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Short communication

Synthesis of AlN porous-shell hollow spheres by a combustion route

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Abstract

Aluminum nitride (AlN) porous-shell hollow spheres with diameters ranging from 2 to 3 μm and porous-shell thickness of about 120 nm were successfully prepared via a facile combustion synthesis route in the presence of polytetrafluoroethylene (PTFE), in which porous-shell was composed of a large number of irregular nanoparticles. These synthesized spheres were characterized by X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM) measurements. The possibility of the reactions of PTFE with Al particles was also investigated by thermogravimetry-differential scanning calorimetry (TG-DSC). It was found that PTFE was not only an active agent for the nitridation of Al particles, but also a structure-directing agent for the formation of this hollow structure. Based on the experimental results, a possible model for the growth of AlN porous-shell hollow spheres was proposed.

Keywords: Combustion synthesis; Hollow spheres; Microstructure; Powder technology

1. Introduction

Hollow micro/nanospheres of inorganic materials are a new class of materials and have attracted immense interest owing to their unique properties and potential applications in catalysis, light filter, waste removal, energy storage and microvessels for drug delivery [1,2]. As one of the most popular semiconductor nitrides, aluminum nitride (AlN) has aroused great attention for its potential applications in electronic, light- and field-emission devices [3,4]. Recently, many efforts have been devoted to synthesis and assembly of micro/nanostructured AlN to improve its performance in currently existing applications. Up to now, various AlN micro/nanosturctures such as nanowhiskers [5,6], nanorods [7–9], nanobelts [10], nanotubes [11], nanobrushes [12,13] and micro/nanoflowers [14,15] have been prepared by different methods. However, there are few literatures on the preparation of AlN hollow micro/nanostructures. Ma et al. prepared polycrystalline AlN hollow nanospheres through a self-template synthesis approach with Al nanoparticles precursor [16]. Zhang et al. fabricated AlN hollow nanospheres by a chemical vapor deposition reaction between $AlCl_3$ and NH_3 [17]. To the best of our knowledge, the preparation of AlN hollow micro/nanostructures via a combustion synthesis route has not been reported. Herein, we demonstrated that AlN hollow spheres with porous-shell could be fabricated by a facile combustion synthesis process. Furthermore, a possible mechanism for the formation of the hollow structures was proposed.

2. Experimental procedure

The starting materials were Al powders (spherical particles, 2–3 μm) with the oxygen content of about 0.35 wt%, AlN powders (hollow structures, self-prepared by the same procedure as this work) as diluent and polytetrafluoroethylene (PTFE, $(C_2F_4)_n$) powders. In a typical procedure, Al, AlN and PTFE powders were mixed lightly in mortar with a weight ratio of 28:64:8, and the molar ratio of Al and AlN powders were fixed as to 4:6. After sieving to disperse any large agglomerates, 20 g of the powder mixture was transferred into a porous graphite crucible and ignited under a nitrogen gas pressure of 0.2 MPa.

Phase purity of the synthesized powders were examined by X-ray diffraction (XRD, X-Pert Pro) with Cu $K\alpha$ radiation at

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a scanning rate of 0.2°/min. Morphologies of the powders were observed using a field emission scanning electron microscopy (FESEM, Hitachi S4800). Thermogravimetry-differential scanning calorimetry (TG-DSC, SDT Q600) of the reactants was carried out from 50 to 1300 °C in N_2 atmosphere.

3. Results and discussion

Fig. 1 shows a typical XRD pattern of the as-synthesized product. All the diffraction peaks can be indexed to the hexagonal wurtzite structure of AlN crystal (JCPDS No. 25-1133). No characteristic peaks of impurities were detected in the pattern. The sharp diffraction peaks indicated the good crystallinity of the product.

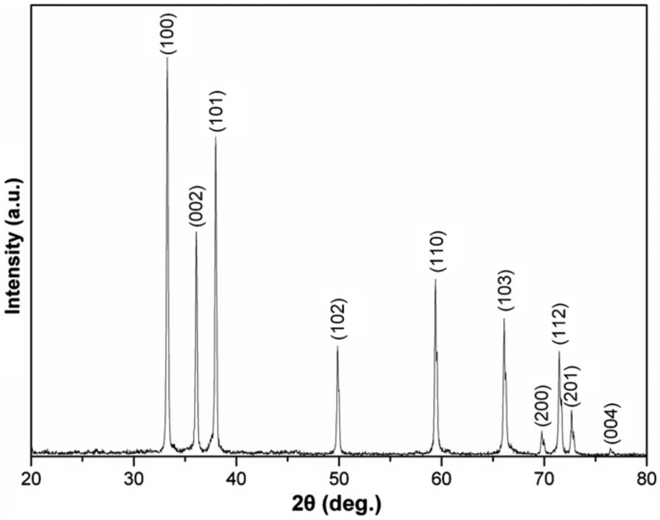

Fig. 1. XRD patterns of the as-synthesized AlN product.

Fig. 2(a) and (b) shows FESEM images of the as-synthesized AlN hollow spheres. The diameter of these spheres was about 2–3 μm, similar as the diameter of the Al powders. This indicated that the Al powders were acted as a template for the growth of AlN hollow spheres. Interestingly, some spheres exhibited broken sites and exposed their hollow interiors, which provided direct evidence that the AlN spheres had a hollow structure, as shown in the inset of Fig. 2(b). A FESEM image of a single hollow sphere is shown in Fig. 2(c). It can be clearly observed that the shell of hollow sphere was porous and composed of a large number of nanoparticles. These nanoparticles were irregular and their size was in the range of 30–120 nm, and the thickness of the shells was about 120 nm (Fig. 2(d)).

Our experimental results suggested that the use of PTFE may play a key role in the formation of the AlN porous-shell hollow spheres. To clarify this point, several parallel experiments with different amount of PTFE or none of it were performed and the results are exhibited in Fig. 3. We found that without PTFE additive, the combustion cannot be triggered. When the amount of PTFE was increased up to 4 wt%, a large number of hollow spheres with closed shells was obtained (Fig. 3(a)), and the thickness of the closed shells was about 400 nm (Fig. 3(b)). With the amount of PTFE further increased to 12 wt%, the sphere-like particles were nearly disappeared and replaced by many fibrous particles (Fig. 3(c)). XRD pattern indicated that the product

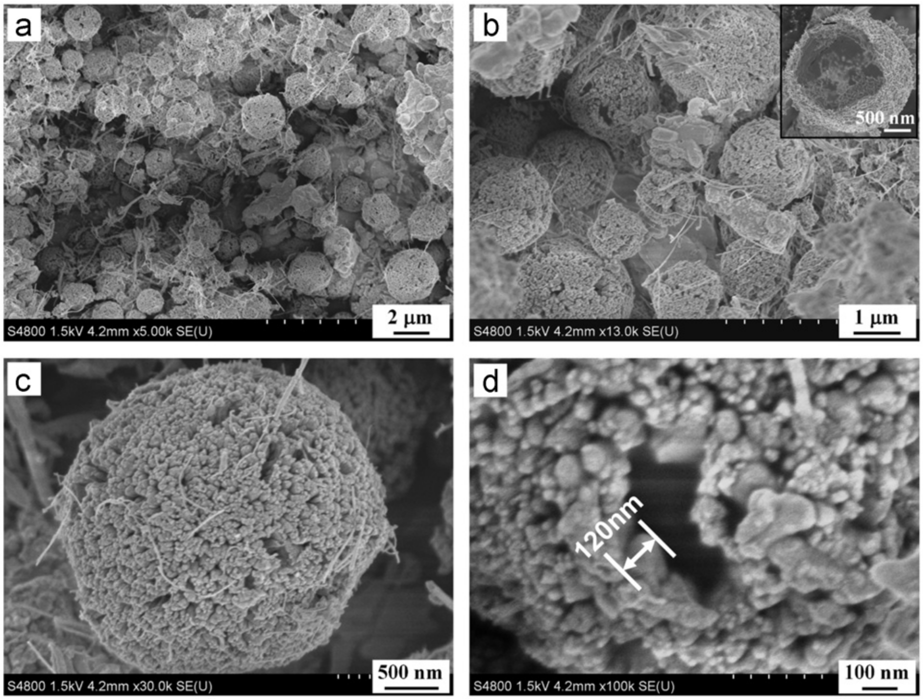

Fig. 2. FESEM images of (a, b) AlN porous-shell hollow spheres with different magnifications (inset of (b): a hollow sphere with broken shell), (c) a single hollow sphere and (d) the surface of the spheres.

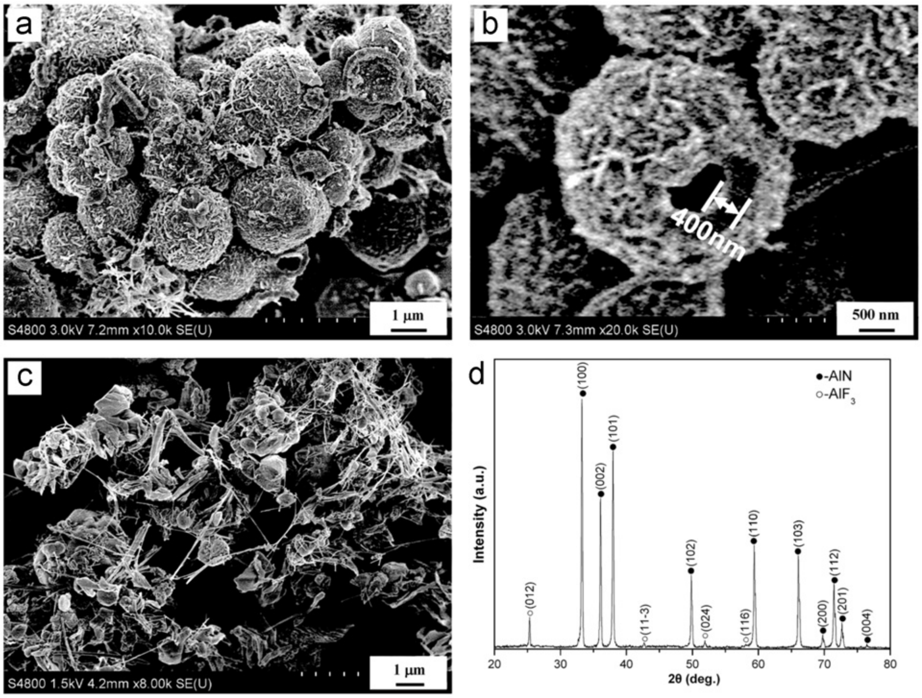

Fig. 3. FESEM images of the AlN products synthesized with the addition of 4 wt% PTFE (a, b), 12 wt% PTFE (c) and its XRD pattern (d), respectively.

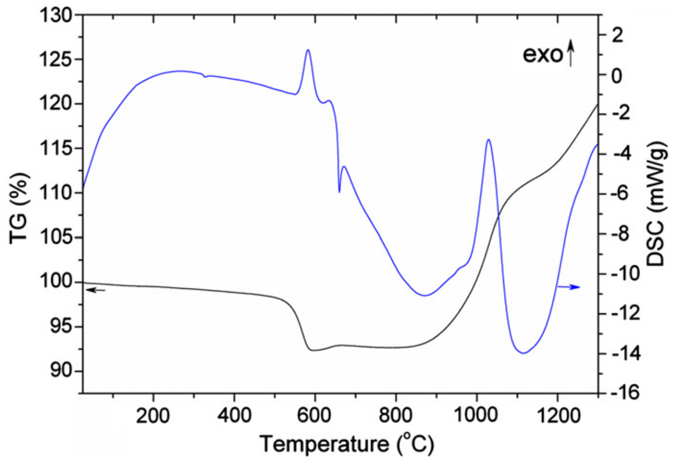

Fig. 4. The TG-DSC curves of the reactants with the weight ratio as the typical procedure.

synthesized with the addition of 12 wt% PTFE was nearly pure hexagonal AlN phase with a trace of AlF_3 (JCPDS No. 44-0231) impurity, as shown in Fig. 3(d).

Fig. 4 shows the TG-DSC result of the reactants with the weight ratio as the typical procedure. The minimum endothermic peak at 322 °C was the phase change of PTFE from solid to liquid. An abrupt weight loss of about 8% at the temperature of 500–600 °C could be attributed to the decomposition of PTFE. However, no corresponding endothermic peak was detected and an exothermic peak at 583 °C was observed. This should be caused by the reaction between PTFE and the oxide shell (Al_2O_3) of the Al particles [18,19]. The reaction can be expressed as follows:

$$Al_2O_{3(s)}+3(C_2F_4)_{n(g)}\rightarrow 4nAlF_{3(s)}+6CO_{(g)} \qquad (1)$$

which was a strong exothermic reaction with $\Delta H=-1373$ kJ/mol, and therefore the endothermic decomposition of PTFE was compensated. Peak at 658 °C corresponded to the melting point of Al particles. Then, the weight gain started at 820 °C because of the nitridation of the Al particles. A strong exothermic peak at about 1025 °C indicated the combustion synthesis could be triggered.

On the basis of the experimental results, the effect of PTFE on the formation of AlN porous-shell hollow spheres can be explained, and a possible growth mechanism is illustrated in Fig. 5. Firstly, nitridation of the Al particle was activated in the presence of PTFE because it can peel off the Al_2O_3 shell surrounding the Al particle (Eq. (1)). Then, the nitridation occurred rapidly at the surface of the Al particle via a direct nitridation pathway:

$$Al_{(l)}+N_{2(g)}\rightarrow 2AlN_{(s)} \qquad (2)$$

which was a strong exothermic reaction ($\Delta H=-657$ kJ/mol) and emitting a large amount of heat to melt the Al core. This was in agreement with the DSC result in Fig. 4. Due to the low solubility of nitrogen in Al particle, the direct nitridation and supersaturation of Al particle with nitrogen led to the multiple nucleation of AlN crystals on the surface of the Al particle [20]. Therefore, an AlN porous-shell surrounding the molten Al core was formed. The addition of PTFE to starting materials offered an alternative reaction pathway for the nitridation of the

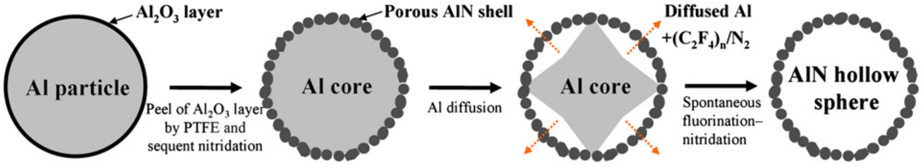

Fig. 5. A possible growth mechanism for the formation of AlN porous-shell hollow spheres by combustion synthesis.

outwardly diffused Al atoms, which involved spontaneous fluorination–nitridation sequences [18]. The encountered reactions can be described according to the following reactions along with Eqs. (1) and (2):

$$4nAl_{(l)}+3(C_2F_4)_{n(g)}\rightarrow 4nAlF_{3(s)}+6nC_{(s)} \quad (3)$$

$$2AlF_{3(s)}+N_{2(g)}\rightarrow 2AlN_{(s)}+3F_{2(g)} \quad (4)$$

$$2Al_{(l)}+3F_{2(g)}\rightarrow 2AlF_{3(s)} \quad (5)$$

As a result, the inner Al core was gradually evacuated, and finally the AlN porous-shell hollow spheres were obtained. Actually, many gray powders were observed in the combustion chamber after the reactions. XRD result (not shown here) indicated that these powders were hexagonal AlN phase, and carbon phase could not be detected, which might be due to the limitations of the measurement technique. Remarkably, addition of appropriate amount of PTFE was very important for the formation of AlN porous-shell hollow spheres. If PTFE was not enough, the Al core tended to react with N_2 via a direct nitridation route to form a thicker and closed shell, as shown in Fig. 3(a) and (b). For the addition of excess PTFE, most of the Al core was nitrided by the spontaneous fluorination–nitridation sequences, which strongly promoted the AlN fibers growth [18]. However, the filled N_2 gas was not enough for the complete nitridation of the formed $AlCl_3$, and therefore the impurity phase was detected in the product, as shown in Fig. 3(d).

4. Conclusions

In conclusion, we have demonstrated a facile combustion synthesis route for preparing AlN porous-shell hollow spheres in the presence of PTFE. The possible formation mechanism of the as-synthesized AlN hollow structures was proposed. It was found that PTFE was not only an active agent for the nitridation of Al particles but also a structure-directing agent for the formation of the hollow structures. This simple synthesis route required no expensive and precise equipment, will offer great opportunities for the scale-up fabrication of hollow structure materials.

Acknowledgments

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References

[1] Q. Zhang, W.S. Wang, J. Goebl, Y.D. Yin, Self-templated synthesis of hollow nanostructures, Nano Today 4 (6) (2009) 494–507.
[2] X.W. Lou, L.A. Archer, Z.C. Yang, Hollow micro-/nanostructures: synthesis and applications, Advanced Materials 20 (21) (2008) 3987–4019.
[3] Y. Taniyasu, M. Kasu, T. Makimoto, An aluminium nitride light-emitting diode with a wavelength of 210 nm, Nature 441 (7091) (2006) 325–328.
[4] L.M. Sheppard, Aluminum nitride: a versatile but challenging material, American Ceramic Society Bulletin 69 (11) (1990) 1801–1812.
[5] J.A. Haber, P.C. Gibbons, W.E. Buhro, Morphological control of nanocrystalline aluminum nitride: aluminum chloride-assisted nanowhisker growth, Journal of the American Chemical Society 119 (23) (1997) 5455–5456.
[6] Z.Q. Shi, M. Radwan, S. Kirihara, Y. Miyamoto, Z.H. Jin, Morphology-controlled synthesis of quasi-aligned AlN nanowhiskers by combustion method: effect of NH_4Cl additive, Ceramics International 35 (7) (2009) 2727–2733.
[7] Y.B. Tang, H.T. Cong, Z.G. Zhao, H.M. Cheng, An array of Eiffel-tower-shape AlN nanotips and its field emission properties, Applied Physics Letters 86 (23) (2005) 153104.
[8] Z.Q. Shi, M. Radwan, S. Kirihara, Y. Miyamoto, Z.H. Jin, Combustion synthesis of rod-like AlN nanoparticles, J, Journal of the Ceramic Society of Japan 116 (1357) (2008) 975–979.
[9] L.S. Yu, Y.Y. Lv, P.Y. Liu, X.Q. Yu, Synthesis of rhombic and triangular cross-sectional AlN nanorods on Si substrate via thermal CVD, Materials Letters 65 (10) (2011) 1499–1502.
[10] Q. Wu, Z. Hu, X.Z. Wang, Y. Chen, Y.N. Lu, Synthesis and optical characterization of aluminum nitride nanobelts, The Journal of Physical Chemistry B 107 (36) (2003) 9726–9729.
[11] Q. Wu, Z. Hu, X.Z. Wang, Y.N. Lu, X. Chen, H. Xu, Y. Chen, Synthesis and characterization of faceted hexagonal aluminum nitride nanotubes, Journal of the American Chemical Society 125 (34) (2003) 10176–10177.
[12] Z. Chen, C.B. Cao, H.S. Zhu, Controlled growth of aluminum nitride nanostructures: aligned tips, brushes, and complex structures, The Journal of Physical Chemistry C 111 (5) (2007) 1895–1899.
[13] Z.Q. Shi, M. Radwan, S. Kirihara, Y. Miyamoto, Z.H. Jin, Enhanced thermal conductivity of polymer composites filled with three-dimensional brushlike AlN nanowhiskers, Applied Physics Letters 95 (22) (2009) 224104.
[14] Y.B. Tang, H.T. Cong, Z.M. Wang, H.M. Cheng, Catalyst-seeded synthesis and field emission properties of flowerlike Si-doped AlN nanoneedle array, Applied Physics Letters 89 (25) (2006) 253112.
[15] Z.Q. Shi, W.L. Yang, G.J. Qiao, J.F. Yang, Z.H. Jin, Growth of flower-like AlN by combustion synthesis assisted with mechanical activation, Materials Science Forum 695 (2011) 413–416.
[16] Y.W. Ma, K.F. Huo, Q. Wu, Y.N. Lu, Y.M. Hu, Z. Hu, Y. Chen, Self-templated synthesis of polycrystalline hollow aluminium nitride nanospheres, Journal of Materials Chemistry 16 (27) (2006) 2834–2838.

[17] F. Zhang, Q. Wu, P. Xiao, Y.W. Ma, Y.M. Hu, X.Z. Wang, C.Y. Wang, Z. Hu, Synthesis of AlN hollow nanospheres via an in situ generated template method, The Journal of Physical Chemistry C 112 (30) (2008) 11331–11335.

[18] T.H. Lee, H.H. Nersisyan, H.G. Jeong, K.H. Lee, J.S. Noh, J.H. Lee, Efficient synthesis route to quasi-aligned and high-aspect-ratio aluminum nitride micro- and nanostructures, Chemical Engineering Journal 174 (1) (2011) 461–466.

[19] D.T. Osborne, M.L. Pantoya, Effect of Al particle size on the thermal degradation of Al/Teflon mixtures, Combustion Science and Technology 179 (8) (2007) 1467–1480.

[20] L.S. Yu, Z. Hu, Y.W. Ma, K.F. Huo, Y. Chen, H. Sang, W.W. Lin, Y.N. Lu, Evolution of aluminum nitride nanostructures from nanoflower to thin film on silicon substrate by direct nitridation of aluminum precursor, Diamond and Related Materials 16 (8) (2007) 1636–1642.