Facile Preparation of Mesoporous Titanium Nitride Microspheres for Electrochemical Energy Storage

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ABSTRACT In this study, mesoporous TiN spheres with tunable diameter have been fabricated via a facile template-free strategy. Under ammonia atmosphere, mesoporous TiO₂ spheres are directly converted into mesoporous TiN spheres with the addition of cyanamide to retain the original morphology. The electrochemical performance of the resultant mesoporous TiN spheres demonstrates that this material can be a promising electrode material for nonaqueous supercapacitors with high energy densities.

KEYWORDS: titanium nitride • mesoporous spheres • cyanamide • template-free method • supercapacitors • electrochemical performance

INTRODUCTION

Titanium nitride (TiN) has drawn considerable attention for its interesting properties and various applications (1), such as abrasives and protective coating materials (2). Recent reports have found its potential use as catalyst (3–6), sensors for electroanalysis (7–9), supercapacitors (10), and also a conductive additive for lithium-ion batteries with minor capacity (1, 11). During the past decades, substantial researches have been carried out for the synthesis of materials with porous nanostructures beneficial for energy storage applications (12–19), as these materials possess high surface/volume ratio, good accessibility of the pores, and a short distance of ion diffusion or mass transport. Therefore, it is reasonably expected that a mesostructure of TiN can be potential for enhancing its electrochemical performance for lithium batteries and supercapacitor applications.

TiN nanoparticles are often prepared from titanium oxide using nitrogen sources (such as ammonia or nitrogen) at high temperature (20–27). However, it is challenging to prepare mesoporous structure, because the collapse of the nanopores during conversion and recrystallization severely hinder the formation of mesoporous TiN (28). To address this issue, the general synthetic strategies have mostly relied on the use of multiple templates (28–33). Two recently reported procedures intended for preparation mesoporous TiN deserve highlighting: (1) the use of SBA-15 and graphitic carbon nitride as sacrificial templates to fabricate 2D hexagonal mesoporous TiN/C composites (28), (2) the use of hollow Zn₂TiO₄ spheres formed by nebulization as an in situ templating to prepare hollow TiN mesoporous spheres (33). However, these approaches substantially require a tedious and time-consuming process of template formation and the necessity of template removal. Therefore, it is urgent to explore new template-free synthetic methods for preparing mesoporous nanostructure of TiN.

Herein, we reported a facile route to directly converted TiO₂ mesoporous spheres into TiN mesoporous spheres under ammonia atmosphere using cyanamide to retain the morphology. In this approach, cyanamide plays a significant role in the procedure of ammonia reduction. First, cyanamide confines the aggregate of spheres at high temperature, prevents the nanopores structure from collapse during recrystallization (4), and finally thermally decomposes without additional purification. Second, cyanamide also serves as an excess of nitrogen source to promote the nitrogenization reaction during decomposition (21, 31). Therefore, TiN can be obtained with well-maintained mesoporous spheres structure.

In addition, mesoporous TiN spheres offer an electronic conducting framework which can be expected to be an effective and fast charge-separation network desirable for the electrochemical energy storage application (34, 35). A highly effective electronic conducting network is expected to ensure a rapid electronic diffusion while the mesoporous structure can be favorable for accessible diffusion of electrolyte. Therefore, in the present study, the electrochemical
The performance of mesoporous TiN spheres for nonaqueous symmetric supercapacitor was also explored.

**EXPERIMENTAL SECTION**

**Synthesis of Mesoporous TiO₂ Spheres.** All chemicals were used as received without further purification. Mesoporous TiO₂ spheres were prepared as described by Zhong and co-workers with minor revision (36). In the first step, titanium glycolate precursor spheres were synthesized. The exact composition of the used precursor solutions are given in Table 1. In the second step, the titanium glycolate is refluxed with 20 mL of water at 80 °C, and titanium glycolate reacts with water to form the nanoporous TiO₂. After refluxing for 3 h, the white precipitate was obtained by centrifugation, followed by washing with water five times and subsequently drying at 50 °C for further usage.

**Preparation of Mesoporous TiN Spheres.** The mesoporous titanium nitride spheres were prepared by using the above-described mesoporous TiO₂ spheres and cyanamide. In a typical synthesis experiment, 120 mg of the TiO₂ powder was mixed with 95 wt % of cyanamide (NH₂CN, Aldrich) dissolved in 5 mL of absolute ethanol. The mixture was magnetically stirred for 2 h and dried at 80 °C to get a homogeneous bulk. Three TiO₂/cyanamide composites were subsequently heated to 800 °C under ammonia atmosphere. The TiO₂/cyanamide composites were subsequently heated at 200 °C under ammonia atmosphere. Antonietti et al. have reported the mechanism of cyanamide severing as nanoconfinement in the process of preparing nanoparticles (31, 37) and porous materials (28). During the thermal treatment, cyanamide was condensed into carbon nitride (occurring at 550 °C) as a confining matrix. When the temperature was higher than 650 °C, carbon nitride decomposition occurred and the minor amount of carbon residue could also serve as a confinement matrix. Finally, the metal oxide spheres confined in the matrix was consequently converted into the nitride with the morphology well preserved. In a control experiment, without the addition of cyanamide (as shown in Figure S1 in the Supporting Information), microspheres aggregated together with a smooth surface and totally lost their mesoporous structure. By changing the amount of water in the process of preparing titanium glycolate spheres, we can tune the diameters of mesoporous spheres from 100 to 800 nm. It is assumed that increasing amount of water will speed up the hydrolysis rate of precursor. Therefore, the nucleation reaction can quickly reach equilibrium to prevent the sphere size from growing larger (38). Three kinds of mesoporous spheres with different diameter range (50–100, 200–300, and 600–800 nm) were prepared and denoted hereafter as TiN-1, TiN-2, and TiN-3, respectively (Figure 1b, d, f).

**RESULTS AND DISCUSSION**

As a main precursor of mesoporous TiN spheres, mesoporous TiO₂ spheres were fabricated by a facile aqueous route reported by Zhong and co-workers (36). As shown in scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images a, c, and e in Figure 1, the mesoporous TiO₂ spheres consist of interconnected nanoparticles 10–20 nm in size. These results are consistent with the morphology of previous report (36).

For the preparation of mesoporous TiN spheres, as shown in Scheme 1, as-prepared TiO₂ spheres were immersed with cyanamide dissolved in absolute ethanol. Cyanamide could penetrate through the pores and enter into the mesoporous spheres. The TiO₂/cyanamide composites were subsequently heated to 800 °C under ammonia atmosphere. When the temperature was higher than 650 °C, carbon nitride decomposition occurred and the minor amount of carbon residue could also serve as a confinement matrix. Finally, the metal oxide spheres confined in the matrix was consequently converted into the nitride with the morphology well preserved. In a control experiment, without the addition of cyanamide (as shown in Figure S1 in the Supporting Information), microspheres aggregated together with a smooth surface and totally lost their mesoporous structure.

<table>
<thead>
<tr>
<th>Table 1. Composition of the Solutions for the Synthesis of Titanium Glycolate Spheres in Step One</th>
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<tbody>
<tr>
<td><strong>materials</strong></td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>TiN-1</td>
</tr>
<tr>
<td>TiN-2</td>
</tr>
<tr>
<td>TiN-3</td>
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Combined measurements using inductively coupled plasma and elemental analysis are applied to investigate charge/discharge measurements conducted with a charge–discharge tester (LAND).
According to elemental analysis, traces of carbon can be detected. The amount of carbon residue is minor compared with that of previously reported TiN (4), TiN nanoparticles (31), and TiVN (ternary metal nitride) nanoparticles (37) using cyanamide or carbon nitride as the only nitrogen source. Furthermore, some oxygen element is also detected, which may result from surface oxidation as mentioned in elemental composition of the resulting materials (Table 2). According to elemental analysis, traces of carbon can be detected. The amount of carbon residue is minor compared with that of previously reported TiN (4), TiN nanoparticles (31), and TiVN (ternary metal nitride) nanoparticles (37) using cyanamide or carbon nitride as the only nitrogen source. Furthermore, some oxygen element is also detected, which may result from surface oxidation as mentioned in
previous reports (35, 38). However, the present of TiN-TiO solid solution also can not be ruled out (further discussed in the next paragraph) (25).

Figure 3 shows that XRD patterns of the resultant black powders can be indexed to the typical pattern of the cubic TiN, belonging to the space group Fm3m. No peaks corresponding to rutile or anatase TiO2 are observed in the XRD patterns. Therefore, the presence of large amount of titanium oxide can be excluded. However, the diffraction peaks shift to higher angles with the increasing size of mesopores, which indicates a decrease of lattice parameters. Indeed, the lattice parameters calculated from the three XRD patterns 4.20 Å (a = b = c), 4.19 Å, and 4.18 Å for TiN-1, TiN-2, and TiN-3, correspondingly. These results are smaller than that of TiN phase osbornite typical pattern (JCPDS 38-1420, 4.24 Å) and previous reports by Kumta et al. (4.219-4.234 Å) (10) and Antonietti et al. (4.21 Å) (28). According to Zukalova and Kavan et al. (25), it is ascribed to a partial formation of TiN-TiO solid solution and nonstoichiometric TiN. This result may be due to the incompletely nitridation of TiO2 spheres with the increasing size. It is also worth noting that with decreasing spheres size, a progressively broadening of the diffraction peaks is observed in the samples. From [220] peak of XRD patterns, the average crystals size of TiN can be calculated to be approximately 2.9, 3.0, and 4.5 nm for TiN-1, TiN-2, and TiN-3, correspondingly, using the Scherrer equation.

The porosity of the TiN materials is determined by nitrogen sorption measurement (Figure 4 and Figure S3 in the Supporting Information). The N2 adsorption–desorption isotherms of all materials are identified as Type IV isotherm indicating characteristics of mesoporous materials. Table 3 summarizes the surface areas, pore volumes, and average pore sizes determined from the BET isotherms. It can be seen that the surface area of TiN materials decrease from 92 to 56 m2 g−1 with increasing size of the TiN spheres. The average pore sizes of Barrett–Joyner–Halenda (BJH) are obtained from the isotherm range from 14 to 27 nm, corresponding to TiN-2, TiN-3, and TiN-1, respectively. All these data strongly confirm the fact that the spheres have a mesoporous structure.

Cyclic voltammograms (CVs) tests were performed on mesoporous TiN spheres to evaluate their electrochemical performance for nonaqueous symmetric supercapacitors. As shown in Figure 5a, the CV curve is approximated to a rectangle which is reflective of an ideal capacitive behavior. Most of the capacity can be attributed to interface storage according to previous reports by J. Maier et al. (39–41). The specific capacitance of symmetric supercapacitor (C) is calculated according to the equation:

$$C = \frac{I \Delta t}{m \Delta V}$$  \hspace{1cm} (1)

where m is the total mass of the two electrodes, and I, Δt, and ΔV are the average current of charge and discharge, time and voltage, respectively. The single-electrode specific capacitance (C₀) can be calculated by the equation:

Table 2. Elemental Composition of the Mesoporous TiN Spheres with Different Diameter Ranges

<table>
<thead>
<tr>
<th>Materials</th>
<th>Ti%</th>
<th>N%</th>
<th>C%</th>
<th>O%</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiN-1</td>
<td>73.6 ± 2.0</td>
<td>16.5 ± 0.1</td>
<td>1.2 ± 0.3</td>
<td>7.2 ± 0.3</td>
</tr>
<tr>
<td>TiN-2</td>
<td>69.5 ± 1.2</td>
<td>16.8 ± 0.1</td>
<td>0.7 ± 0.2</td>
<td>5.0 ± 0.1</td>
</tr>
<tr>
<td>TiN-3</td>
<td>68.5 ± 0.8</td>
<td>15.9 ± 0.2</td>
<td>0.6 ± 0.1</td>
<td>6.2 ± 0.1</td>
</tr>
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</table>

Table 3. Porous Characteristics of the Mesoporous TiO2 with Different Particle Sizes

<table>
<thead>
<tr>
<th>Materials</th>
<th>Surface area S BET (m² g⁻¹)</th>
<th>Pore volume (cm³ g⁻¹)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiN-1</td>
<td>92</td>
<td>0.57</td>
<td>27</td>
</tr>
<tr>
<td>TiN-2</td>
<td>70</td>
<td>0.28</td>
<td>14</td>
</tr>
<tr>
<td>TiN-3</td>
<td>56</td>
<td>0.29</td>
<td>20</td>
</tr>
</tbody>
</table>

FIGURE 3. XRD patterns of the mesoporous TiN spheres (black line refers to TiN-1, green line refers to TiN-2, red line refers to TiN-3).

FIGURE 4. (a) Nitrogen adsorption and desorption isotherms of mesoporous TiN micro-spheres TiN-2 and (b) their pore-size distribution obtained from adsorption branch of the isotherm using the BJH method.
where $m_s$ is the mass of single electrode. Therefore, the single electrode $C_s$ of the TiN-2 is 133 F g$^{-1}$ at the scan rate of 2 mV s$^{-1}$.

Galvanostatic charge–discharge experiments were further carried out to test the mesoporous TiN spheres symmetric supercapacitors. The charge–discharge curves and cycling performance of TiN-2 supercapacitors under rates varied from 0.05 to 1 A g$^{-1}$ are shown in Figure 5b (the electrochemical performances of TiN-1 and TiN-3 supercapacitors are shown in the Figure S4, Supporting Information). The single electrode $C_s$ of the TiN-2 measured from galvanostatic charge–discharge tests can also be calculated by eq 1 when $I$ represents the current of discharge. Thus the $C_s$ of the TiN-2 are 144.0, 112.3, 69.1, 54.2, 44.2, and 39.4 F g$^{-1}$, corresponding to current densities of 0.05, 0.1, 0.25, 0.5, 0.75, and 1 A g$^{-1}$, respectively (Figure 5c). It should be noted that this result is a little higher than that obtained by the CV test, which is also in agreement with a previous work (42). Energy density and power density, as important parameters for the electrochemical performance of supercapacitor, have been also presented for a detail evaluation of TiN materials. The power density and energy density can be calculated from the following equations (43)

$$E = \frac{1}{2} C (\Delta V)^2 \quad (3)$$

$$P = \frac{Q \Delta V}{2 m \Delta t} = \frac{E}{t} \quad (4)$$

where $P$ (kW kg$^{-1}$), $C$ (F g$^{-1}$), $V$ (V), $Q$ (C), $m$ (kg), $\Delta t$ (s), and $E$ (W h kg$^{-1}$) are the power density, specific capacitance, potential window of discharge, charge delivered of discharge, mass of active materials, discharge time, and energy density, respectively. Ragone plot of TiN-2 (Figure 5c insert) showed that the energy densities reduce slightly with increasing power densities. The energy density of TiN-2 can reach 45.0 W h kg$^{-1}$ at a power density of 150 W kg$^{-1}$ (based on the mass of active materials), and still remains 12.3 W h kg$^{-1}$ at a power density of 3 kW kg$^{-1}$, which indicate mesoporous TiN spheres are potential candidates for a high-energy supercapacitor.

CONCLUSION

In summary, we have fabricated mesoporous titanium nitride spheres through a facile template free strategy. Using cyanamide as a structural confinement agent, TiO$_2$ mesoporous spheres were directly transformed into mesoporous TiN spheres at high temperature under an ammonia atmosphere. Through changing the amount of water during the procedure of preparing titanium glycolate spheres, mesoporous spheres with tunable diameters were obtained. It is also demonstrated that the mesoporous TiN spheres can serve as a promising electrode material for high energy supercapacitors. Furthermore, this mesoporous structure of TiN is potential framework for synthesizing composites with 3D mixed (electron and ion) conducting networks by introducing electroactive materials (e.g., MnO$_2$, RuO$_2$, Si, Sn) on the surface of mesoporous TiN spheres. Therefore, an excellent electrode material based on mixed conducting composites with a higher specific energy and power density can be expected, which is highly desirable for Li-ion batteries and supercapacitor applications.

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Supporting Information Available: SEM and TEM images of TiN prepared without the addition of cyanamide (Figure S1), low-magnification SEM images of the three mesoporous TiN spheres samples (Figure S2), nitrogen adsorption/desorption isotherms and the pore-size distribution of TiN-1 and TiN-3 (Figure S3), and electrochemical performance of TiN-1 and TiN-3 (Figure S4) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES