Convenient Fabrication and Property Investigations of Uniform TiN Hollow Nanocages

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Crystalline TiN hollow nanocages with pure cubic phase were prepared in large scale using TiO_2, $N_2H_4{\cdot}2HCl$, and Mg as reactants in autoclaves in 300–500 °C for 12 h. These hollow nanocages mainly have diameters of 300 to 500 nm and shell thicknesses from 20 to 35 nm. The product obtained with target temperature of 500 °C has a BET surface area of 68.13 m^2/g and pore volume of 0.17 cm^3/g.

The high-temperature plasticity, high hardness, good electrical and thermal conductivity, and chemical stability[1] endow titanium nitride (TiN) a good material for wide applications such as in coating or cutting tools and wear resistance materials.[2] TiN is also an important material used as for bioreplacements,[3] and gate electrodes for deep submicro CMOS.[4,5]

It is known that hollow materials with well-defined shapes may open new opportunities in exploring their novel properties,[6,7] as one kind of nanostructure, TiN hollow nanocages exhibit widespread potential applications in catalysis, drug delivery, lightweight filler, photonic crystals, and so on.[8] Conventionally, bulk TiN was produced via a CVD process by directly reacting metallic titanium (or metal hydride) with nitrogen (or a mixture of nitrogen and hydrogen, or ammonia) at high temperatures or by reacting $TiCl_4$ with ammonia.[9,10] Bulk TiN was also synthesized by the carbothermal reduction process at 1200 °C in N_2 atmosphere under high pressure using TiO_2 as titanium source.[11,12] Nanocrystalline TiN was made by the solid-state metathesis reactions of $TiCl_4$ (or $TiCl_3$)[13] with various nitrogen sources, such as Li_3N,[14] NaN_3,[13] Ca_3N_2,[15] NH_4Cl/Na[16] or by heat treatment of the precursor (obtained by reacting liquid $TiCl_4$ with NH_3 in anhydrous organic liquids).[17,18] TiN nanopowders were also prepared by using TiO_2 and cyanamide (or urea) at 900 °C under nitrogen atmosphere.[19]

There have been few reports about the fabrication of TiN hollow cages, for example, hollow spherical TiN particles have been produced by employing $TiCl_4$ and $NaNH_2$ at room temperature; however, their shells are mainly composed of nanoparticles and their crystallinity still needs further improvement.[20] In this letter, we report a simple but effective method for producing crystalline TiN hollow nanocages by using TiO_2, $N_2H_4{\cdot}2HCl$, and Mg as reactants in autoclaves in 300–500 °C for 12 h. The sample obtained at 500 °C was measured to have a BET surface area of 68.13 m^2/g and pore volume of 0.17 cm^3/g.

In this experiment, $N_2H_4{\cdot}2HCl$ was used after drying at 60 °C for 30 min in vacuum. In a typical procedure, $N_2H_4{\cdot}2HCl$ (5.0 g), TiO_2 (1.6 g), and Mg (2.5 g) powder were put in to a stainless-steel autoclave of 20-mL capacity. The autoclave was heated from room temperature to 300 °C (labeled as Sample 1), 400 °C (Sample 2), and 500 °C (Sample 3) with an increasing rate of 10 °C/min and maintained at the target temperature for 12 h. Then, the raw products were collected, filtered, and washed with distilled water and 1 M HCl solution. Finally, the samples were dried in a vacuum at 60 °C for 4 h.

The samples were characterized by using a Bruker D8 advanced X-ray diffractometer. The transmission electron microscope (TEM) images, selected area electron diffraction (SAED) pattern, and high-resolution TEM (HRTEM) images were measured on a JEOL-2100 microscope. SEM images were studied using a thermal FE scanning electron microscope (Oxford Scientific Co., U.K.). Thermal stability of the products was taken on a Mettler Toledo TGA/SDTA 851 thermal analyzer.

Figure 1 shows the typical XRD pattern of Sample 3. The strong intensive peaks with *d* spacings of 2.434, 2.108, 1.494, 1.275, and 1.222 Å could be indexed as the diffraction crystal-planes of (111), (200), (220), (311), and (222) from cubic TiN, respectively. The calculated lattice constant $a = 4.224$ Å was in good agreement with the reported value (JCPDS, card No. 65-0715). XRD patterns of Samples 1 and 2 gave similar results.

The structure and morphology of Sample 3 were examined by TEM, SAED, and HRTEM. Figure 2a shows the typical

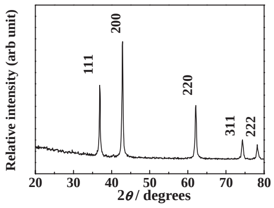

Figure 1. XRD pattern of Sample 3.

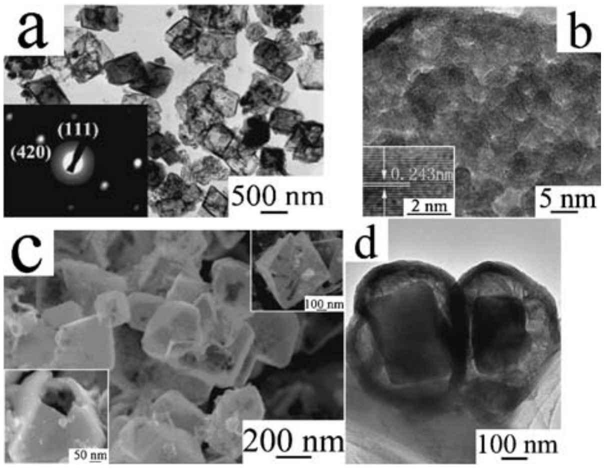

Figure 2. (a) TEM image of Sample 3, inset in left corner is the SAED pattern of a TiN hollow nanocage; (b) magnified TEM image of part of a hollow nanocage, insert in left corner is the HRTEM image of part of hollow nanocage; (c) typical SEM images of Sample 3; (d) TEM image of the raw product that produced at 500 °C without any purification.

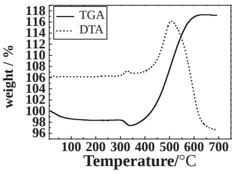

Figure 3. Differential thermal analysis/thermogravimetric analysis (DTA/TGA) plot of Sample 3 under air atmosphere.

TEM image of Sample 3. It can be seen that there is an obvious contrast between the dark edge and the pale center of the nanocages, revealing their hollow core characteristics.[21] These TiN hollow nanocages, shown in Figure 2a, mainly have diameters of 300 to 500 nm and shells thicknesses of 20 to 35 nm. The left-bottom corner inset in Figure 2a shows the typical SAED pattern of a hollow nanocage of Sample 3, in which two diffraction spots with *d* spacings of 2.43 and 0.94 Å could be indexed as the (111) and (420) of cubic TiN, respectively. It can be clearly seen from the magnified TEM image (Figure 2b) that the shells of a hollow nanocage have many pores and that the pore diameters are 2–7 nm. Insert in Figure 2b shows the HRTEM image of part of a randomly selected individual TiN hollow nanocage. The lattice fringes that are regularly arranged can be clearly seen, which reveals the well crystalline of the hollow TiN nanocage. The interplanar spacing is about 0.243 nm, which corresponds to (111) spacing of cubic TiN (JCPDS card No. 65-0715). The morphology of Sample 3 was also examined by FESEM (Figure 2c). Most of these nanocages have smooth surfaces, while some of them were broken (left-bottom corner) or have large holes (right upper corner). The typical TEM image of the product obtained at 500 °C but without any treatment process is shown in Figure 2d, which displays the core–shell structure characteristics. The inner contents of the core–shell product were deduced to be MgO or/and Mg related compounds according to the XRD and EDS analysis.

Figure 3 shows the typical DTA/TGA curves of Sample 3. It is obvious that only minor weight change occurred below 300 °C. The drastic decrease in the weight loss curve in 300–340 °C might be attributed to the loss of little residual chlorine-related impurities.[22] Figure 4 shows the N_2 adsorption–desorption isotherm (Figure 4a) and pore diameter distribution (Figure 4b) of Sample 3. Its BET surface area was $68.13\,\mathrm{m^2/g}$, which is much lower than the reported values of TiN powder ($135\,\mathrm{m^2/g}$),[23] and the total pore volume was $0.17\,\mathrm{cm^3/g}$. It can be seen from Figure 4b that the pore diameters of the TiN hollow nanocages are mostly distributed in the range of 2–7 nm, which is consonant with the TEM observation results (Figure 2b).

According to the results of thermodynamic calculations, the reaction is spontaneous and highly exothermic.[24] The overall reaction in this experiment is proposed as follows:

$$\begin{aligned} &2\mathrm{TiO_2} + 6\mathrm{Mg} + 2\mathrm{N_2H_4{\cdot}2HCl} \\ &\quad = 2\mathrm{TiN} + \mathrm{N_2} + 6\mathrm{H_2} + 2\mathrm{MgCl_2} + 4\mathrm{MgO} \end{aligned} \tag{1}$$

In this experiment, it is found that TiN hollow nanocages could be obtained by heating at 500 °C only for 1 h, and their yield increased along with the prolonged reaction time (from 1 to 12 h). The yield of the hollow nanocages was also found to increase significantly along with the increasing reaction temperature (300, 400, and 500 °C), and its maximum proportion approaches about 75% at 500 °C. However, the higher reaction temperature usually resulted in the larger sizes of the as-obtained hollow nanocages. When NaN_3 was used instead of $N_2H_4{\cdot}2HCl$, only solid TiN nanoparticles could be obtained. The effect of Mg powder in this experiment was also explored; no TiN could be produced when Mg powder was substituted by Na, and pure cubic TiN with hollow cage-like morphology could only be obtained when the using amount of Mg powder was excessive about 15 to 20% according to that of TiO_2. Combined with the analysis results from Figure 2d, it is likely that MgO or/and Mg related intermediate compound plays a crucial role on the formation of hollow TiN nanocages.

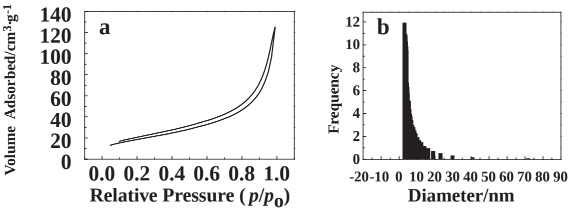

Figure 4. (a) Nitrogen adsorption–desorption isotherm, and (b) pore diameter distribution of Sample 3.

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