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FULL PAPER

2D Nb_4N_5 nanosheets synthesized by template method

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Abstract: Niobium nitrides possess superconductivity and stable chemical stability, which render them desirable candidates for energy storage. Therefore, they deserve exploration in potential application for energy storage. Here we report on synthesis of 2D Nb_4N_5 nanosheets by ammonization of NbS_2 nanosheets as template at 700 °C. The obtained 2D Nb_4N_5 nanosheets retain hexagon shape and display porous structure with pore size of 3.716 nm. These 2D Nb_4N_5 nanosheets exhibit capacitor behavior as electrode materials for energy storage. This study opens a new avenue in synthesizing 2D materials based on 2D templates.

Introduction

Nitrides have drawn much attention owing to their wide range of applications.[1] Among them, transition metal nitrides are a class of interstitial compounds formed by transition metals and nitrogen, including metal elements in the group of IVB-VIB in the periodic table,[2] such as TiN,[3] VN[4] and Mo_2N[5]. Due to nitrogen atoms occupy interstitial sites of transition metals, they have ionic bond, metallic bond and covalent bond.[6] Therefore, they display a combination of excellent properties, including high hardness, chemical and mechanical stability.[7] Moreover, they possess superconductivity[8] and excellent catalytic activity[9]. Based on these excellent properties, they have been explored in many applications, such as supercapacitors[10], hydrogen evolution reaction, batteries[11] and others[12].

Niobium nitrides, as a typical kind of transition metal nitrides, display superconductivity, high chemical and mechanical stability.[13] Fritz et al. reported that niobium nitrides exhibit excellent electrochemical stability in acidic environment after 2000 cycles in proton-exchange membrane fuel cells.[13a] Porous niobium nitride have shown superior cycling stability as a capacitor anode material in Li-ion hybrid capacitor.[14] There are kinds of niobium nitrides, including Nb_2N, Nb_4N_3, NbN, Nb_4N_5, and Nb_5N_6. However, as reported, only niobium nitrides with high-valence states, such as Nb_4N_5 and Nb_5N_6 might be good candidates as electrode materials for energy storage because redox reactions with adsorbed ions in the electrolyte.[15] Currently, a few approaches were explored to synthesize niobium nitrides, including magnetron sputtering,[16] metal-organic chemical vapor deposition (MOCVD),[17] nitridation of metal precursors (transition metal oxides, chloride,[18] sulphide[19] and bromide[20]) in the NH_3 atmosphere.[2] Among them, nitridation of metal precursors with different structure is common method. To date, Nb_4N_5 with high-valence states have been synthesized by nitridation of niobium hydroxide nitride nanobelt arrays,[21] Nb_2O_5 nanochannels[15] and Nb_2O_5 powders[14]. Based on different metal precursors, Nb_4N_5 have different structures, such as nanochannel,[15] nanosize crystal[22] and nanobelts[23]. However, there is no reports on the synthesis of 2D Nb_4N_5 nanosheets. 2D nanosheets provide large surface area for electrode materials. Nanostructured electrode materials with large surface area could improve the performance of energy storage.[24] A common approach to synthesize nanostructured electrode materials is tailored template method.[25] Therefore, 2D Nb_4N_5 nanosheets deserve fully exploration in synthesis and application for energy storage.

Here, template method was developed to synthesize 2D Nb_4N_5 nanosheets. In our experiment, 2D NbS_2 nanosheets were used as templates to grow 2D Nb_4N_5 nanosheets in ammonia (NH_3) atmosphere. In addition, electrochemical performance of 2D Nb_4N_5 nanosheets as electrode materials was investigated.

Results and Discussion

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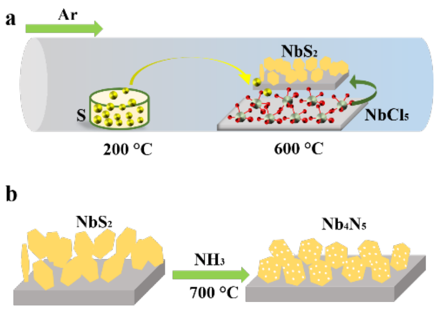

Figure 1. Schematic illustration of growth process of 2D Nb_4N_5 nanosheets. (a) Synthesis of NbS_2 naonsheets as the templates. (b) Synthesis of 2D Nb_4N_5 nanosheets based on NbS_2 nanosheets templates.

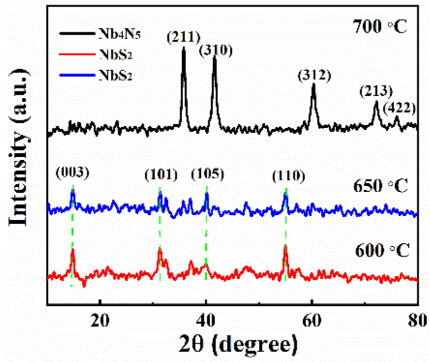

Figure 2. XRD diffraction patterns of NbS_2 nanosheets templates ammoniated at different temperatures (600 °C, 650 °C and 700 °C) in NH_3 atmosphere.

The schematic illustration of growth process of 2D Nb_4N_5 nanosheets is shown in Figure 1. The details of experiments are in the Experiment Section. Figure 1a shows the synthesis of NbS_2 templates. To determine the ammonization condition of the NbS_2 nanosheets in NH_3 atmosphere, several ammonization temperatures have been attempted firstly. X-ray diffraction (XRD) was conducted to confirm these ammoniated samples. Figure 2 displays the XRD diffraction patterns of these ammoniated samples under 600 °C, 650 °C and 700 ° C. For NbS_2 nanosheets ammoniated at 600 ° C and 650 ° C, only several typical diffraction peaks of NbS_2 nanosheets were detected in the XRD pattern. These typical diffraction peaks of NbS_2 are indexed as (003), (101), (015) and (110), which are located at 15° , 31.4° , 40.2° , and 55.2° , respectively.[26] This indicates that NbS_2 nanosheets could not be successfully transformed to Nb_4N_5 nanosheets at 600 ° C and 650 ° C. However, as ammoniated temperature increased to 700 ° C, several typical diffraction peaks of Nb_4N_5 nanosheets could be detected in the XRD pattern, indicating that Nb_4N_5 nanosheets have been successfully synthesized by NbS_2 nanosheets templates in ammonia environment. The diffraction peaks of Nb_4N_5 nanosheets are indexed as (211), (310), (312), (213) and (422), which are located at 36.1°, 41.7°, 60.9°, 73.2°, 76.4° (JCPDS no. 51-1327). Based on the XRD results, we could conclude that Nb_4N_5 nanosheets have been synthesized successfully by NbS_2 nanosheets templates at 700 °C.

To confirm the nitridation of NbS_2 nanosheets to Nb_4N_5 nanosheets, energy dispersive X-ray spectroscopy (EDX) in SEM was used to identify the atomic compositions of samples. The atomic composition of NbS_2 nanosheets templates and ammoniated NbS_2 nanosheets at 650 °C and 700 °C were shown in Table 1 (normalized to the Nb=1.00). As the ammoniated temperature increases, the ratio of N increases with ratio of S decrease. For NbS_2 nanosheets templates, Nb:S ratio is 1:2. After ammoniated at 650 °C, nitrogen atoms replace the S atoms and the Nb:S ratio changes to 1:0.21. As annealed temperature increased to 700 °C, Nb:S ratio changes to 1:0.01 and Nb:N ratio increases to 1:1.3, indicating synthesis of Nb_4N_5 nanosheets.

Table 1. Elemental analysis from EDX of NbS_2 nanosheets templates and samples ammoniated at different temperatures in NH_3 atmosphere. Atomic ratios is normalized to Nb = 1.00.

	Nb	S	N
NbS_2 nanosheets	1.00	2.00	-
NbS_2 650 °C	1.00	0.21	0.367
NbS_2 700 °C	1.00	0.01	1.3

Scanning electron microscopy (SEM) was performed to reveal the morphology and detailed microstructure of nanosheets. Figures 3a-c show the morphologies of NbS_2 nanosheets ammoniated at different temperatures (600 °C, 650 °C and 700 °C). In Figure 3a, NbS_2 nanosheets show hexagon shape, which can be clearly observed in the inset pictures (framed in red in Figure 3a). The average lateral sizes of NbS_2 nanosheets are about 400 nm. As growth temperature increased to 650 °C, NbS_2 nanosheets could still maintain hexagon shape (Figure 3b). Once ammoniated temperature increased to 700 °C, NbS_2 nanosheets were transformed into Nb_4N_5 nanosheets. As shown in Figure 3c, Nb_4N_5 nanosheets also display hexagonal shape. However, they show porous structures with different pore size, which can be seen clearly in the insert picture (framed in red cycles in Figure 3c). These porous structure results from different configuration structure of NbS_2 and Nb_4N_5 nanosheets. The nitrogen adsorption-desorption isotherms of the NbS_2 nanosheets and Nb_4N_5 nanosheets synthesized at 700 °C were collected (Figure S1). The BET surface area of NbS_2 nanosheets and Nb_4N_5 nanosheets are 160.949 m^2/g and 381.592 m^2/g, respectively (Table S1). The increased the BET surface area for Nb_4N_5 nanosheets is due to the formation of porous. Compared to the total pore volume (0.03 cc/g) and average pore diameter (1.5 nm) for NbS_2 nanosheets, the total pore volume and average pore diameter for Nb_4N_5 nanosheets are increased to 0.059 cc/g and 3.716 nm (Table S1).

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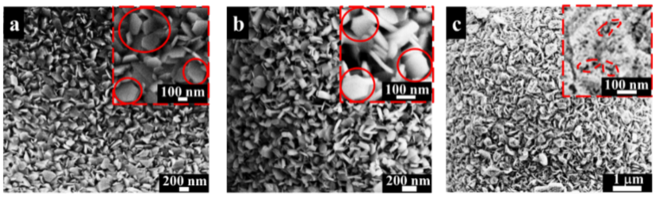

Figure 3. SEM images of NbS_2 nanosheets ammoniated under different temperatures. NbS_2 nanosheets were ammoniated at (a) 600 °C and (b) 650 °C and (c) 700 °C in NH_3 atmosphere for 30 min.

Furthermore, detailed microstructure Nb_4N_5 nanosheets was identified by transmission electron microscopy (TEM) (Figure 4). Nb_4N_5 nanosheets are porous structure with pore size of ~ 20 nm in Figure 4a. High resolution TEM (HRTEM) image shows lattice fringes of nanosheets with space of 0.217 nm (Figure 4b) which agrees well with (310) crystal planes.[27] TEM images also demonstrate that 2D Nb_4N_5 nanosheets were synthesized via NbS_2 nanosheets template CVD.

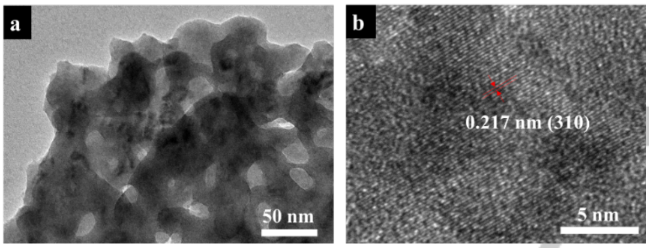

Figure 4. (a) TEM micrograph and (b) High-resolution (HR) TEM micrograph of 2D Nb_4N_5 nanosheets.

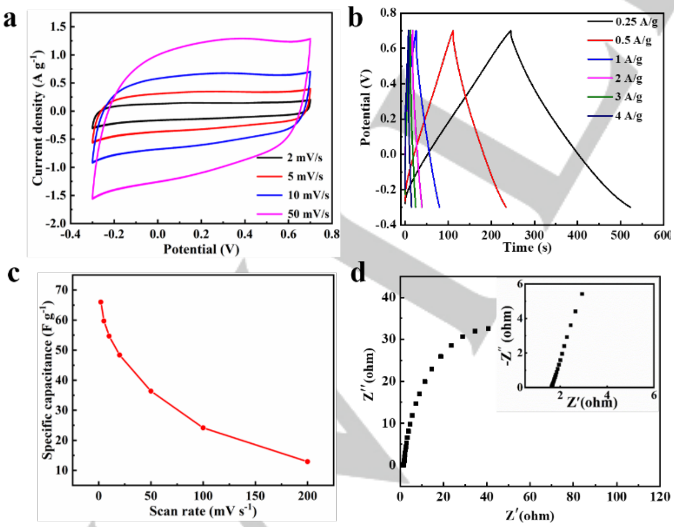

Figure 5. Electrochemical properties of 2D Nb_4N_5 nanosheets as electrode materials. (a) Cyclic voltammetry curves at different scan rate (2, 5, 10 and 50 mV/s) in 0.5 M H_2SO_4 electrolyte. (b) Galvanostatic charge-discharge curves at different current densities (0.25, 0.5, 1, 2, 3, 4 A/g). (c) The variation of specific capacitance with scan rate from 2 to 200 mV/s. (d) Nyquist plots variation as a function of frequency of Nb_4N_5 nanosheets.

To investigate performance of 2D Nb_4N_5 nanosheets for supercapacitor as electrode materials, electrochemical performances of Nb_4N_5 nanosheets were tested in 0.5 M H_2SO_4 using three-electrode system. The performances of Nb_4N_5 nanosheets are displayed in Figure 5. The CV curves of the Nb_4N_5 nanosheets (Figure 5a) are nearly rectangular when scanning is carried out from − 0.3 to 0.7 mV at a scanning rate of from 2 mV/s to 50 mV/s, indicating Nb_4N_5 nanosheets are promising candidates as electrode material for supercapacitor. The galvanostatic charge/discharge (GCD) curves of Nb_4N_5 nanosheets collected at different current density ranging from 0.25 to 4 A/g are shown in Figure 5b. The GCD curves at all current density are nearly symmetric, indicating a high charge/discharge columbic efficiency and low polarization of electrode. As a decreasing current density, the nonlinearity of potential and time curves turn sharp. This indicates that the process is involved with pseudo-constant charge/discharge over the entire potential window. Gravimetric capacitance of the Nb_4N_5 nanosheets as electrode materials (Figure 5c) are calculated from the GCD curves (Figure 5b). The gravimetric capacitance of Nb_4N_5 nanosheets at 2 mV/s is 66 F g^{-1}. As the current density increased from 2 mV s^{-1} to 200 mV s^{-1}, gravimetric capacitance decreases from 66 F g^{-1} to 12.9 F g^{-1}. As shown in Figure 5d, the Nyquist plots show that the equivalent series resistance (ESR) is only 1.6 Ω. This lower value means consistent interfacial contact of the electrode. These electrochemical properties indicate that these 2D Nb_4N_5 nanosheets have potential application in field of energy storage as electrode materials.

Conclusion

In conclusion, a novel template method was explored to synthesize 2D Nb_4N_5 nanosheets. 2D Nb_4N_5 nanosheets can be successfully fabricated by ammonization of NbS_2 nanosheets in NH_3 atmosphere. 2D Nb_4N_5 nanosheets are hexagon shape and porous structure with pore size of ~20 nm. In addition, 2D Nb_4N_5 nanosheets exhibit capacitor behavior as electrode materials. More importantly, the current research results provide an effective strategy to produce other non-layered 2D metal nitride nanosheets with porous structures for high-performance energy storage and conservation.

Experimental Section

Preparation of 2D Nb_4N_5 nanosheets:

First, NbS_2 nanosheets templates were synthesized. Niobium chloride ($NbCl_5$) and sulfur (S) powders were used as metal and sulfur precursors, respectively. $NbCl_5$ powder (50 mg) in a ceramic boat was placed in center of the quartz tube and melamine foam (1x1 cm^2) as the substrate was placed above $NbCl_5$ powder. S powder (100 mg) in another ceramic boat was placed on the upstream relative to the gas flow direction in the quartz tube. The distance between $NbCl_5$ powder and S powder was about 30 cm.

The $NbCl_5$ powder was heated to 600 °C at 10 °C /min under an Argon environment (200 sccm, standard cubic centimeter per minute). After it was heated target temperature, S power was moved into low-temperature zone (about 200 °C). Then S source was carried into high-temperature zone by Ar gas and reacted with $NbCl_5$ vapor to grow NbS_2 nanosheets. After 30 minutes, S powder was moved away from low-temperature zone. Figure 1b shows the synthesis of 2D Nb_4N_5 nanosheets. Second, the obtained NbS_2 nanosheets templates was ammoniated in NH_3 environment. During this process, different nitridation temperatures were studied. NbS_2 nanosheets were heated up to 600 °C, 650 °C and 700 °C at 10 °C /min in Ar gas, respectively. After that, Ar gas was closed and NH_3 gas was provided to synthesize 2D Nb_4N_5 nanosheets for 30 min. Finally, the furnace was cooled to room temperature gradually and samples were collected.

Characterization of niobium nitride nanosheets:

The morphology of samples was characterized under scanning electron microscopy (SEM). Microstructure and composition of samples were conducted by X-ray diffraction analysis (XRD) using Cu Kα radiation. Transmission electron microscopy (TEM) (JEOL JEM-2100F) was utilized to obtain atomic resolution images of niobium nitride nanosheets.

Electrochemical performance of niobium nitride nanosheets:

The electrochemical performances were performed in a three-electrode system in a 0.5 M H_2SO_4 electrolyte. Niobium nitride nanosheets, black carbon and PVDF with the ratio of 90:5:5 were mixed and then attached on Ti foil as work electrode. Ag/AgCl electrode and black carbon electrode were reference electrode and counter electrode, respectively. Electrochemical performance for supercapacitors was conducted, including cyclic voltammetry curve, galvanostatic charge-discharge curves, Nyquist plots variation using the electrode system.

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Keywords: 2D Nb_4N_5 nanosheets; template method.

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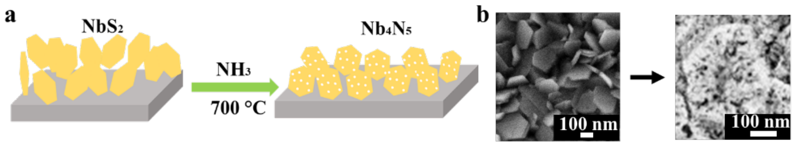

A new approach was explored to synthesize the Nb_4N_5 nanosheets by template method. First, NbS_2 nanosheets were fabricated by chemical vapor deposition method. Then Nb_4N_5 nanosheets were synthesized by ammonization of NbS_2 nanosheets in the NH_3 atmosphere at 700 °C. Nb_4N_5 nanosheets show capacitor behavior as electrode materials for energy storage.