A Simple Approach to Synthesize Mo_2N Nanocrystals

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Mo_2N nanocrystals were successfully synthesized through a simple reaction route. The synthesis was carried out in an autoclave in the temperature range of 450–550 °C, using $MoCl_5$ and NaN_3 as the reactants. Characterized by XRD, XPS, and TEM, the composition and morphology of the products were confirmed. This work contributes an effective and facile method for preparing the refractory metal nitride.

In the past decades, there has been much interest in the synthesis and characterization of the metal nitrides, especially those of transition metals, because of their fundamental physical properties, such as their hardness and high melting point, which lead to the applications in protective coatings for cutting tools,[1,2] ultrahigh-vacuum system components,[3] and reinforced ceramic tools.[4] Molybdenum nitride (Mo_2N), one of the transition metal nitrides, was regarded as active catalysts for a range of reactions typically occurring on the hydrodenitrogenation (HDN) of indole[5–7] and vacuum gas oil (VGO) hydrodesulfurization (HDS) of thiophene as well as in the reaction of cyclohexene with hydrogen.[8,9] Up to now, various strategies to the synthesis of Mo_2N have been invented. Soignard and co-workers[10] reported the high-pressure synthesis and low-compressibility of Mo_2N. Li et al.[11] reported the synthesis molybdenum nitride by temperature-programmed reaction (TPR) between $H_3PMo_{12}O_{40}{\cdot}26H_2O$ and NH_3. Roberson and co-workers[12] prepared thick polycrystalline Mo_xN films with small average grain size of 10 nm on previously nitrided Ti substrates via conversion of MoO_3 films in NH_3, while Wei et al.[13] reported the temperature-programmed reaction of MoO_3 with NH_3. Wu et al.[14] reported laser-promoted nitridation reaction. Li_3N was also used as nitriding agent through the liquid–solid reaction via benzene-thermal method.[15] However, impurity of carbon may be produced because of the decomposing of benzene.[16] Herein, by substituting NaN_3 for Li_3N, and employing $MoCl_5$ as molybdenum source, we report a more simple solid-state reaction route to synthesize nanocrystalline Mo_2N. Additionally, NaN_3 has been proven to be a useful nitriding agent since it can add a nitrogen overpressure to the reactions.

The reaction is carried out in an autoclave in the temperature range from 450 to 550 °C for 12 h. To the best of our knowledge, this is a synthesis route not been reported previously, which may provide a new route to the synthesis of other metal nitrides.

Molybdenum chloride ($MoCl_5$) and sodium azide (NaN_3) were purchased from Aldrich and Shanghai Chem. Co., respectively, and used without further purification. All the manipulations were carried out in a dry glove box with Ar flowing. In the typical process, 0.01 mol of $MoCl_5$ and 0.08 mol of NaN_3 were placed into a stainless steel autoclave. Then the autoclave was sealed and heated for 12 h at the temperature of 450, 500, and 550 °C, respectively, followed by cooling to room temperature on standing. The product was washed with dilute absolute ethanolic dilute HCl and distilled water for several times to remove the impurities. The final product was vacuum-dried at 60 °C for 4 h. Dark brown powders were obtained.

The obtained samples were characterized by X-ray powder diffraction (XRD) on a Rigaku Dmax-γA X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54178$ Å). The morphology of nanocrystalline Mo_2N was examined 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 nonmonochromatized Mg Kα X-rays as the excitation source.

In our process, Mo_2N nanocrystals with different size but in the same phases can be obtained through changing the reaction temperature from 450 to 550 °C.

Figure 1 shows the powder XRD patterns of the samples prepared at 550 °C for 12 h. All the diffraction peaks can be indexed to the 112, 200, 004, 220, 204, and 312 crystal planes of Mo_2N with tetragonal symmetry, respectively. The lattice parameters of the product are $a = 4.198$ and $c = 8.002$ Å, they are well consistent with the JCPDS files (No. 25-1368) ($a = 4.188$ and $c = 8.048$ Å).

To investigate the effects of reaction temperature in this reaction system, the above-mentioned reaction is carried out at different temperatures 450, 500, and 550 °C, respectively. The morphology and structure of the prepared Mo_2N nanocrystals at different temperature (named sample A, B, and C here) were further characterized using transmission electron microscopy (TEM). It can be easily seen that adapting different reaction temperature can control the sizes of these nanocrystals, and we found that the size of the nanocrystals increases with increasing reaction temperature. As shown in Figure 2a (sample A), there are a large amount of monodispersive crystallites with diameters ranging from 10 to 15 nm. Compared with sample A, there are a few rod-like nanocrystals existed in sample B [indicated by the arrow in Figure 2b], but a large amount of nanoparticles are still found. Nearly all the shapes can be contribute to rod-like in sam-

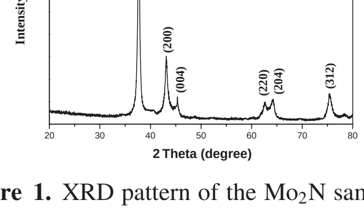

Figure 1. XRD pattern of the Mo_2N samples.

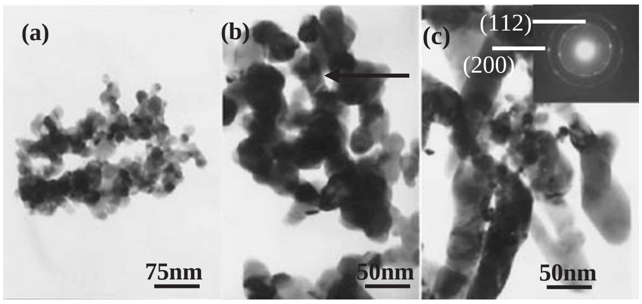

Figure 2. TEM images of the samples as prepared at: (a) 450 °C; (b) 500 °C; (c) 550 °C; and SAED of sample C (inset c).

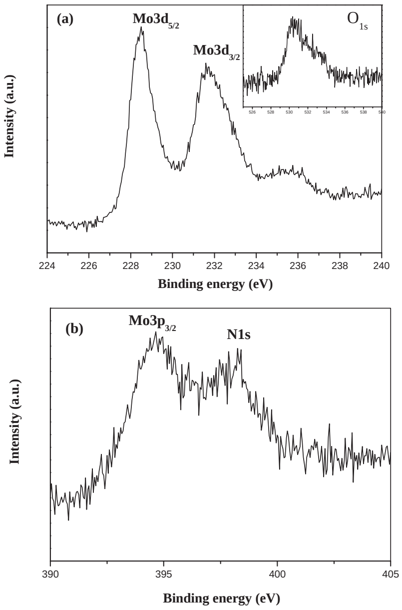

Figure 3. XPS spectra of the Mo_2N nanocrystals: (a) $Mo3d_{3/2}$,$3d_{5/2}$ and O1s peaks (inset), (b) $Mo3p_{3/2}$ and N1s peaks.

ple C with diameters about 20–40 nm and lengths range from 150 to 200 nm (Figure 2c). It can also be seen that the rod-like shapes are formed by some small nanocrystals assembled in one-dimensional order. This result indicates that the reaction temperature plays a leading role in determining the sizes and morphology of the Mo_2N nanocrystals, and this result is similar to that reported previously.[17] All of above show that the rod shapes of Mo_2N aggregates tend to more visible and the nanocrystals tend to more integrate with the increasing of the reaction temperature. The diffraction rings (inset in Figure 2c) recorded from the sample C reveal the characteristic of nanocrystalline tetragonal phase Mo_2N.

It is also found that if the time is shorter than 6 h, the reaction becomes incomplete and the crystallinity is poor. However, varying the reaction time in the range of 12–24 h at 550 °C does not significantly affect the shape and size of the products. The yield of the products is nearly 100%.

Figure 3 gives the XPS spectra of the as-prepared Mo_2N sample C. The Mo3d, N1s and Mo3p core-level regions were examined. It is found that the binding energies of N1s at 398.00 eV and $Mo3d_{5/2}$ are at 398.00 and 228.45 eV, respectively. The latter accords well with the reported binding energies for Mo_2N, confirming further the formation of Mo_2N.[18] The quantification of the peak intensities reveals that the atomic ratio of Mo to N slightly less than the chemical stoichiometry of Mo_2N, it may be due to surface oxidation of the products (as inset in Figure 3a).[19] This result agrees well with previous report.[13]

The possible reaction mechanism of our approach to Mo_2N nanocrystalline is proposed. A previous report on the research of NaN_3 indicated that N_3 radicals could be generated from the decomposition of NaN_3.[20] The resulted N_3 can be regarded as the intermediate reactants and immediately reacted with $MoCl_5$ to form Mo_2N nanocrystals.

In summary, via a thermal liquid–solid metathesis reaction route, rod-shaped aggregates of Mo_2N nanocrystals have been successfully synthesized at 550 °C, which is a moderate temperature compared with traditional methods to our knowledge. The change in temperature can also control the shape and size of the products. This work also verifies that the thermal solid-state reaction synthesis technique is an effective and facile method for preparing the refractory metal nitride.

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