminescent devices. The synthesis mechanism is also speculated and further supported by the similar synthesis of hollow AlN nanospheres from regular Al particles.

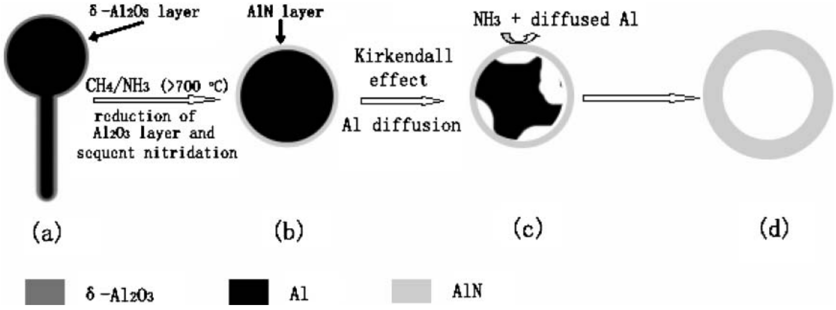

Fig. 7 Schematic diagram of the self-templated route for the synthesis of the hollow h-AlN nanospheres. (a) An irregular Al nanoparticle with a thin outer layer of δ-Al_2O_3; (b) the formation of the core–shell nanostructure of Al/AlN; (c) the growth of the AlN shells through the reaction of outwardly diffused Al with NH_3 through the Kirkendall effect; (d) the formation of the polycrystalline hollow AlN nanospheres.

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