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Syntheses of metal nitrides, metal carbides and rare-earth metal dioxymonocarbodiimides from metal oxides and dicyandiamide

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Abstract

We design a facile and efficient solid-state reaction method by selecting an organic reagent dicyandiamide and metal oxides as precursors to prepare metal nitrides, carbides and rare-earth metal dioxymonocarbodiimides in sealed ampoules. Some fine divided nitride and carbide nanoparticles with small and uniform size can be easily obtained at the relatively low temperatures. It is interesting to find that dicyandiamide is not only a highly efficient nitridation reagent but also a highly efficient carburization reagent, and can be used as a precursor to directly synthesize rare-earth metal dioxymonocarbodiimides. A possible mechanism is proposed to explain the results of the reactions between the organic reagent and metal oxides.

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Keywords: Inorganic materials; Nitride materials; Nanostructured materials; TEM

1. Introduction

In the past decade, metal nitrides and carbides have been attracting much attention due to their fundamental and technological importance [1–3]. Compared to metal oxides, they have superior properties in some respects, such as excellent electronic characteristics, extreme corrosion and wear resistance, and good catalytic properties [3–8]. In general, metal nitrides are obtained by the reactions of metal and nitrogen or ammonia directly. Metal carbides are conventionally made by combination of the elements at elevated temperatures during extended time periods [9]. However, high-energy consumption, long reaction duration, large (micrometers) grains of low specific surface area and incomplete conversions are often encountered in these conventional methods. Therefore, it is highly desired to search some routes to nitrides and carbides at lower temperature and shorter

reaction time to meet the demand of industrial applications. An effective and general route to synthesize nitrides and carbides, rapid solid-state methathesis (SSM) has been developed in the past decade [10–13]. Other routes including solvothermal, carbothermal, sonochemical and electrochemical methods, gasphase reactions, metal-organic polymeric precursors routes are successful in synthesizing some nitrides and carbides [14–22].

Compared with halides used in SSM reactions, oxides are more chemically stable, cheaper and much common in nature. So, some methods to prepare metal nitrides and carbides using metal oxides as starting materials have been investigated [23,24]. However, the preparative route through reactions between organic compounds and oxides has been rarely investigated. In this paper, by an efficient and facile solid-state reaction, we successfully synthesized a series of metal nitride and carbide nanoparticles using an organic reagent dicyandiamide ($C_2N_4H_4$) and metal oxides as starting materials. It is found that dicyandiamide exhibits both powerful nitridation and carburization abilities, and metal oxides are completely converted into the corresponding metal nitrides and carbides at moderate temperatures. In addition, by this facile route, we directly synthesized

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Table 1
Summary of the metal nitrides and carbides through the reactions between metal oxides and dicyandiamide

Metal oxide	Molar ratio	Temperature (°C)	Product	Space groups	ICDD-PDF	Cell constants (Å)	Average size (nm)
Ga ₂ O ₃	4:1	750	GaN	P6 ₃ mc	50-0792	<i>a</i> =3.186, <i>c</i> =5.176	40
V_2O_5	8:1	850	VN	Fm3m	35-0768	a=4.138	6
Cr ₂ O ₃	10:1	1050	CrN	Fm-3m	76-2494	a=4.143	120
Al_2O_3	12:1	1150	AlN	$P6_3mc$	25-1133	a = 3.111, c = 5.007	90
Nb ₂ O ₅	8:1	850	NbN	Fm-3m	65-0436	a=4.385	5
B_2O_3	4:1	1100	BN	P-6m2	73-2095	a = 2.504, c = 6.663	30
Ta_2O_5	8:1	900	TaN	Fm3m	49-1283	a=4.327	20
TiO ₂	20:1	1250	TiN	Fm3m	38-1420	a=4.239	150
WO ₃	10:1	850	WN	P-6m2	25-1256	a = 2.889, c = 2.831	4
MoO ₃	8:1	900	Mo ₂ N	141/amd	25-1368	a = 4.183, c = 8.041	4
Nb_2O_5	8:1	1100	NbC	Fm3m	38-1364	a=4.463	15
Ta_2O_5	8:1	1150	TaC	Fm3m	35-0801	a=4.459	25
WO ₃	10:1	1150	WC	P-6m2	25-1047	a = 2.899, c = 2.834	4
MoO ₃	12:1	1150	MoC	P-6m2	45-1015	a = 2.897, c = 2.814	200
V_2O_5	8:1	1150	VC	F23	74-1220	a=4.296	5

some rare-earth metal dioxymonocarbodiimides. A possible mechanism of this route is discussed and investigated.

2. Experimental

In the standard synthesis, firstly, 8 mmol dicyandiamide ($C_2N_4H_4$) and 2 mmol Ga_2O_3 were mixed together and then pressed to a pellet. The pellet was put into a silica ampoule (out diameter, 15 mm; inner diameter, 12 mm). Secondly, the ampoule with the pellet was evacuated to 1×10^{-5} Pa and sealed at length of 10 cm. Subsequently, the ampoule was heated to 750 °C at the rate of $3 \,^{\circ}C \min^{-1}$. Then the whole system was kept at 750 °C for half an hour. At last, the ampoule was cooled naturally to room temperature and gray powder was found after cooling. The typical smell of ammonia was detected after opening the ampoule up, which was due to condensation of dicyandiamide ($C_2N_4H_4$). This phenomenon can be found in the syntheses of other as-prepared samples. By the similar methods, other 9 metal nitrides, 5 metal carbides and 10 rareearth metal dioxymonocarbodiimides can be also synthesized by the reaction of dicyandiamide ($C_2N_4H_4$) and corresponding metal oxides, respectively, at moderate temperatures. The experimental conditions and sample data are listed in Tables 1 and 2.

Powder X-ray diffraction (XRD) data used for structural analysis is collected on a MAC-M18XHF diffractometer with Cu K α radiation (50 kV, 200 mA), and a continuous mode is employed with a scan speed of 10° min⁻¹. The morphology and chemical composition of the products were characterized using a FEI XL30 S-FEG field-emission scanning electron microscope (FE-SEM) equipped with energy-dispersive X-ray spectroscopy (EDX). The magnified morphology size and high-resolution lattice fringe of samples were conducted on a JEOL 2010 transmission electron microscope (TEM) operation at 100 and 200 keV, respectively. The samples for TEM were dispersed in ethanol by sonication and deposited on carbon-coated copper grids.

3. Results and discussion

Table 1 lists the experimental conditions and structural information of the samples in this work including as-prepared 10 metal nitrides and 5 transition metal carbides. The powder X-ray diffraction (XRD) data of these metal nitrides and carbides are shown in Figs. 1 and 2, respectively. The XRD patterns of these products clearly indicate that the products are well crystalline and can be indexed well with the corresponding metal nitrides and carbides, suggesting that these metal oxides are completely converted into the corresponding nitrides and carbides under the X-ray diffractometer's resolution. These samples were further characterized by TEM and HRTEM. TEM images (Figs. 3 and 4) show that, except the sample AlN, CrN, TiN and MoC, the other samples are composed of finely divided nanoparticles having very small nanosize with a fairly narrow size distribution, typically as VN, NbN, Mo₂N, NbC and WC with size of 6, 5, 4, 15 and 4 nm, respectively. High-resolution lattice micrographs clearly exhibit the different plane spacing for the respective metal nitrides and carbides (the inset in Figs. 3 and 4), which is in good agreement with the known data in the ICDD-PDF reference patterns listed in Table 1, unambiguously confirming the corresponding XRD results.

Dicyandiamide is an important starting material for several industrial applications. The interesting pyrolysis of dicyandiamide sealed in the silica ampoule was investigated. Dicyandi-

Table 2

Summary	of the rare	-earth metal	dioxymonoc	vanamides tl	hrough the	e reactions	between rai	re-earth metal	oxides and	dicyandiamide
										-

Metal oxides	Molar ratio	Temperature (°C)	Product	Space groups	Cell constants (Å)	Volume (Å ³)
Nd ₂ O ₃	6:1	900	Nd ₂ O ₂ CN ₂	P-3m1	<i>a</i> = 3.887, <i>c</i> = 8.314	108.79
Sm ₂ O ₃	6:1	900	Sm ₂ O ₂ CN ₂	P-3m1	a = 3.828, c = 8.267	104.91
Eu ₂ O ₃	6:1	900	Eu ₂ O ₂ CN ₂	P-3m1	a = 3.803, c = 8.248	103.31
Gd_2O_3	6:1	900	Gd ₂ O ₂ CN ₂	P-3m1	a = 3.777, c = 8.222	101.58
Tb_4O_7	10:1	950	Tb ₂ O ₂ CN ₂	P-3m1	a = 3.740, c = 8.192	99.24
Dy ₂ O ₃	6:1	900	$Dy_2O_2CN_2$	P-3m1	a = 3.724, c = 8.175	98.17
Ho ₂ O ₃	6:1	900	Ho ₂ O ₂ CN ₂	P-3m1	a = 3.705, c = 8.169	97.09
Er ₂ O ₃	6:1	900	$Er_2O_2CN_2$	P-3m1	a = 3.682, c = 8.318	95.53
Tm_2O_3	6:1	900	$Tm_2O_2CN_2$	P-3m1	a = 3.659, c = 8.128	94.26
Yb ₂ O ₃	6:1	900	Yb ₂ O ₂ CN ₂	<i>P</i> -3 <i>m</i> 1	<i>a</i> =3.637, <i>c</i> =8.110	92.93



Fig. 1. XRD patterns of the obtained metal nitrides: (a) GaN; (b) VN; (c) CrN; (d) AlN; (e) NbN; (f) TaN; (g) BN; (h) TiN; (i) WN; (j) Mo_2N . The observed peak C denotes the by-product amorphous carbon decomposed by the excessive dicyandiamide.



Fig. 2. XRD patterns of the obtained transition metal carbides: (a) NbC; (b) TaC; (c) WC; (d) MoC; (e) VC.

amide was reported to first release NH₃ and some intermediate condensed phases such as so-called melamine $(C_3N_3(NH_2)_3)$, melam $((C_3N_3)_2(NH_2)_4(NH))$, melem $(C_6N_7(NH_2)_3)$, melon $((C_6N_7)_3(NH_2)_3(NH)_3)$, graphitic carbon nitride materials (g- C_3N_4) [25], and then further release some chemically reactive hydrogen-, carbon-, and nitrogen-containing atomic species such as $C_3N_3^+$, $C_2N_2^+$, $C_3N_2^+$ and NCNH⁺ at higher temperatures [26–28]. Therefore, dicyandiamide may play triple role as the reduction, nitridation and carburization reagent.

To validate the effectiveness of this reaction process using dicyandiamide as precursor, we firstly select the synthesis of GaN from Ga₂O₃ as an example. It is found that, if the furnace temperature is 650 °C, Ga element and trace amount of GaN are obtained, which demonstrates that the reduction process indeed exists. This phenomenon can be also found in the synthesis of all the other metal nitrides by the experimental observation. When the furnace temperature is increased to 750 °C, pure GaN is obtained. It can be seen from the XRD pattern of the asprepared GaN (Fig. 1a) that the well crystalline sample can be indexed as hexagonal GaN (a = 3.186 Å and c = 5.176 Å), agreeing well with the calculated diffraction pattern (ICDD-PDF No. 50-0792), and no other impure peaks is detected. Energy dispersive X-ray analysis (EDX) (Fig. 5a) indicates the product consists of Ga, N and trace amount of O elements. The O element maybe comes from the O₂ and H₂O adsorbed on the surface of the product. The TEM image (Fig. 3a) further reveals the sample consists of some well-crystallized nanoparticles having average size of about 40 nm with a narrow size distribution, which is consistent with the broadening of the XRD peaks. The corresponding HRTEM micrograph (the inset in Fig. 3a) displays that the interplanar spacing of the lattice planes is 0.277 nm, which matches well with the distance value of (100) lattice planes of the hexagonal GaN, providing further evidence for the formation of GaN.

Some metal nitrides, such as NbN, TaN, CrN, requires much higher temperatures and higher pressure to be prepared by direct reactions, otherwise some other nitrides such as Nb₄N₃, Ta₃N₅ and Cr₂N will be the main formation of the products. In this work, some mono-nitrides can be easily obtained through this route. For example, NbN is prepared successfully by this method. The XRD pattern of the product (Fig. 1e) is indexed to be cubic cell and the lattice constant is calculated to a = 4.385 Å, agreeing well with the cubic NbN (ICDD-PDF) No. 65-0436). The EDX measurement indicates that the product mainly consists of Nb, N and C element (Fig. 5b). The C element can be identified as the by-product amorphous carbon decomposed by the excessive dicyandiamide. The corresponding high-magnification TEM image indicates that the sample is composed of finely divided nanoparticles with average size of 5 nm, agreeing well with the broadening of the XRD peaks. The high-resolution TEM (HRTEM) images shown in the inset of Fig. 3e clearly exhibits the lattice fringe spacing for (111) planes of cubic NbN ($d_{111} = 0.255$ nm), giving further evidence that the as-prepared sample is NbN with good crystallinity.

It is interesting to find that, with increasing the furnace temperature, some transition metal nitrides (NbN, TaN, WN, Mo₂N and VN) are firstly reduced into the corresponding metal elements, and further transmitted into transition metal carbides (NbC, TaC, WC, MoC and VC) at the higher temperatures. For example, WN is obtained at 850 °C (Fig. 1i). However, if the temperature is increased to1000 °C, W element and trace of WN can be found. When the furnace temperature is as high as 1150 °C, well-crystallized WC is prepared. These results indicate that WN is firstly reduced into W element, and then the as-reduced W element is further converted into WC at the higher temperature. The EDX result (Fig. 5d) demonstrates that the sample contains W, C and some trace impurity O element, and no N element detected in the sample WN (Fig. 4c) can be found in the sample WC. It can be seen from Fig. 2c that all the diffraction peaks are indexed to be hexagonal phase and lattice parameter is calculated to be a = 2.899 Å and c = 2.834 Å, which is in good agreement with hexagonal WC (ICDD-PDF No. 25-1047). TEM image of the



Fig. 3. TEM micrographs of the obtained metal nitrides: (a) GaN; (b) VN; (c) CrN; (d) AlN; (e) NbN; (f) TaN; (g) BN; (h) TiN; (i) WN; (j) Mo₂N. The inset of each images imply the lattice of the corresponding metal nitride nanoparticles.



Fig. 3. (Continued).

sample (Fig. 4i) reveals the sample consists of well-crystallized nanoparticles with average size of 4 nm. HRTEM (the inset in Fig. 4i) clearly exhibits the lattice space are 0.250 nm for (100) planes of hexagonal WC.

These results demonstrate that the overall pathway of synthesizing metal nitrides is involved in a two-step process: reduction process and nitridation process. For the formation of metal carbides, further reduction process and carburization process will indeed occur. In the previous reports, g-C₃N₄ that can decompose into some carbon nitride species was used as precursor to synthesize some nitrides and carbides [3,29]. It is thought that these carbon nitride species play crucial roles in the syntheses of metal nitrides and carbides. However, the reactions between g-C₃N₄ and oxides fail to produce some nitrides and carbides such as NbN, TaN, AlN and MoC. In this work, hydrogen-, carbon-, and nitrogen-containing atomic species may play crucial roles in the synthesis of these nitrides and carbides. On the other hand, NH₃ is released by the pyrolysis of dicyandiamide. NH₃ that can keep the pressure in the ampoule may play another important role in the reaction processes. However, because of the lack of thermodynamic data for these intermediate carbon nitrides produced, we cannot calculate the precise theoretical energy released from the reactions of carbon nitride species and oxides, as well as the absolute temperatures of the reactions.

Moreover, whether NH_3 released by the pyrolysis of dicyandiamide is involved in the reaction processes is unknown. The exact reaction mechanism needs to be further investigated.

In addition, we directly synthesize 10 rare-earth dioxymonocarbodiimides such as $Ln_2O_2CN_2$ (Ln = Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb) through the reactions between the corresponding rare-earth metal oxides and dicyandiamide at 900 °C. The experimental conditions and structural information of the as-prepared samples are listed in Table 2. The XRD patterns of these samples (Fig. 6) are well consistent with the data reported in the ICDD-PDF reference patterns or the literature [30,31]. These compounds crystallize in the trigonal space group P-3m1 with layer structures composed of $Ln_2O_2^{2+}$ layers and the interlayer carbodiimide ion (CN_2^{2-}) . The $Ln_2O_2^{2+}$ layers are pile perpendicular to the *c* axis, and the linear ions, -N=C=N-, are inserted in parallel to the c axis. Hashimoto et al. prepared some rare-earth dioxymonocarbodiimides by heating rare-earth oxides in a graphite boat under flowing ammonia gas at high temperature for several times [31]. It is thought that, in their syntheses, the C atoms in the graphite boat react with NH3 gas to form some hydrogen-, carbon-, and nitrogen-containing atomic species and then further react with the rare-earth oxides because the graphite boat can be corroded by ammonia gas at high temperature. Generally, the reaction mechanism underlying our



Fig. 4. TEM micrographs of the obtained metal nitrides: (a) NbC; (b) TaC; (c) WC; (d) MoC; (e) VC. The inset of each images imply the lattice of the corresponding metal carbide nanoparticles.



Fig. 5. EDX measurements of the obtained samples: (a) GaN; (b) NbN; (c) WN; (d) WC.



Fig. 6. XRD patterns of the obtained rare-earth metal dioxymonocarbodiimides: (a) $Nd_2O_2CN_2$; (b) $Sm_2O_2CN_2$; (c) $Eu_2O_2CN_2$; (d) $Gd_2O_2CN_2$; (e) $Tb_2O_2CN_2$; (f) $Dy_2O_2CN_2$; (g) $Ho_2O_2CN_2$; (h) $Er_2O_2CN_2$; (i) $Tm_2O_2CN_2$; (j) $Yb_2O_2CN_2$.

route is similar to the explanation mentioned above. The carbon nitride species produced at high temperature replace the reactants obtained by the reaction through the graphite boat and NH_3 gas, and the NH_3 released by the condensation of dicyandiamide play the same protecting role as the flowing NH_3 . These oxides are captured one oxygen atom by the carbon nitride species due to the high stability of rare-earth oxides. Then, the as-reduced $Ln_2O_2^{2+}$ ions further bond the carbon nitride species to form these rare-earth dioxymonocarbodiimides. However, the exact reasons are unknown and need to be further investigated.

4. Conclusions

By an efficient and facile solid-state reaction, we successfully synthesized 10 important metal nitrides and 5 metal carbides through the reactions between metal oxides and an organic reagent dicyandiamide ($C_2N_4H_4$). The experimental results indicate that dicyandiamide can be used as both powerfully nitridation and carburization reagent, and metal oxides are completely converted into the corresponding metal nitrides and carbides at the temperatures lower than reported in the conventional methods. Especially, some metal nitride and carbide nanoparticles such as VN, Mo_2N , NbC and WC with small nanosize may be more desire in ceramic and catalytic applications. It is found that the highly active carbon nitride species condensed by dicyandiamide might play the crucial roles in the reduction, nitridation, and carburization processes. In addition, 10 rare-earth metal dioxymonocarbodiimides can be directly synthesized through this route. These results maybe provide a new clue to prepare other metal nitrides, carbides and dioxymonocyanamides by this facile solid-state route.

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