

A Thermal Reduction-Nitridation Synthesis and Ultraviolet-light Emission of Nanocrystalline VN

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18 nm vanadium nitride (VN) nanocrystallites were synthesized through a reduction-nitridation reaction between VCl_4 , NH_4Cl and metal Mg. The XRD showed the product was pure cubic VN ($a = 4.14 \text{ \AA}$). Ultraviolet emissions at about 337 and 346 nm were observed from the nanocrystalline VN at room temperature.

Vanadium nitride (VN) is well-known for its typical combination of properties, including high melting point, extreme hardness, high thermal conductivity, low electrical resistivity and high chemical and thermal stability.^{1,2} Most of the VN materials are in the form of thin films as wear-resistant³ and solar-control⁴ coatings. It is equally important to produce nanocrystalline VN powder, because it can be utilized as effective industrial catalysts⁵ and has potential applications in mechanical, electrical and optical fields.⁶ However, there have been few reports on the composition, structure and physical properties of the VN nanocrystallites, indicating that there is a great challenge in synthesis and characterization of VN.⁷

Traditionally, VN nanocrystallites can be synthesized through various methods, such as carbothermal reduction of vanadium pentoxide in N_2 at about 1500°C ⁸ and direct nitridation of metal vanadium in N_2 at 1200°C .² A high-temperature combination of NH_3 (or H_2/N_2 mixture) with various vanadium sources such as metal vanadium, NH_4VO_3 ,¹ its oxide,⁹ chloride,¹⁰ and sulfide¹¹ at temperatures around 1000°C can also be applied to preparation of VN particles. Vanadium nitride powder can also be prepared through the microwave-assisted combustion method¹² and solid state metathesis (SSM) method¹³ at elevated temperatures.

Herein, we reported a low temperature thermal reduction and nitridation to synthesize nanocrystalline VN in an autoclave at 500°C . All the reagents were analytically pure. In a typical procedure, in a dry glovebox with N_2 flowing 0.01 mol of VCl_4 , 0.01 mol of NH_4Cl and 0.025 mol of powdered Mg were put into a stainless steel autoclave of 50 mL capacity. The autoclave was sealed and maintained at 500°C for 12 h and then cooled to room temperature on standing. After that, the product was washed with absolute alcohol, 0.5 mol/L HCl and distilled water in turn. A black-brown product was collected and dried in vacuum at 60°C for 4 h.

The crystalline structure of the as-obtained product was identified by X-ray powder diffraction (XRD), using a DanDong X-ray diffractometer with graphite-monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The size and shape of the product was also observed by a Hitachi H-800 transmission electron microscope (TEM), applying an accelerating voltage of 200 kV. The surface of the product was examined by X-ray photoelectron

spectroscopy (XPS) using a VGESCALAB MKII photoelectron spectrometer using $\text{Mg K}\alpha$ radiation (1253.6 eV). The UV-vis absorption spectrum was recorded on a Shimadzu UV-2401PC UV-vis spectrophotometer. The photoluminescence (PL) spectrum was measured by a Hitachi 850 fluorescence spectrometry with a Xe lamp at room temperature.

A typical XRD pattern of the product was shown in Figure 1. All the diffraction peaks could be indexed as (111), (200), (220), (311) and (222) reflections of NaCl type VN (JCPDS No. 78-1315), respectively. No impurity XRD peaks, such as V_2N , V_2O_3 , V_2O_5 and V, were detected in the experiment range. The lattice parameter was calculated to be $a = 4.14 \text{ \AA}$, which was close to the reported value of $a = 4.1398 \text{ \AA}$ of stoichiometric VN.¹⁴ The crystallite size was estimated to be 18 nm, according to (200) reflection by the Debye-Scherrer equation with a shape factor of 0.9. The TEM images (not shown here) indicated that the product was about 10–20 nm and in irregular shape.

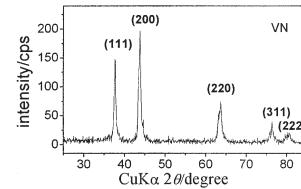


Figure 1. XRD pattern of the product prepared on the reaction of VCl_4 , NH_4Cl and Mg at 500°C for 12 h.

XPS spectrum (Figure 2) of the as-prepared product indicated the presence of V, N and surface contamination of C and O due to the absorbed gaseous molecules. The main C1s peak was set to 284.6 eV. In the inserted high-resolution spectra, the peak cores at 397.15 eV and 515.05 eV corresponded to N1s and V2p_{3/2}, respectively, which were close to the reported binding energies.¹¹ However, the V2p peaks were broad, which may be attributable

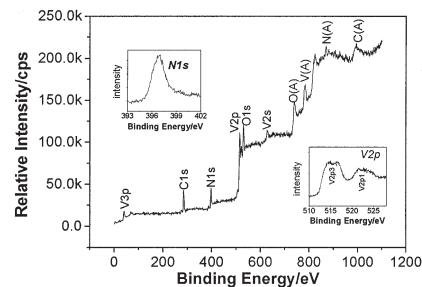


Figure 2. XPS spectra of the same sample as in Figure 1, the inserted figures were higher resolution spectra of V2p and N1s.

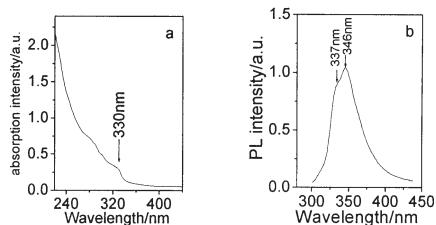
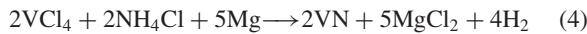
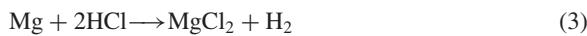


Figure 3. Room temperature UV-vis absorption (a) and photoluminescence emission (b) spectra of the same product as in Figure 1.

to a slight oxidation of the sample. By measuring peak areas of the N and V cores, the ratio of N/V was calculated to be 0.94 and close to chemical stoichiometry. This also implied some nitrogen vacancies in the as-prepared product. Thus, this product can be formulated as VN. The yield of the VN was about 85% based on the VCl_4 .

The UV-vis absorption and PL emission spectra of the VN nanocrystallites were shown in Figure 3. The onset of the absorption appears at about 330 nm in Figure 3(a). The photoluminescence spectrum (Figure 3(b)) of the VN nanocrystallites excited at 239 nm shows a main emission at 346 nm (3.60 eV) and a shoulder emission at 337 nm (3.68 eV), which may be ascribed to the transitions between the hybridized $\text{V}3\text{d}$ - $\text{N}2\text{p}$ bands.¹⁴ Previously, Callenas and Johansson had studied band structure of the bulk $\text{VN}_{0.89}$ by ultraviolet photoelectron spectroscopy (UPS).¹⁵ There, the UPS emission peak at about 4.4 eV was close to the band energy (3.6 eV) between the Δ_5 initial-state band and the Fermi level in bulk VN.¹⁵ Therefore, the PL emissions at 3.6–3.68 eV were consistent with theoretical band energy.^{14,15} The presence of shoulder emission may result from the nitrogen vacancies.

In our experiments, NH_4Cl decomposed generating NH_3 and HCl gases at 500 °C. Then, the pressure in the vessel increased up to 3.7 MPa, as estimated by the ideal gas law from the decomposed NH_3 , HCl and VCl_4 ($\text{bp} = 152^\circ\text{C}$)¹⁶ gases. The gaseous VCl_4 and NH_3 could react with the surface of Mg powder to produce VN. The oxidation state of the vanadium was reduced from +4 to +3 and the elemental magnesium was oxidized to MgCl_2 simultaneously. The produced HCl gas was strongly absorbed by the Mg powder to form MgCl_2 and H_2 . Therefore, the possible thermal reduction-nitridation reaction may be expressed as following.



The reaction temperature and time play very important roles on the formation of VN. Although the reaction (Eq 4) from VCl_4 , NH_4Cl and Mg to VN is thermodynamically spontaneous ($\Delta G = -230.59 \text{ kcal}\cdot\text{mol}^{-1}$) and exothermic ($\Delta H =$

$-224.025 \text{ kcal}\cdot\text{mol}^{-1}$),¹⁶ crystalline VN cannot form at a temperature lower than 400 °C. An increase of the reaction temperature over 650 °C result in an increase of the crystallite size more than 30 nm. The reaction was usually incomplete and the crystallinity was very poor in too short time (<3 h). However, varying the reaction time between 6 and 24 h did not significantly affect the crystallinity or the crystallite size. Thus, the optimal reaction parameters are at a temperature over 500 °C and not less than 6 h.

In summary, a convenient low temperature reduction-nitridation method was successfully applied to production of nanocrystalline VN powder at 500 °C, using NH_4Cl as nitrogen source, VCl_4 as vanadium source and powdered Mg as chlorine absorbent. The reaction temperature and time played important roles on the product. The product mainly consisted of cubic VN with size of 10–20 nm. The PL spectra of the VN nanocrystallites showed the ultraviolet light emission at about 337–346 nm, which was reported for the first time. Since the VN is one of the refractory materials, this nanocrystalline VN may be applied as high temperature luminescent materials.

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