

A room-temperature synthesis of nanocrystalline vanadium nitride

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Abstract

Vanadium nitride was synthesized by the reaction of VCl_4 and NaNH_2 at room temperature. X-ray powder diffraction could be indexed as cubic VN with the lattice constant of $a = 4.134 \text{ \AA}$. Transmission electron microscopy image showed particle and hollow sphere morphology. The optical properties of the as-prepared VN were investigated.

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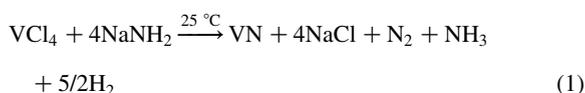
1. Introduction

Metal nitrides, especially those of transition metals, have received increasing attention in recent years because of their interesting and attractive chemical and physical properties [1]. The traditional applications of these materials range from cutting tools and structural materials [2,3] to magnetic and electric components [4] and superconducting devices [5–7]. Among them, vanadium nitride (VN) is an important material due to its typical properties including wear resistance, high melting point, extreme hardness, high thermal conductivity, excellent oxidative stability and corrosion resistance, low electrical resistivity [8,9].

Conventionally, VN has been synthesized by various high temperature methods, such as the direct reaction of metal vanadium with nitrogen at $1200 \text{ }^\circ\text{C}$ [9], carbothermal reduction of vanadium pentoxide in N_2 at about $1500 \text{ }^\circ\text{C}$ [10], and solid-state metathesis (SSM) routes at elevated temperature [11]. However, most of these reactions involve processing temperatures high than $1000 \text{ }^\circ\text{C}$ and for extended time periods. Recently, Parkin et al. [12] have reported

chemical vapor deposition of VN film from reaction of VCl_4 with NH_3 . Our group has successfully synthesized nanocrystalline VN by a reduction–nitridation reaction between VCl_4 , NH_4Cl and Mg [13].

Herein, we report a facile approach to prepare VN at room temperature, using vanadium tetrachloride (VCl_4) as the vanadium source and sodium amide (NaNH_2) as nitrogen. The reaction can be formulated as follows:



2. Experimental procedure

All the manipulations were carried out in a dry glove box with Ar flowing. All the reagents used were of analytical-grade purity. In a typical procedure, NaNH_2 (0.04 mol) was added into a crucible and then VCl_4 (0.01 mol) was dripped into the crucible at room temperature ($25 \text{ }^\circ\text{C}$). When the VCl_4 was added, NaNH_2 immediately reacted with VCl_4 . The obtained product was washed with distilled water and absolute ethanol for several times to remove the impurities. The final product was vacuum-dried at $60 \text{ }^\circ\text{C}$ for 4 h.

X-ray powder diffraction (XRD) pattern was carried out

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on a Rigaku Dmax- γ A X-ray diffractometer with Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$). The morphology of nanocrystalline VN was observed from transmission electron microscopy (TEM) images taken with a Hitachi H-800 transmission electron microscope. X-ray photoelectron spectra (XPS) were recorded on a VGESCALAB MKII X-ray photoelectron spectrometer, using non-monochromatized Mg K α X-rays as the excitation source. The ultraviolet and visible light (UV–vis) spectra and photoluminescence (PL) spectra were recorded on JGNA Specord 200 (Japan) PC UV–vis spectrophotometer and Hitachi 850 fluorescence spectrophotometer, respectively.

3. Results and discussion

Fig. 1 shows the XRD pattern of the product. All of the four peaks at d -spacings of 2.398, 2.072, 1.462, 1.247 \AA can be indexed as cubic VN ((111), (200), (220), (311)). The lattice constants are $a = 4.134 \text{ \AA}$, in good agreement with $a = 4.137 \text{ \AA}$ (JCPDS card# 78-1315). No evidence of V_2O_3 , NaCl and other impurities are observed. The broadened nature of the peaks indicates that the grain sizes of the sample are on the nanometer scale.

Further evidence for the XPS spectrum of the as-prepared VN sample is shown in Fig. 2. The chemical binding energies of $\text{V}2p_{3/2}$ and N1s are located at the positions of 514.2 and 397.1 eV, respectively. The N1s peak at 397.1 eV and the $\text{V}2p_{3/2}$ peak at 514.2 eV, in good agreement with those in the literature [14].

The TEM image and selected area electron diffraction (SAED) pattern of as-prepared VN are shown in Fig. 3. From Fig. 3a, the material exhibits particle and hollow sphere morphology. It can be seen that there is an obvious contrast between the dark edge and the center of the sphere, revealing that the core is hollow. The as-prepared VN sphere has diameter about 120 nm, with thickness of the shell is about 20 nm. The SAED pattern (Fig. 3b) of the VN hollow

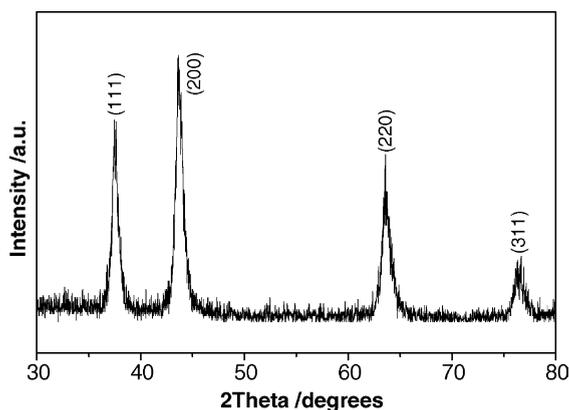


Fig. 1. XRD pattern of the VN sample.

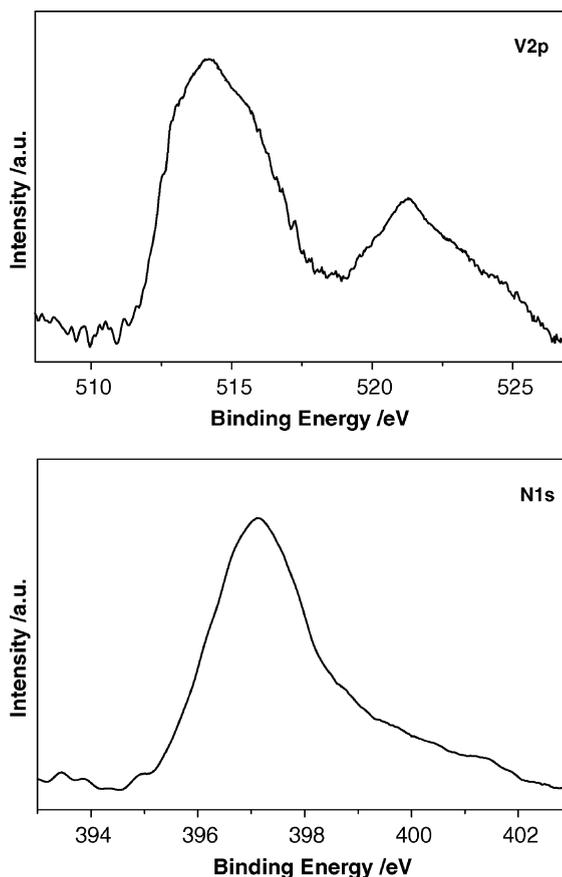


Fig. 2. XPS spectra of the VN sample.

sphere shows three clear diffraction rings corresponding to the (111), (200), (220) planes of cubic VN. This result suggests that the shell of VN hollow sphere is constructed by VN polycrystallines.

The UV–vis absorption and PL emission spectra of the nanocrystalline VN are shown in Fig. 3. The onset of the absorption appears at about 271 nm in Fig. 4a. The PL spectrum (Fig. 4b) of nanocrystalline VN excited at 293 nm shows an emission at 364 nm, which may be ascribed to the transitions between the hybridized $\text{V}3d$ – $\text{N}2p$ bands [15].

According to free energy calculations, the reaction is thermodynamically spontaneous and highly exothermic ($\Delta G = -935.4 \text{ kJ mol}^{-1}$ and $\Delta H = -852.5 \text{ kJ mol}^{-1}$) [16]. A great deal of heat is generated during the reaction process and results in an instantaneous local high temperature, which favors the formation of nanocrystalline VN. Strongly exothermic reaction raises the local temperature near the surface and leads VCl_4 (b.p. $148 \text{ }^\circ\text{C}$) to vaporize to form many small droplets. Then the reaction can occur on the surface of the VCl_4 droplets in the atmosphere of NaNH_2 , which may result in the formation of a VN shell around the VCl_4 core. With the VCl_4 droplets further

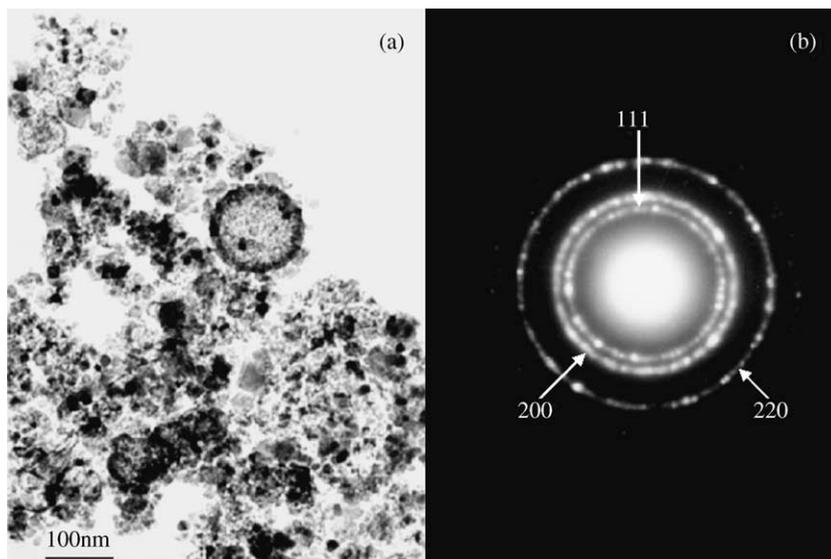


Fig. 3. (a) TEM image and (b) SAED pattern of the VN sample.

reacting with NaNH_2 , the shell becomes thicker. In this process VCl_4 droplets may serve as a template with the VN shells formed near the liquid–solid interface.

4. Conclusions

In summary, we have succeeded in synthesizing nanocrystalline VN by the reaction of NaNH_2 and VCl_4 at room temperature. The XRD pattern can be indexed as cubic VN with the lattice constant of $a = 4.134 \text{ \AA}$. The TEM image shows particle and hollow sphere morphology. The PL spectra of the nanocrystalline VN shows an emission at 364 nm.

Acknowledgements

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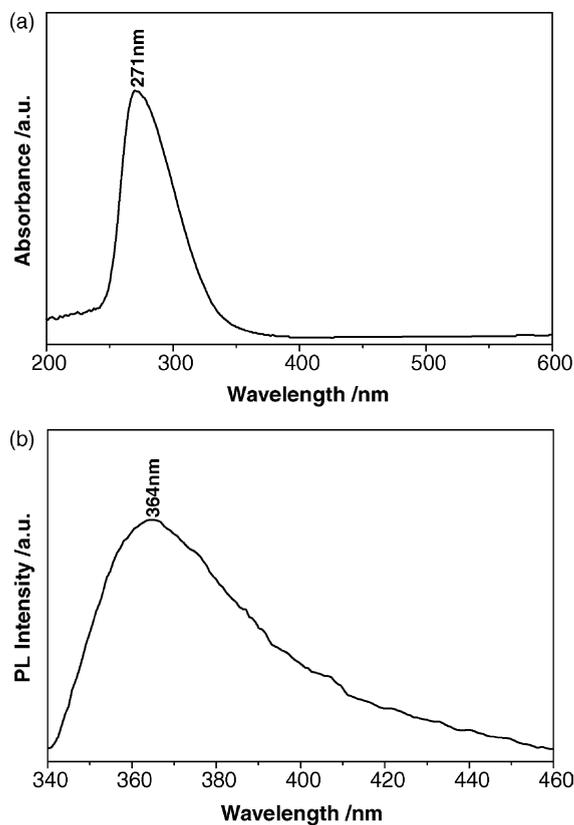


Fig. 4. (a) UV–vis spectra and (b) PL spectra of the VN sample.

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