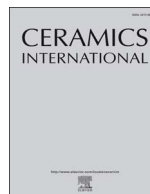




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Hierarchically nanostructured vanadium nitride microspheres assembled with porous nanosheets fabricated by a template-free route

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ABSTRACT

In this research, hierarchically nanostructured vanadium nitride (VN) microspheres were successfully prepared by a template-free method. ZnO, behaving as a sacrificial phase, was selectively leached out during nitridation of $\text{Zn}_3(\text{OH})_2(\text{V}_2\text{O}_7)(\text{H}_2\text{O})_2$ microspheres with NH_3 , inducing a network structure. The VN microsphere was assembled with porous nanosheets. Extraordinary, the VN microsphere mimicked the morphology of the initial precursor and exhibited a rose-like morphology. The diameter of the microsphere was in the range of 1–3 μm , and the thickness of the porous nanosheets was typically approximately 30 nm. In addition, this facile and novel synthetic strategy can be further extended to the preparation of other hierarchically nanostructured transition metal nitrides.

1. Introduction

In recent years, transition metal nitrides (TMNs) have been studied widely due to their interesting chemical and physical properties [1–3]. As a typical TMN, Vanadium nitride (VN) possesses many desirable characteristics including high melting point (2619 K), extreme hardness (1500 kg/mm²), excellent wear resistance, high electrical conductivity (10⁶ S/m), and excellent corrosion resistance [4–6]. Thus, VN can be applied in wear-resistant coating and electronic devices fields [7,8]. In addition, several other applications of VN, such as electrodes for energy storage devices including supercapacitors (SCs) [9], lithium-ion batteries [5,10], lithium-sulfur batteries [11], dye-sensitized solar cells [12] and fuel cells [13,14], have also been reported. Furthermore, VN belongs to the family of intermetallic compounds, where N atoms occupy the interstitial lattice sites, leading to the increase of d-electron density. As a result, VN has a similar electronic structure to noble metals and can be used as practical catalysts for some hydrogen-involved reactions [15]. To maximize the above performance of VN, nanoscale particles are favored. However, as the size of the VN nanoparticles decreases, nanoparticles agglomeration usually occurs and leads to the lowering of the specific surface area and high contact resistance [16]. An effective approach to avoid agglomeration is to control the morphology of VN, for example, to form VN with hierarchical structure.

Various synthesis methods, such as nitridation of V metal or metal chlorides, oxides, and sulfides [17–20], carbon thermal reduction/nitridation of oxides [21], solid-state metathesis synthesis [22,23], self-propagating high-temperature synthesis (SHS) [24], and so on, have been established to prepare VN. Unfortunately, VN particles prepared by the above methods are severely agglomerated, producing nanoparticles with non-uniform morphologies and low specific surface area. Additionally, those conventional methods are impractical for the synthesis of hierarchically nanostructured VN. Prior work in the preparation of hierarchically porous TMNs basically focused on template methods. However, the use of pre-formed templates and post-processing are prerequisite in these methods.

As a promising technique, the template-free route has been proven to be an effective method to prepare porous inorganic materials. Selective leaching of sacrificial phases is a typical template-free method to achieve porous inorganic materials [25,26]. Up to now, single-crystal GaN nanotubes [27], porous TiN microspheres and nanofibers [28,29], porous metals and oxides [26], as well as mesoporous TMNs [4,30,31] have been successfully synthesized by selectively etching ZnO from the corresponding precursors. However, there are few attempts to fabricate hierarchically nanostructured VN materials. To the best of our knowledge, preparing hierarchically nanostructured VN microspheres by this method has not been reported.

Herein, a novel VN with hierarchical nanostructure features was

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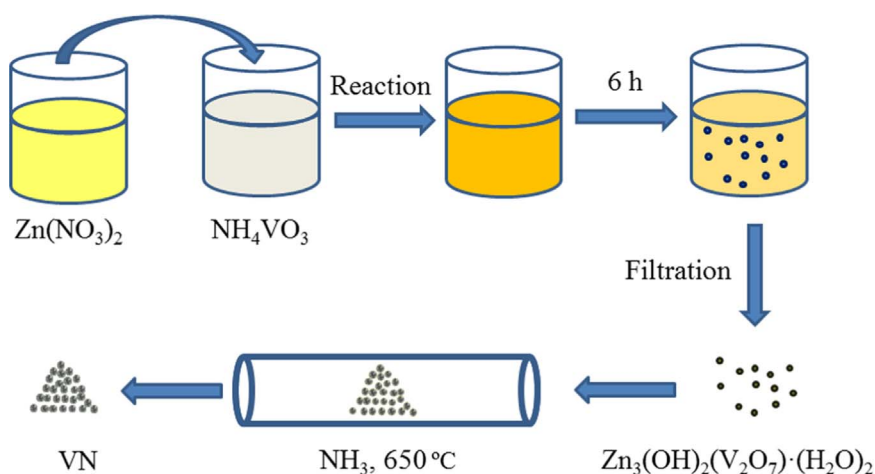


Fig. 1. Diagram for the formation of hierarchically nanostructured VN microspheres.

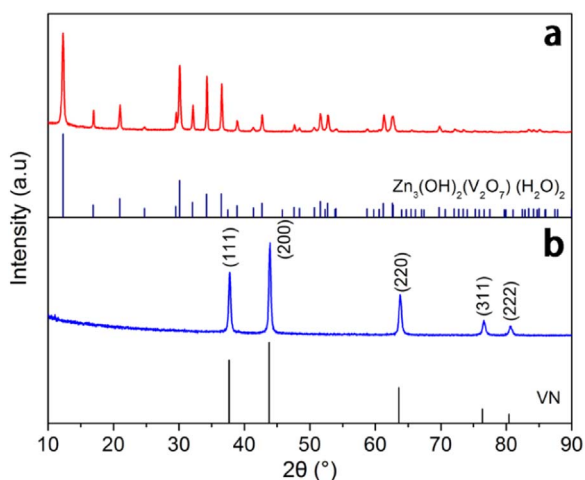


Fig. 2. XRD patterns of (a) $\text{Zn}_3(\text{OH})_2(\text{V}_2\text{O}_7)\cdot(\text{H}_2\text{O})_2$ and (b) VN.

prepared through nitridation of hierarchically nanostructured $\text{Zn}_3(\text{OH})_2(\text{V}_2\text{O}_7)\cdot(\text{H}_2\text{O})_2$ microspheres. As a sacrificial phase, ZnO was selectively removed during nitridation process, thus creating porous structure. VN microspheres assembled with porous nanosheets were obtained. Its phase structure, composition and microstructure were characterized. The formation process was also investigated.

2. Experimental

2.1. Synthesis of hierarchical VN microspheres

$\text{Zn}_3(\text{OH})_2(\text{V}_2\text{O}_7)\cdot(\text{H}_2\text{O})_2$ microspheres were prepared by a simple liquid phase precipitation procedure similar to the process reported by Wang [32]. For example, $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (1.2 mmol) and NH_4VO_3 (0.8 mmol) were dissolved in 10 mL of deionized water at room temperature. Then, NH_4VO_3 solution was added to $\text{Zn}(\text{NO}_3)_2$ solution under magnetic stirring. After the suspension was stirred for 0.5 h, followed by aging for 6 h, the precipitates were filtered and washed three times with deionized water and ethanol, respectively. Subsequently, the product was dried in an oven at 60 °C for 24 h.

Then, the dried $\text{Zn}_3(\text{OH})_2(\text{V}_2\text{O}_7)\cdot(\text{H}_2\text{O})_2$ microspheres were placed into a corundum tube furnace and annealed for 8 h under NH_3 flow (400 mL/min) at 650 °C with a progressive heating ramp (4 °C/min). Finally, the hierarchical VN microspheres were obtained.

2.2. Materials characterization

The morphology and chemical composition of the precursor and the final product were characterized by a scanning electron microscope (SEM, JSM-7001F, 15 kV) equipped with energy dispersive X-ray spectroscopy (EDS). The powders were homogeneously spread out over a carbon background to achieve SEM images. The microstructure of the final product was observed by a transmission electron microscope (TEM, JEM-2010, 200 kV). The dispersion of VN powder was coated onto a 300 mesh copper grid to obtain TEM images. The X-ray diffraction (XRD) patterns were obtained on a PANalytical B.V instrument by using Cu K α radiation ($\lambda = 1.5419 \text{ \AA}$), operating at 40 kV and 20 mA. X-ray photoelectron spectroscopy (XPS) characterization was carried out on an ESCALAB 250Xi (Thermo Fisher Scientific Inc.) spectrometer using an Al K α source. Specific surface areas and pore distribution were measured by Brunauer-Emmett-Teller (BET) nitrogen adsorption-desorption at 77 K on a NOVA3200e gas adsorption analyzer.

3. Results and discussion

In order to generate hierarchically nanostructured VN materials, the hierarchical $\text{Zn}_3(\text{OH})_2(\text{V}_2\text{O}_7)\cdot(\text{H}_2\text{O})_2$ microspheres were used as precursor. The schematic of the synthesis procedure of VN is depicted in Fig. 1. An aqueous solution containing Zn salt (Zinc nitrate hexahydrate) and metavanadate reacted to precipitate $\text{Zn}_3(\text{OH})_2(\text{V}_2\text{O}_7)\cdot(\text{H}_2\text{O})_2$. Then, the precursor, nanostructured $\text{Zn}_3(\text{OH})_2(\text{V}_2\text{O}_7)\cdot(\text{H}_2\text{O})_2$ microspheres, were obtained after aging for 6 h. Subsequently, hierarchically nanostructured VN were prepared by nitridation of the precursor at 650 °C.

Fig. 2a shows the XRD patterns of $\text{Zn}_3(\text{OH})_2(\text{V}_2\text{O}_7)\cdot(\text{H}_2\text{O})_2$. It can be seen that the patterns match expected PDF files of 01-087-0417 [33]. In addition, no obvious extra diffraction peaks attributed to NH_4VO_3 or $\text{Zn}(\text{NO}_3)_2$ were identified, indicating that a relatively pure $\text{Zn}_3(\text{OH})_2(\text{V}_2\text{O}_7)\cdot(\text{H}_2\text{O})_2$ phase was generated. The patterns of VN are presented in Fig. 2b. Five diffraction peaks corresponding to the (111), (200), (220), (311) and (222) planes at 37.65°, 43.76°, 63.61°, 76.34°, and 80.40°, respectively, match well with the characteristic peaks of cubic VN phase (PDF file 01-078-1315) [34]. No impurity peaks were detected, indicating that VN with high purity was obtained. The lattice constant of the VN samples was calculated using the least square refinement technique and it was found to be 4.1309 Å, which is in agreement with the bulk lattice parameter of cubic VN of 4.105–4.140 Å [35]. The sharp diffraction peaks in Fig. 2b indicate the good crystallinity of the VN obtained. The crystallite size of VN, calculated using the Scherrer formula from the integral breadth of the Lorentzian contribution determined from the peak profile analysis using

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