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Original Research Paper

## A smart processing of silicon oxynitride ceramic powders with variable morphology controlled by hard template assistance

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## ABSTRACT

Spherical and rod-like Si<sub>2</sub>N<sub>2</sub>O ceramic powders were successfully prepared using a hard template strategy to meet different application background. The mesoporous silica spheres and rod-like silica (SBA-15) particles were selected as hard templates and also served as reactants. Highly active mesoporous silica is reacted through a combination of sucrose-nano-casting and carbothermal reduction nitridation (CRN) to successfully synthesize spherical and rod-like powders. Temperature and holding time of calcination are found to be significant factors for the formation of pure and well-crystallized powders. Insufficient temperature and holding time cause an incomplete reaction between silica, carbon and nitrogen, and also lead to the formation of amorphous phase. In the processing, sucrose was used as carbon source to incorporate evenly into mesopores of templates to assist CRN reaction. Big surface areas and high porosity of mesopores in SiO<sub>2</sub> provide an additional driving force to decrease the formation temperature of Si<sub>2</sub>N<sub>2</sub>O phase to 1280 °C. As-synthesized powders inherit same morphology as their parental mesoporous templates, which indicate that two mesoporous templates play an important role in guiding the growth of ceramic particles. In the research, we develop a smart processing for synthesis of oxynitride powders with variable morphology controlled by template.

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## 1. Introduction

Si<sub>2</sub>N<sub>2</sub>O is a significant compound in silicon–oxygen–nitrogen system [1], as an advanced engineering material which can keep low thermal conductivity, excellent oxidation resistance in air, high flexural strength, and low dielectric constant and loss [2–8]. Having these excellent properties, Si<sub>2</sub>N<sub>2</sub>O has been a promising candidate in varied applications. For example, the powders with rod-like morphology or fiber will benefit the reinforcement of fracture toughness in engineering material matrix [9,10]. On the contrary, the powders with low aspect ratio will be more suitable to use in areas requiring relative low dielectric constant and loss [11]. Herein, synthesizing morphology-controllable Si<sub>2</sub>N<sub>2</sub>O powders crucially affects their further development and extended applications.

As for particle shape control of ceramic powders, there are essentially three ways to approach: (1) growth directed syntheses typical of precipitation processes [11–15]; (2) template directed syntheses, wherein the growth is directed by epitaxy via a pre-existing structure upon which nucleation and growth take place [16–18]; (3) parameters-adjusted wet chemical methods. [19,20]. However, among the three methods, the template directed way is relatively easy and simple to control, while the finding of effective templates is full of challenges.

Since ordered mesoporous SiO<sub>2</sub> was successfully synthesized [21,22], the preparation and application of various mesoporous materials have attracted great attention of researchers, including SiO<sub>2</sub>-series [23–25], other oxides (Al<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, etc.) [26–28], and even non-oxides (carbon, ZnS, CdS, etc.) [29–31]. With hot focus on mesoporous materials of SiO<sub>2</sub> (such as MCM-type, SBA-type, and KIT-type), owing to their good stability and diversity of selectable structural-guide agents, hard template directed methods using mesopore channels of SiO<sub>2</sub> have shown the effectiveness in directing particle growth. To date, considerable works have devoted to control macrostructure/microstructure of different products using hard template approach. Kim and Cho [32] reported

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the preparation of mesoporous SnO<sub>2</sub> lithium battery anode materials using KIT-6 and SBA-15 templates (two kinds of mesoporous SiO<sub>2</sub>), in which the shapes and pore sizes of SnO<sub>2</sub> changed with different templates. Wang et al. [33] employing two kinds of mesoporous silica (SBA-15 and spheres) synthesized morphology-controllable Co<sub>3</sub>O<sub>4</sub> and CeO<sub>2</sub>. The Mesoporous MFI zeolite using CMK carbon templates was reported recently [34]. In a word, the hard template method with morphology flexibility from a copy of template structure can readily realize the precise morphological control. Based on advantages mentioned above, the “migrating” of hard template method into preparation of ceramic powder will potentially solve the difficulties in precisely morphology controlling and limited kinds of powder shapes in present methods.

Very importantly, carbon can be readily introduced into the nanosized channels or skeletons of mesoporous SiO<sub>2</sub>. Previous studies have also demonstrated that in situ composited carbon in mesoporous SiO<sub>2</sub> and large specific surface area of mesoporous SiO<sub>2</sub> are greatly helpful to decrease the synthesis temperature of pure  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> and  $\beta$ -SiAlON powders through carbothermal reduction and nitridation method (CRN), utilizing SBA-15 powders as starting active SiO<sub>2</sub> raw materials [35,36].

Predictably, using SiO<sub>2</sub> hard template for synthesis of morphological controlled Si<sub>2</sub>N<sub>2</sub>O powder would give a novel technical method to further extend the applications of Si<sub>2</sub>N<sub>2</sub>O, in which SiO<sub>2</sub> serves as not only a structural guide agent but also Si source. In the present work, by utilizing two different kinds of mesoporous silica hard template (SBA-15 and spheres), rod-like and spherical Si<sub>2</sub>N<sub>2</sub>O powders were successfully synthesized at lower temperature of 1280 °C.

## 2. Experimental

### 2.1. Materials preparation

AR grade sucrose (as carbon source), sulfuric acid, tetraethyl orthosilicate (TEOS, Si source), ammonia, cetyltrimethylammonium bromide (CTAB, structural guide agent), and C<sub>2</sub>H<sub>5</sub>OH were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), and used without further purification. Additive Y<sub>2</sub>O<sub>3</sub> (99.9 wt%) was purchased from Shanghai Yuelong Rare Earth New Materials Co. Ltd (Shanghai, China). The rod-like mesoporous silica SBA-15, one of hard templates, was purchased from Fudan University of China and mesoporous silica sphere (MSS), another hard template, was prepared in our laboratory. Before usage as templates, SBA-15 and MSS were fired at 550 °C for 6 h to remove the remaining impurities.

To make a comparison with rod-like SBA-15 hard-template prepared in rigid bolaform surfactants by Zhao et al. [37], MSSs were synthesized in our laboratory using a similar method reported by Teng [38], aiming at preparation of spherical Si<sub>2</sub>N<sub>2</sub>O. Generally, ethanol-to-water volume ratio was selected as 0.56 with an aqueous ammonia solution (25 wt% NH<sub>3</sub> in water). Then, TEOS was added drop-like into the above solution with stirring time of 12 h.

As for the synthesis of Si<sub>2</sub>N<sub>2</sub>O powders, SBA-15 and the as-synthesized MSS particles were used as silica source and hard templates to control the morphology of final products. Sucrose was selected as carbon source, with a C:SiO<sub>2</sub> molar ratio of 4:1. A typical procedure of processing is as follows: 1.8 g sucrose and 0.2 g H<sub>2</sub>SO<sub>4</sub> were dissolved in deionized water and 1.0 g SiO<sub>2</sub> (SBA-15 or MSS) was added subsequently, followed with stirring and drying. Afterwards, Y<sub>2</sub>O<sub>3</sub> was added in the amount of 3.0 mol% (relative to the mesoporous silica source) and the solution was stirred for 30 min. After carbonized at 800 °C for 4 h in nitrogen flow of 0.3 L/min, the mixture powders form a SiO<sub>2</sub>-C composite with carbon introduced into the nanosized channels or skeletons

of mesoporous SiO<sub>2</sub> (Fig. 1a and b). This composite consequently underwent further nitridation in a graphite furnace at 1250–1300 °C for 5–7 h with a 0.8 L/min nitrogen flow. The residual carbon was removed by heating at 600 °C for 6 h in air environment. It has to be emphasized herein that Y<sub>2</sub>O<sub>3</sub> assistant is required to be added before carbonization to obtain a stable and highly-pure Si<sub>2</sub>N<sub>2</sub>O phase. The role of Y<sub>2</sub>O<sub>3</sub> additive has been explained in a separate literature [39]. Generally, the addition of Y<sub>2</sub>O<sub>3</sub> guarantees the CRN reaction occurred below 1300 °C due to the formation of an eutectic intermediate phase as Y<sub>2</sub>SiO<sub>5</sub>, which was the reaction product of Y<sub>2</sub>O<sub>3</sub> and mesoporous SiO<sub>2</sub>.

### 2.2. Characterization

Nitrogen adsorption–desorption isotherms were measured on a Micromeritics ASAP2010 surface area and pore size analyzer at liquid nitrogen temperature (77 K). Prior to measurements, the samples were dehydrated at 373 K and then outgassed at 473 K in vacuum for 4 h. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas (*S*<sub>BET</sub>). The pore volume (*V*<sub>BJH</sub>) and the mean pore size (*D*<sub>BJH</sub>) were derived from the adsorption branches of the isotherms using the Barrett–Joyner–Halanda (BJH) method. X-Ray powder diffraction patterns were collected on a Rigaku D/MAX-c  $\beta$  instrument using Cu K $\alpha$ <sub>1</sub> ( $\lambda$  = 0.15406 nm) radiation at 40 kV and 60 mA. Morphology of the particles was observed with field emission scanning electron microscope (FSEM, JSM-6700F JEOL, Japan, 10.0 kV) equipped with EDS analysis.

## 3. Results and discussions

### 3.1. Texture of hard templates

To identify the difference between rod-like SBA-15 particles and mesoporous silica spheres (MSS), the textural parameters of two templates were analyzed using nitrogen adsorption–desorption isotherms and results are listed in Table 1. Both templates possess relatively high BET surface areas and relatively high pore volume. While MSS has a higher surface about 994 m<sup>2</sup>/g and SBA-15 possess a bigger pore diameter about 6.6 nm. The particle morphology of two templates is shown in Fig. 1c and d.

### 3.2. Phase formation of Si<sub>2</sub>N<sub>2</sub>O

To compare the different phase formation behavior of Si<sub>2</sub>N<sub>2</sub>O by two hard template guiding, mesoporous SBA-15 and MSS were used either as silica sources or as templates. And XRD analysis was carried out to record the phase formation of Si<sub>2</sub>N<sub>2</sub>O resulted from the two mesoporous SiO<sub>2</sub> templates. However, based on our experimental results, only SBA-15 derived Si<sub>2</sub>N<sub>2</sub>O phase formation is discussed in detail herein, because of a very similar phase formation and reaction mechanism shown from the two mesoporous silica precursors as starting materials.

#### 3.2.1. Calcination temperature effect

Fig. 2 provides XRD patterns of final powders Si<sub>2</sub>N<sub>2</sub>O with SBA-15 and MSS as starting material of SiO<sub>2</sub>, calcined at 1250 °C, 1260 °C, 1280 °C, and 1300 °C, respectively, for 7 h. As the temperature of CRN increases, SBA-15 is gradually transformed into Si<sub>2</sub>N<sub>2</sub>O (JCPDS Card No. 47-1627). When the temperature is below 1280 °C, the unreacted amorphous SBA-15 clearly exists, indicated by a big “broad” diffraction band. When the calcination temperature or CRN temperature is above 1280 °C, considerable  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> phase appears as a detectable impurity in the matrix of Si<sub>2</sub>N<sub>2</sub>O. As a result, the optimal temperature is fixed at 1280 °C. A phase

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