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Synthesis and application of nano-structured metal nitrides and carbides: A review

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ABSTRACT

Transition metal nitride and carbide have several similarities in their preparatory methods, properties, and applications. Synthetic parameters have remained the main factors that determine the effectiveness of nitrides and carbides in electrochemical storage devices, photocatalysis, environmental remediation, gas sensing and medicinal agents. This review addresses aspects of relevance to electronic structure and chemical bonding, and recent advances made in the synthesis approaches. The syntheses approaches that are particularly relevant for reducing (i) production cost, (ii) energy consumption, and (iii) synthesis time for these materials systems are discussed in detail. Furthermore some of the recent techniques like solid-solid state separation, carbothermal, gas-phase, electrochemical, sonochemical, solvothermal, sol-gel reaction and solid state reaction that offer new avenues for researchers (including a sustainability-oriented exploration) are mentioned. We discuss synthetically tunable properties (morphology, electronic characteristics, energy storage capacity, corrosion resistance, catalytic ability and gas sensing properties), heat treatment aspects, and relevant applications of these systems. We expect this review to be useful to the ever growing community of researchers that are interested in nitrides and carbides, and their applications.

1. Introduction

Metal nitrides and carbides are increasingly being used to replace conventional materials in many applications, especially in electrochemical devices, environmental remediation, gas sensing, photocatalysis, applied ceramics, and medicine. Also several important classes of the materials (eg. composites), have a number transition metal carbide and nitride nanoparticles incorporated in them. Recently nanoparticle materials with different morphologies, and possessing hollow structures (spheres, needles, capsules, particles, fibers, cube and plates) have attracted much interest from researchers owing to their (i) low density, (ii) thin walls, (iii) large surface areas, (iv) high toughness, (v) flexibility, (vi) ionic conductivity, (vii) enhance chemical activity, and (viii) electrical properties [1–8]. Solid state reaction has hitherto been considered as an economical and eco-friendly synthetic method for synthesizing metal nitrides and carbides; another prominent advantage of this approach is that the final products are often crystalline [9]. Metal carbide and nitride have superior properties like (i) high melting point [10], (ii) extreme corrosion and wear resistance [11,12] (iii) excellent electronic properties [13], and (iv) good catalytic properties [14] when compared to several pristine metal oxides. For instance TiC, HfC, ZrC, and SiC have been used in a number of ceramic applications due to its high melting point and wear resistance [15].

Metal carbides have high melting point due to covalent carbon networks that exist within the structure [16]. This is also the reason for the high mechanical strength and wear resistance which may due to the strong covalent bonds present in these materials [17]. One of the relevant numerical indices here, the ratio of hardness to the melting point (in Kelvin scale) of TiC, ZrC, VC and NbC are 3000/3340 K, 2900/3718 K, 2480/2921 K and 2150/3886 K while their counterpart TiN, ZrN, VN and NbN have 2000/3220 K, 1520/3250 K, 1500/2620 K and 1400/2900 K [18], respectively. These indicate that for refractory and high stress environment, both carbides and nitrides offer unique advantages.

In addition to the above, it is helpful to note that metal carbides and nitrides have relatively high thermal stability and conductivity. For instance HfC has thermal conductivity around (20 W/mK) [19] which may due to bonding and antibonding orbitals resulting from bonds between carbide or nitride 2p orbitals and metal d-orbital and the vibrational properties thereof [20].

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Advancements in materials chemistry and technology have resulted in several synthetic procedures that are relevant for the synthesis of carbides and nitrides. These techniques currently used include (i) conventional direct element combination, (ii) solvothermal, (iii) carbothermal, (iv) sonochemical, (v) gas-phase, (vi) electrochemical, (vii) solid state metathesis and solid state metal-organic polymeric precursor (vii) hydrazine sol-gel [21–29]. Furthermore organic carburization reagents like cyanamide (CN_2H_2) have been used as precursors with various transition metal oxides to synthesize corresponding metal carbide via solid state reaction [30].

In this review paper, we will focus on (i) chemistry of synthetic methods, (ii) apparatus used for synthesis/fabrication, (iii) method-morphology-property correlations, and (iv) eventual applications of the materials. These three aspects are particularly important considering emerging directions in carbide and nitride science. Recent papers, for instance studies by Lie et al. [31] and 2012, Yang et al. [32] are indicators of fresh directions in this area wherein there is effort in making (i) the processes *chimie douce* (soft chemical) and (ii) the materials multifunctional (often times through use of morphology control and dopants).

1.1. Electronic structure and bonding insights relevant to synthesis and catalytic applications

Recently, titanium carbide (TiC) and titanium nitride (TiN) have been reported to have ionic character as the dominant bonding mechanism based on the ab initio calculations [33]. Notable reports here are the studies by Calais [34], Neckel [35] and Schwarz [18]. This investigation into the nature of bonding has implications to the (i) way these materials are synthesized or processed, and (ii) applied (in any of the various applications listed before). Hence synthesis approaches designed benefit from insights about the eventual intended engineering application.

Investigations are interestingly revealing similarities between the nature of bonding in both carbides and nitrides this indicates why similar synthesis approaches oftentimes work for these two families of materials. For example in case of titanium nitride (TiN), metallic character exists between Ti-Ti. On the other hand, ionic character is due to charge transfer occurring between Ti and N. However there is substantial covalent character too in the bond between Ti and N [36]. This mixed character has been observed and well established for titanium carbide (TiC) too. From a ceramic processing standpoint, these insights are obviously helpful since bonding directly determines material properties like melting point, surface energy, thermal expansion, bulk modulus etc. For example, today it is very obvious that the high melting point (normally above 1000 °C) and high hardness ($\geq 2000\,kg\,mm^{-2}$) of the carbides and nitrides can also be attributed to bonding of mixed character [36].

In fact in recent times, bonding and electronic structure based arguments have helped rationalize and develop better synthetic techniques for functional nitrides and carbides. For example, for electrocatalytic purposes, the electronic properties are tuned based on arguments relying on (1) direction and amount of charge transfer, and (2) the modifications in the metal d-band in the ceramic [36]. A measure of these bonding related changes is the increase in metal-metal bond length, when carbon/nitrogen occupies the interstitial positions in the parent lattice (as shown in Fig. 1a). For instance, in case of the vanadium carbide the lattice constant increases from 0.26 to 0.42 nm. The variation in lattice parameter for other carbides and nitrides are given in Table 1 [37]. Interestingly the extent of increase in the metal-metal bond distance can be an important parameter in improving catalytic properties. In particular, the contraction of the metal d-band is known to increase the density of states (DOS) near the Fermi level [38,39] (ref: Fig. 1b), which in turn gives rise to catalytic properties that are comparable to those of group VIII noble metals (eg. Pt) [40,41]. The combination of both carbon and nitrogen have also shown improved catalytic properties. For example tungsten carbonitride (WN_xC_y) is found to have better catalytic performance for hydrazine decomposition [42]. This immediately opens new avenues for intelligent catalytic design and synthesis. For example, tungsten and molybdenum carbides have been identified as promising alternatives to platinum as a hydrogen evolving reaction (HER) catalyst [43,44]. TiC is also interesting in terms of HER catalyst as it is reported to have surface oxidation potentials ranging from 0.8-1.0 V in aqueous H_2SO_4. The exchange current density of TiC has been measured to be $3.5 \times 10^{-4}\,mA\,cm^{-2}$ in $1\,M\,H_2SO_4$ solution [45]. The values of exchange current density obtained for the TiC electrodes are comparable with those of other metals. In fact in acidic medium, Ferri et al. has showed that TiC is as efficient as Pd which is an important result [46]. This is in fact an example of result wherein bonding and electronic structure based arguments have helped in gaining insights into a new and important application for an otherwise well known carbide. Such examples are likely to increase in times to come considering the increasing importance of ab-initio calculations and their role in rationalizing material-property correlations. However there is certainly scope to perform more detailed investigations into electronic structure-synthesis correlations in carbide and nitride science.

Considering the correlations between the electronic structure of nitrides and carbide it is not surprising that nitride catalysts, are reported to be promising too. For instance, the catalytic character for molybdenum nitride for hydrocarbon hydrogenolysis is reported to approach that of platinum [47]. Reasons for this require more detailed computational and theoretical studies; however it is very likely to do with the modifications occurring to the d band due to the presence of nitrogen in the lattice. From an experimental standpoint, Nagai et al. [48], have extensively studied the effect of nitriding temperature, starting materials and gas flow rate on the molybdenum nitride phase formation. MoN and Mo_2N phases exhibit good electrochemical stability up to +0.67 V *vs.* RHE in acidic solution (pH = 0) [48]. Notably another important nitride, TiN is found to exhibit very good corrosion resistance in acidic solutions; the chemical stability is comparable to that of Pt-modified glassy carbon electrode [49]. This makes these nitrides good candidate materials wherein surface stability is a requirement. For example, Tungsten nitrides have been studied mostly for their fuel cell and batteries applications, but Choi et al. [50] have investigated and reported that one of the phases WN can be used as HER catalyst [50,51]. There is a recent review paper which gives information on the development of transition metal based carbides and nitrides as HER electrocatalysts [52] in detail.

2. Synthetic methods for metal carbide and nitride

2.1. Direct element combination

This synthetic method involves high temperature reaction whereby nonmetal and metal are directly reacted together. However this approach has several setbacks such as high temperature usage, irregular grain sizes of the final nanoparticle, incomplete reaction, long reaction time and lack of mesoporous nature of the final nanoparticles Lie et al., [31]. In summary this approach has not gained much interest from researchers due to lack of promising properties of final product, high energy consumption and long reaction time.

2.2. Solid-solid separation method

This report reviews a recent study on the preparation of metal nitrides via solid-solid separation method. This synthetic approach is carried out through ammonolysis of bulk ternary oxides under ammonia gas flow at moderate temperature ranging from 600 °C to 800 °C. Various kinds of metal nitrides like TiN, NbN, VN and Ta_3N_5 with large surface area and pore sizes (~10–40 nm) are successfully synthesized through this economical and eco-friendly synthetic method [53].

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