Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2014, Article ID 203837, 8 pages
http://dx.doi.org/10.1155/2014/203837

Review Article

An Overview on Structure and Field Emission Properties of Carbon Nitride Films

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Received 26 February 2014; Revised 29 April 2014; Accepted 29 April 2014; Published 21 May 2014

Academic Editor: Jun Yang

Carbon nitride films have excellent properties and wide application prospects in the aspect of field emission properties. In this review structure characteristics and a variety of synthetic methods of carbon nitride film will be described. In the carbon nitrogen films, we mainly from the following three points: sp^2/sp^3 ratio, surface morphology and N content to discuss the change of field emission properties. Appropriate sp^2/sp^3 (about 1.0–1.25) ratio, N content (about 8 at.%–10 at.%), and rough surfaces will strengthen the field emission properties.

1. Introduction

In the 1989, Liu and Cohen [1, 2] theoretically predicted the structure and physical properties of β-C_3N_4 whose bulk modulus and hardness, compared with diamond, are more outstanding. Although great effort has been made in synthesis of this material, in most cases amorphous carbon nitrogen (a-CN_x) films instead of crystalline C_3N_4 were obtained. Either crystalline C_3N_4 or a-CN_x films have excellent performance. Studies have shown that carbon nitrogen (CN_x) films have excellent properties in terms of high hardness [3], wear resistance [4], hydrogen storage performance [5], and excellent field emission properties [6]. In the past three decades, diamond-like carbon films incorporated with nitrogen or called CN_x films have been extensively studied owing to their potential application as cold cathode materials in field emission displays (FED). In the case of the previous reports, the threshold fields of the pure DLC film were usually 3–20 V/μm [7–9] and decreased to 1–12 V/μm after nitrogen incorporation [10–12]. In the past few years, there has been considerable interest in electron field emission from CN_x films. In addition, the structures and synthesis methods of CN_x films are diverse, so they have attracted much attention.

2. The Structures of CN_x Films

2.1. The Structures of Crystalline Phase CN_x Films. Teter and Hemley through the theoretical calculation have predicted five kinds of crystalline phase structures of C_3N_4: alpha C_3N_4 (α-C_3N_4), beta C_3N_4 (β-C_3N_4), cubic C_3N_4 (c-C_3N_4), pseudo-cubic C_3N_4 (pc-C_3N_4), and graphite C_3N_4 (g-C_3N_4) [13]. In addition, these crystal structures have been found and reported in experiments [14–17]. The α-C_3N_4 is earlier obtained by Yu et al. [18]. They used the calculation method of quantum mechanics clusters model and got α-C_3N_4 by optimization crystal structure of simulative C_3N_4. The α-C_3N_4 has crystal plane cascade order of crystal structure, by ABAB pattern to stack. In the structure of α-C_3N_4, C and N atoms connection by sp^3 key formed a tetrahedron structure. Liu and Cohen [1] predicted the existence of β-C_3N_4 using band theory of first principles and prepared β-C_3N_4 based on β-Si_3N_4 crystal structure. They previewed that the structure of β-C_3N_4 is the hexagonal containing 14 atoms per unit cell. As a new kind of superhard material, β-C_3N_4 got more extensive research; its structure is shown in Figure 1. The c-C_3N_4 was first reported by Teter and Hemley [13]. They suggested the structure of c-C_3N_4 using the conjugate gradient method

Table 1: The structure parameters of crystal, bulk moduli B, and total energies E_0 for five kinds of the predicted carbon nitride crystals.

	α-C_3N_4	β-C_3N_4	Cubic-C_3N_4	Pseudocubic-C_3N_4	Graphite-C_3N_4
Space group	P31c(159)	P3(143)	$I\bar{4}3d$(220)	$p\bar{4}2m$(111)	$P\bar{6}m2$(187)
Z	4	2	4	1	2
a (Å)	6.4665	6.4017	5.3973	3.4232	4.7420
c (Å)	4.7097	2.4041			6.7205
B_0 (GPa)	425	451	496	448	
E_0 (eV/unit)	−1598.669	−1598.403	−1597.388	−1597.225	−1598.71

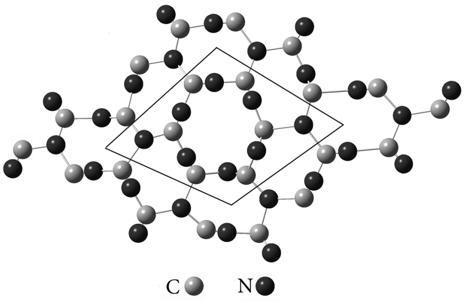


Figure 1: Schematic atomic structure of β-C_3N_4.

and found it has a similar structural characteristic with the Zn_2SiO_4. Liu and Wentzcovitch [19] proposed pc-C_3N_4 crystal structure based on the structure of cubic ZnS removed a quarter of Zn atom. They found that pc-C_3N_4 and β-C_3N_4 have similar crystal structures. The g-C_3N_4 has a variety of structures model. Liu and Wentzcovitch [19] proposed a rhombus g-C_3N_4 crystal structure described as ABCABC... pattern to stack by calculation. However, Teter and Hemley [13] believed the mode of g-C_3N_4 is hexagonal graphite structure in which the arrangement of atoms is along the C axis and crystal structures are based on the ABAB pattern to stack [20].

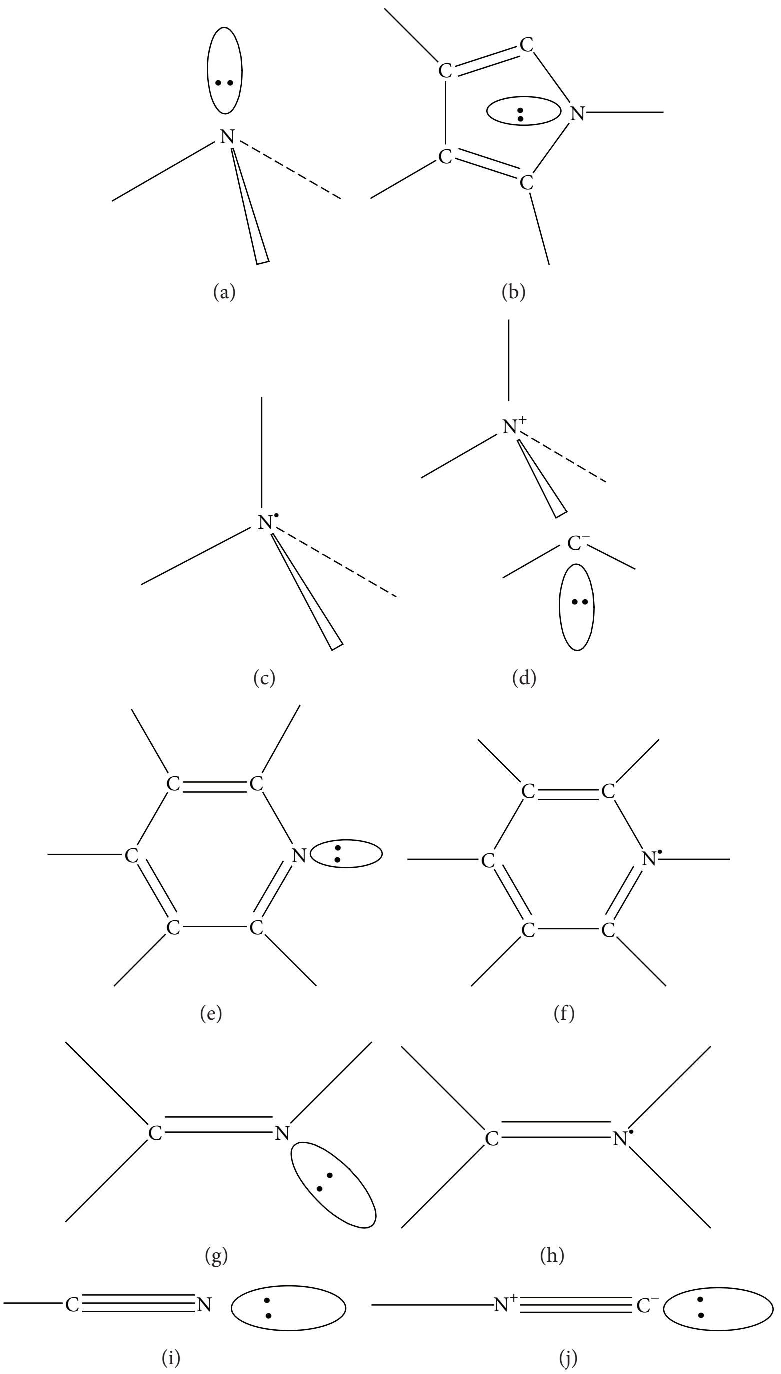
In those structures of C_3N_4, the g-C_3N_4 has the most stable structure, but others have the superhard characteristics that it does not have. In the superhard structures of C_3N_4, α-C_3N_4 is the most stable structure. In a single cell, the volume of g-C_3N_4, α-C_3N_4, β-C_3N_4, c-C_3N_4, and pc-C_3N_4 subsequently decreases; however, their energy increases in turn. Table 1 shows the structure parameters of crystal, bulk modulus B and total energies E_0 for five kinds of the predicted carbon nitride crystals. In order to prepare the C_3N_4 crystalline, carbon and nitrogen ratio of precursors should be as close as possible to the theoretical value of 1.33. The researchers can also adopt appropriate methods to improve the reaction temperature, which can help the molecular fracture of the precursors.

2.2. The Structures of Amorphous CN_x. Because carbon and nitrogen have the characteristic of various valence states forming bonding, therefore, in a-CN_x films there are diverse of valence bond structures, as shown in Figure 2 [21]. In a-CN_x films, N/C ratio depended on preparation methods of the films and parameters of the technique. Studies have found that some C_3N_4 defect structures and amorphous structures of CN_x films are still the metastable structures, but with the increase of N vacancy, these two kinds of structure of CN_x material reduce in bulk modulus. Researches show that the hardness of a-CN_x films which be reached is 15 GPa–50 GPa. At the same time, a-CN_x films have very excellent tribological properties. The structural characteristics, composition of materials, and crystallinity of CN_x films can be characterized and analyzed by XRD, XPS, and Raman, techniques. From the current results, the superior mechanical properties, good heat conductivity properties, and excellent field emission properties make a-CN_x films win a place in the new materials.

3. The Preparation Methods of CN_x Films

The research on syntheses and properties of carbon nitride (CN_x) films has aroused interest of scholars from different countries. CN_x films with particular properties have been synthesized whose structures and characteristics were reviewed [22, 23]. The synthetic methods include physical vapor deposition (PVD), chemical vapor deposition (CVD), and so forth. These methods have led to amorphous CN_x films or in some cases formed carbon nitride crystallites structure embedded in an amorphous CN_x matrix.

3.1. Physical Vapor Deposition (PVD). Physical vapor deposition comprises magnetron sputtering, ion beam deposition (IBD), reaction sputtering, and pulsed laser deposition, and so forth. Reaction sputtering is the basic method for preparation of compound films. When used it to prepare CN_x films, the mass fraction of nitrogen is generally lower than 40%. However, to form β-C_3N_4, system should include enough nitrogen and stoichiometric ratio should reach 57%. Niu et al. [24] obtained the CN_x films on silicon substrate by using pulse laser evaporation C target, auxiliary deposition of atom nitrogen. Their studies found that N content reached 40% in the films and then C, N atoms combined with nonpolar covalent bond. Subsequently, Sharma et al. [25] and Zhang et al. [26] also obtained CN_x films by a similar method. Mihailescu et al. [27] using ammonia instead of N_2 produced hard CN_x films with carbon nitrogen single bond, double bond, and triple bond and then got that its optical band gap is 4.5 eV. Through analysis of the current study, people mostly get are mixture films which containing a various of crystal phases. Traditionally, these mixture films are called CN_x films.



(a) (b) (c) (d) (e) (f) (g) (h) (i) (j)

Figure 2: The possible bonding configuration in a-CN$_x$ films: (a)–(d) N sp^3 hybridization; (e)-(f) N atom in benzene; (g)-(h) N sp^2 hybridization (linear); (i) N sp^1 hybridization (nit rile); (j) N sp^1 hybridization (nitrile-like, autocompensation effect).

3.2. Chemical Vapor Deposition (CVD). Chemical vapor deposition achieved good results in the synthesis of carbon nitride films compared with other synthetic methods. CVD method is mainly used for one or more elements belonging to the film, so that these elements generate chemical reaction on the surface of the substrate and then generate films. CVD methods mainly include electron cyclotron resonance, hot filament assisted, DC glow discharge, radiofrequency discharge, and microwave plasma chemical vapor deposition. Bias of auxiliary hot filament chemical vapor deposition (HFCVD) is one of the traditional devices used in the deposition of diamond films. Wang et al. [32, 33] got CN$_x$ films on Ni substrate by using HFCVD method firstly. Because preparation of the films is more likely to generate C–H and N–H bonds under the CVD conditions, so most of the CN$_x$ films are amorphous. Many researches are focused on the mechanical properties and field emission performance of the thin films. Based on previous researches, when CVD methods

Table 2: Optimal sp^2/sp^3 ratio of amorphous carbon films which can be used as a reference of CN$_x$ films.

	sp^2/sp^3 ratio	Preparation method	Turn-on electric field (F_T)	Highest current density	Reference
DLC films	0.85–1.0	Microwave plasma chemical vapor deposition (MPCVD)	10 V/μm (defined as the low-end electric field to emit electrons)	—	[28]
a-C	1.25	MPCVD	4.8 V/μm (0.28 mA/cm^2)	—	[29]
Metal-DLC	1.0	Electrochemical deposition	6.5 V/μm (1 μA/cm^2)	1.2 mA/cm^2 (23.5 V/μm)	[30]
Metal-DLC	1.2016	Electrochemical deposition	8.4 V/μm (1 μA/cm^2)	163.89 μA/cm^2 (12.455 V/μm)	[31]

are used to prepare CN$_x$ films, the choice of substrate materials is critical.

4. Field Emission Properties of CN$_x$ Films

Field emission displays have high brightness, high resolution and vivid colors, fast response speed, and low energy consumption which can make true the advantages of flat displays and make it become the future direction of the display technology [34]. The preparation of cold cathode is the key factor in field emission display technology. Low-dimensional structure cold cathode materials with excellent field emission have broad application prospects in the vacuum microelectronic device. It is known that carbon-based materials such as diamond [28], diamond-like carbon, and carbon nanotubes [35, 36] are good cold cathode field emission materials. However, these materials still have many drawbacks [37–39], for DLC films are limited owing to its low total field emission current and high threshold fields, which have restricted the field emission properties. The incorporation of suitable amount of nitrogen into carbon films formed CN$_x$ films which can enhance field emission properties of the materials. It is attributed to the weak donor activity of nitrogen that make the Fermi level rise [40],work function lower and formation of more sp^2 clusters in films. The sp^2/sp^3 ratio and surface morphology of CN$_x$ films may also affect the field emission properties [41].

4.1. The Influence of sp^2/sp^3 Ratio on Field Emission Properties. From the results of studies, the sp^2/sp^3 ratio in the DLC films increases with the increase of nitrogen doping [30, 42–44]. The sp^2 clusters have high electrical conductivity that has better ability to provide high currents [45]. These sp^2 clusters forming caused electron delocalization and/or improved electron hop between the clusters. Moreover, these clusters were likely to be overlapped, which also further accelerated electrons transportation between the connecting clusters [46, 47]. The electrons would be easily extracted from the film surface while the external electric field was applied, so high content of sp^2 cluster plays a very important role in the field emission properties. These sp^2 clusters with good connectivity act as a conductive channel in amorphous structures so that electrons can be launched into vacuum through this channel under the action of the outer electric field. With the increase of emission electron in films, the Fermi level rise, the work function, and surface potential barrier height of the material are reduced, and then the electron emits from the surface more easily [48, 49]. In addition, the threshold field decreases when the sp^2 clusters size increases [50]. However, Satyanarayana et al. [51–53] hold a different view with most researchers. They suggested that electron emission increases with the higher sp^3 content and the field emission was not enhanced by an excessive amount of sp^2-bonded carbon. This is due to a serious graphitization of films at a higher level of sp^2 content.

From Table 2, it can be concluded that an optimum sp^2/sp^3 bonding ratio provides a high emission current density and a low turn-on electric field (F_T) value. The sp^3 bonding confers on CN$_x$ film with low electron affinity and also a chemical and physical inertness that is invaluable for FED applications, with low electron affinity aid in electron emission to a vacuum. Shi et al. proposed a multiple step emission mechanism and the junction between sp^2 and sp^3 rich clusters provides an intermediate ladder for the electrons to climb up from the sp^2 rich clusters to sp^3 rich ones where they may have enough energy to overcome the small barrier to emit to vacuum [54]. As is shown in Table 3, the sp^2 clusters size plays an important role in electron field emission properties [55]. Table 3 shows that the size of sp^{2}aromatic clusters is in the range of 1.8–2.4 nm, according to the Tuinstra-Koenig (TK) relationship [56, 57]. According to Tables 2 and 3 we suggest that in CN$_x$ films what can effectively improve the field emission properties is the appropriate size and concentration (sp^2/sp^3 ratio is about 1.0–1.25) of sp^{2}clusters [58]; the more conductive sp^2 phase should be surrounded by insulating sp^3 matrix to form a conductive channels, which at the same time can ensure that the electronic can easily be launched into the vacuum, which can effectively improve the field emission properties.

4.2. The Influence of Surface Morphology on Field Emission Properties. The electron emission is strongly related to the surface roughness: rougher surface means that there are more dense protrusions in the film surface. Protrusive structures could further increase the field enhancement factor which can geometrically promote the field emission [63, 64]. The CN$_x$ films prepared by doping nitrogen into DLC films have a more rough surface morphology than DLC films [65, 66]. So these CN$_x$ films have a higher geometric enhancement factor compared with DLC films and also have lower threshold field.

Some methods can be used to process the surface of films, such as ion etching which can create surface roughness to

Table 3: Appropriate size of sp^2 clusters.

	Size of sp^2 clusters (nm)	Preparation method	Turn-on electric field (F_T)/threshold field (F_{th})	Current density	Reference
Ta-C (annealed in nitrogen and acetylene ambient)	2	Filtered cathodic vacuum arc technique	4.8 V/μm (1 μA/cm^2)	—	[50]
N-PPANI	2.2	Pyrolysis of polyaniline	1.7 V/μm (10 μA/cm^2)	—	[59]
CN_x	1.8–2.4	Magnetron sputtering of carbon target	4.0 V/μm (1 μA/cm^2)	10 μA/cm^2 (11.0 V/μm)	[56]

Table 4: Nitrogen content of the CN_x films.

	N content (at.%)	Preparation method	Turn-on electric field (F_T)/threshold field (F_{th})	Current density	Reference
a-C : N films	8.0	Electron cyclotron resonance plasma	—	—	[60]
ta-C : N	10	A pulsed filtered vacuum arc deposition	4 V/μm (1×10^{-6} A/cm^2)	—	[10]
DLC : N	10	Electrodeposition	11.8 V/μm (1 μA/mm^2)	59.5 μA/mm^2 (24 V/μm)	[61]
ta-C : N	10.3	Filtered cathodic vacuum arc deposition	—	—	[62]

cause a field enhancement of the films. Songbo Wei et al. reported that, with increasing the bombarding energy, the film surface changed from smooth to a peak-and-valley structure, and the film surface became rougher. The root mean square (RMS) values of the CN_x films increased from 0.27 nm to 0.78 nm in this process [67]. Hart et al. and Shi et al. believe that hydrogen treatment on the surface of films can create sp^2 clusters which would induce a field enhancement of the surface [54, 68], while Robertson think that, after treating with hydrogen, some areas of the surface will adsorb hydrogen and form C–H dipole which would cause a nonuniform distribution of electric field and produce an electric field enhancement effect which is similar to the metal tip needle [37].

4.3. The Influence of N Content on Field Emission Properties.

It was found that the field emission of CN_x films depended on the N content and this effect dominated the effects of other parameters, such as sp^3 content, band gap of the films, Fermi level position, and resistivity of the films. The effect is negative on field emission no matter too much or too little nitrogen doping into CN_x films and only the appropriate nitrogen content can enhance field emission properties [69]. As shown in Table 4, which is based on previous experimental results, it can be seen that the CN_x film containing 8 at.%–10 at.% nitrogen [10, 60–62, 70] possesses enhanced field emission properties. A minimum for threshold field and a maximum for emission current density at this suitable N content were found. High levels of nitrogen additions are found to reduce field emission properties; from the above description we know that N incorporation into the DLC films favors formation of sp^2 units and leads to serious graphitization of the CN_x films [11, 53]. According to the proposal of Cutler et al.'s three-step field emission model, the emitted electrons are assumed to subject a three-step process. The first step is internal emission, the second step is electron transport, and the third step is vacuum emission [10, 54, 71]. The determinative within third step is the fraction of sp^3 phase, since the sp^3phase carbon has a low electron affinity, and the sp^3 phase is favorable for electron emission into vacuum [54]. So serious graphitization of the CN_x films is not conducive to the field emission. Vacuum emission is a determinative for the whole emission process.

In the first step, the determinative for emission is the value of band gap and Fermi level position. However, in the second step, the injected electrons transport across the CN_x films bulk, which is directly limited by the resistivity of the CN_x films [10]. From Figure 3 it can be seen that as the N content increases, the optical band gap reduces and Fermi level increases of CN_x films [10, 72]. When the N content keeping at an optimum range the resistivity of the films decreases remarkably [62]. However, when the N content becomes higher than the appropriate value, Fermi level and band gap width do not move any more, the resistivity approaches gradually to a saturation value [10, 73].

5. Conclusions

For several decades, a variety of techniques have been used for the synthesis of CN_x films; in this paper PVD and CVD

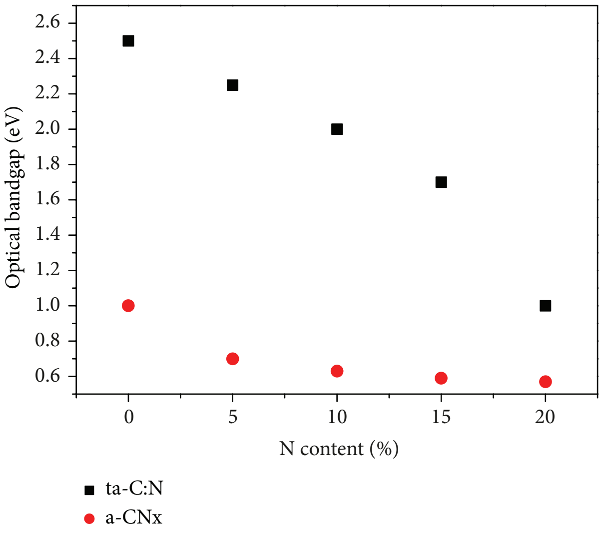


Figure 3: Optical band gap versus nitrogen content. Data from Zhang et al. [10] and Meškinis et al. [72].

methods have been introduced. The structures properties in crystalline and amorphous CN_x films have been elaborated in this paper.

The field emission properties of CN_x films are influenced by ratio of sp^2/sp^3, size of sp^2 clusters, surface morphology, and N content of films. Appropriate sp^2/sp^3 ratio (about 1.0–1.25) and N content (about 8 at.%–10 at.%) will strengthen the field emission properties. When N contents remain at an optimum range, the optical band gap and resistivity reduce and Fermi level of CN_x films increases, which are important for enhancing field emission properties. Appropriate size of sp^2 clusters is about 1.8–2.4 nm. Doping nitrogen can enhance surface roughness of CN_x films; the CN_x films with rougher surface also have lower threshold field. So CN_x films with rough surface can improve the field emission properties.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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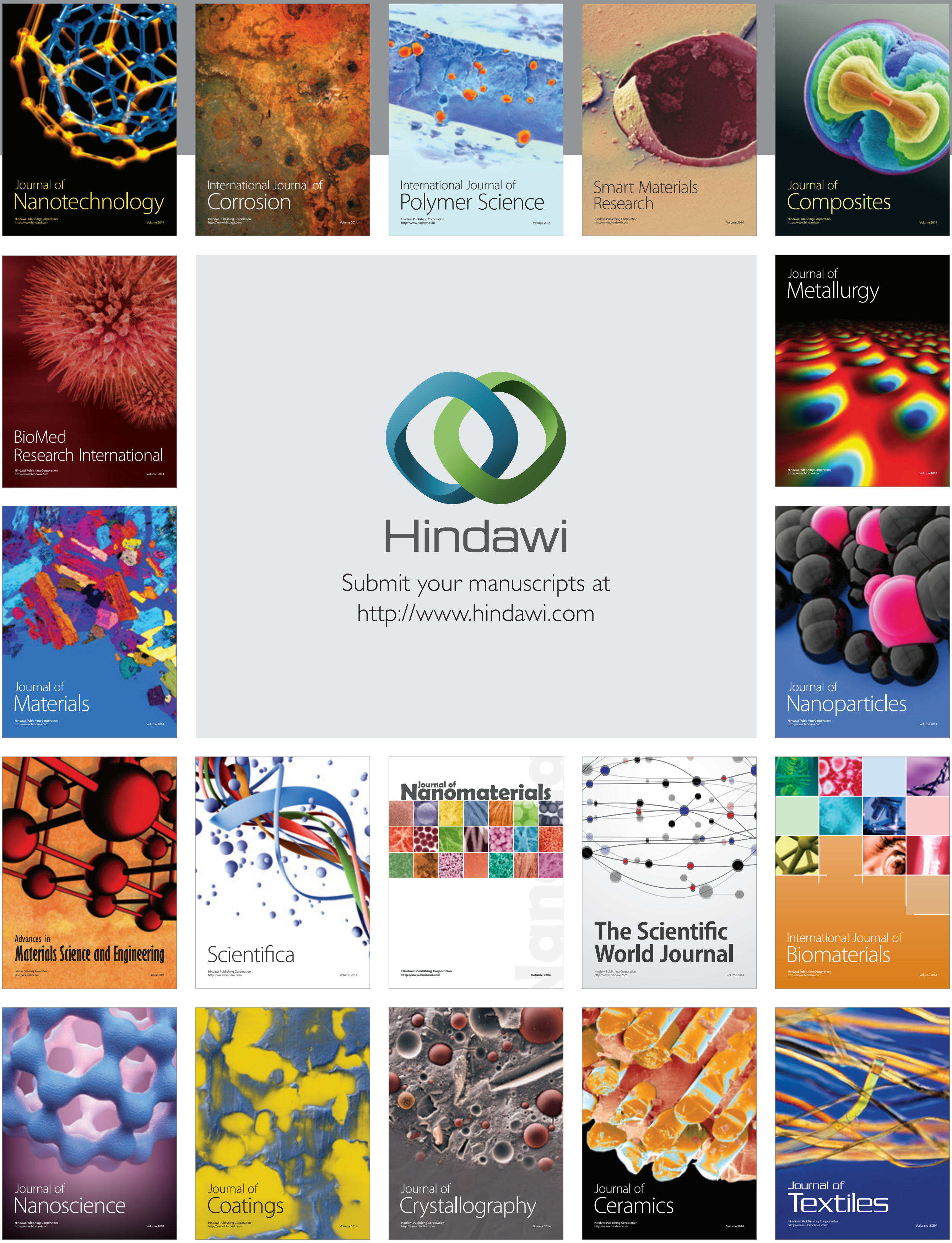
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