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Self-organized graphene-like boron nitride containing nanoflakes on copper by low-temperature N₂ + H₂ plasma†

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A simple and efficient method for synthesizing complex graphene-inspired BNCO nanoflakes by plasma-enhanced hot filament chemical vapour deposition using B₄C as a precursor and N₂/H₂ reactive gases is reported. The results of the field emission scanning electron microscopy, X-ray diffractometer, micro-Raman spectroscopy, Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy have evidenced that the BNCO nanostructures are composed of graphene-like hexagonal boron nitride nanoflakes with carbon and oxygen admixtures. The photoluminescence properties of the BNCO nanoflakes were studied in a Ramalog system using a He–Cd laser, and the results have demonstrated that the BNCO nanoflakes can generate strong green photoluminescence in the range of 515–569 nm, which was attributed to the aggregation of carbon atoms in the BNCO nanoflakes. The growth mechanism of the BNCO nanoflakes was also studied to show that the NH₃⁺ ions generated in plasma play an important role in the formation of the BNCO nanoflakes. The results propose a novel and efficient method for the synthesis of BN-based nanomaterials using B₄C precursors, and contribute to the design of the functional BN-based nanomaterials for various applications including optoelectronics, nanoelectronics, medical equipment, and wear-resistant materials for acceleration channels of electric propulsion thrusters.

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1. Introduction

Since the discovery of the first-ever real two-dimensional (2D) material, graphene, 2D films¹ and metamaterials² have become frontmost structures for intensive fundamental and applied

studies due to their unique physical, optical, and mechanical properties.^{3,4} Hexagonal boron nitride (h-BN) sheets represent a novel graphene-like material featuring a set of unique properties^{5,6} such as high thermal conductivity, structural stability and wide bandgap, which make it extremely promising for a wide range of applications⁷ ranging from lubricants and transistors operating in harsh environments^{8,9} to wear-resistant materials for acceleration channels of electric propulsion thrusters.^{10,11} The 2D BNCO structure was recently designed on the basis of h-BN sheets and demonstrates exceptional composition- and bandgap-tunable properties, with potential extensive applications in many innovative areas including automotive engineering, light-emitting diodes, gas discharge systems, equipment for biological imaging and DNA labelling, etc.^{8,12,13}

The atom connectivity of the BNCO structure is shown in Fig. 1, which is drawn according to the configuration of the BNCO structure.¹² Due to incorporation of carbon and oxygen, the BNCO structure exhibits better stability compared to the h-BN structure. The nitrogen vacancies in the h-BN structure can serve as the activation and absorption centers,¹⁴ which implies that the h-BN structure can interact with oxygen and water under some conditions. However, oxygen in the BNCO structure has a healing effect for the nitrogen vacancies¹⁵ and can improve the inertness toward oxidation on air and water

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Fig. 1 Schematic of BNCO structure.

exposure.¹⁶ In other words, the BNCO structure is more stable than the h-BN structure in air and hydrolytic condition, which is evidenced by the results of Lei *et al.*¹⁶ Due to this fact, the BNCO nanomaterials have attracted much more interests in last years.

Nevertheless, fabrication of such materials is still a challenge. To date, BNCO nanomaterials have mainly been synthesized using chemical vapour deposition (CVD) and liquid-based methods.^{8,12,17} In the liquid-based technique, the BNCO nanomaterials are synthesized at relatively low (<900 °C) temperatures using cheap precursor materials such as boron acid, boron oxide, urea, tetra-ethylene glycol and polyethylene glycol, but long duration of stirring and heating of the precursor materials results in long preparation and eventually, in the significant price increase.^{12,17} When the 2D BNCO sheets are grown by the CVD method, a high (>1000 °C) process temperature is used in line with expensive CH₄, O₂, Ar and BH₃-NH₃ precursors,⁸ thus the process is similar to that of fabricating h-BN sheets using BH₃-NH₃ precursor.^{9,18} Thus a new, fast, cost-efficient technique for the fabrication of hexagonal graphene-like boron nitride-based nanomaterials is vitally needed.

Can the 2D BNCO nanomaterials be synthesized by the chemical vapour deposition at relative low temperatures using cheap precursors? Such a technique would offer a significant progress in enhancing the nanomaterial characteristics and reducing material cost and harm to the environment, thus promoting a wide usage of complex nanomaterials in various advanced applications.¹⁹

Recently, reactive low-temperature plasma has been extensively employed to synthesize various nanomaterials at relatively low temperatures.²⁰ In particular, sophisticated 1D²¹ and 2D nanomaterials such as graphene and MoSe₂-graphene hybrid structures have been successfully synthesized using the reactive plasma.^{22–25} In addition, plasma can enhance the growth rates of nanomaterials due to the motion of ions and charged reactive species under the electric field generated by the plasma.²⁶ These motivated us to synthesize the 2D BNCO nanomaterials using the low-temperature reactive plasma environment and cheap precursors.

Apparently, the boron, nitrogen, carbon and oxygen sources are simultaneously required for the synthesis of 2D BNCO nanomaterials. We have selected B₄C compound as boron and

carbon precursor, which is much cheaper boron source than BH₃-NH₃. Oxygen does not require a separate source in our case, since it is always present in due amount in the CVD system,⁸ *i.e.*, the residual oxygen was used as the oxygen source. It is important that B₄C can be easily oxidized at 800–1600 °C to form B₂O₃ and CO/CO₂ compounds,²⁷ and then B₂O₃ can react with NH₃ to form BN,²⁸ which further serve as building material for the formation of BN sheets. However NH₃ is a toxic gas, so we have replaced it with nontoxic N₂ and H₂ gases since NH₃⁺ ions can be directly formed in the N₂-H₂ plasma.²⁹ Thus, one can expect that the 2D BNCO nanomaterials will be successfully synthesized in a cheap and fast process using N₂-H₂ plasma and B₄C compound as the main precursor.

In this work we used the N₂-H₂ plasma to synthesize the self-organized BNCO nanoflakes on copper foils using B₄C precursor in the plasma-enhanced hot filament chemical vapor deposition system (PEHFCVD). The characterization results show that the BNCO films are composed of h-BN nanoflakes with carbon and oxygen admixtures, thus the 2D BNCO nanomaterials were successfully synthesized. The formation mechanism was also studied to propose a plausible scenario of the 2D BNCO nanomaterial formation in the plasma.

Due to the change in the composition of BNCO nanomaterial as compared to BN sheets and graphene sheets, the bandgaps of BNCO flakes will be altered. As a result, the photoluminescence (PL) properties of BNCO nanomaterial will also be changed, in comparison with those of BN sheets and graphene sheets. Therefore, in this work we have also studied and described the PL properties of BNCO nanomaterials by PL measurements using Ramalog system.

2. Experimental details and characterization

Prior to the growth of BNCO films, copper foils with a thickness of about 10 μm were consequentially ultrasonicated in each solution of acetone and alcohol for 15 min, and then triple washed in deionized water. The growth of BNCO films was carried out in the PEHFCVD system shown in Fig. 2 and described in detail elsewhere.³⁰ In the CVD chamber, the heating system composed of three coiled tungsten filaments and electric biasing system made of a DC power supply were installed. The filaments were heated to ~1800 °C by AC current, thus the heating of the substrate and evaporation of B₄C compound were ensured. Anode and cathode leads of the biasing system were connected to the filaments and substrate holder, respectively, and the discharge sustained by the DC voltage was used for the generation of N₂-H₂ plasma. To avoid blowing off the B₄C powder by the pump, the powder was pressed into the sheets. The B₄C sheets were placed near the copper foil on the substrate holder. Due to a distance between the filaments and substrate (~8 mm), the substrate was fast heated to ~880 °C by the infrared flux from the hot filaments.

After evacuation of the CVD chamber to a basic pressure lower than 2 Pa, N₂ and H₂ gases were supplied to the chamber at the same flow rates of 50 sccm, *i.e.*, the mixing ratio of N₂ with

Fig. 2 Schematic of the experimental plasma-enhanced hot filament chemical vapour deposition system used to synthesize BNCO films on copper foils using B_4C precursor. N_2 and H_2 were used as reactive gases.

H_2 is 1 : 1, and the gas pressure was stabilized at about 2×10^3 Pa using vacuum valve. After that, the tungsten filaments were heated to the operational temperature by AC current. Once the substrate was heated by the filaments to about $880^\circ C$, the DC power supply was turned on to ignite and sustain the plasma in the chamber, and start the 2D BNCO nanomaterial growth experiments. In the main experiment series, the samples were grown for 15 and 20 min, respectively.

The morphology, structure, and composition of the synthesized 2D BNCO nanomaterials were studied using a Utimav X-ray diffractometer (XRD), a Hitachi S-4800 field emission scanning electron microscope (FESEM) operated at 15 kV, a HR 800 micro-Raman spectroscopy using a 532 nm line of semiconductor laser as the excitation source, BIORAD60V Fourier transform infrared spectroscopy (FTIR) and a ESCALAB 250 X-ray photoelectron spectroscopy (XPS) using an Al $K\alpha$ X-ray source, respectively. The PL properties of 2D BNCO nanomaterials were studied at room temperature in SPEX 1403 Ramalog system using the 325 nm line of He–Cd laser as the excitation source.

3. Results and discussion

3.1. Structure and compositions of nanomaterials

Fig. 3 is the FESEM images of the two samples of successfully synthesized 2D BNCO nanostructures. From Fig. 3 one can see that the samples A and B are composed of films. The insets showing the high resolution (HR) FESEM images of samples A and B indicate that the films are constituted of nanoflakes with a thickness of ~ 5 – 6 nm. More SEM images can be found in the ESI, Fig. S1.†

Fig. 4a is the XRD diffraction patterns of samples A and B, which show two XRD peaks at about 43.4° and 50.5° , respectively. For comparison, h-BN has two diffraction peaks located

at about 43.7° and 50.1° (JCPDS: 45-0895), while the diffraction peaks of copper are located at about 43.3° and 50.4° (JCPDS: 04-0836). Furthermore Huang *et al.* attribute the peak at about 43° to the diffraction of h-BN (100).³¹ These mean that the strong peaks in Fig. 4a originate from the diffraction of both BN(101) and Cu(111), or the single diffraction of Cu(111). In other words, it is difficult to determine the composition of the synthesized films by the XRD results only, thus the structure requires further characterization by other instruments.

After the peaks at about 43.4° are fitted using origin software, we obtain the full width at half maximum (FWHM) of these peaks and the FWHM values are about 0.192° and 0.179° for the samples A and B. These data indicate that the sample B has a better crystallinity than the sample A and there are more h-BN phases to be formed with the increase of time (see XPS results).

To accurately confirm the structure and composition of the produced samples, they were additionally studied using Raman spectroscopy and XPS technique. Fig. 4b is the Raman spectra of the same two samples. Each Raman spectrum in Fig. 4b shows the main peak at about 1369 cm^{-1} of h-BN,^{9,18} which evidences that the main component of the fabricated nanostructure is the h-BN phase.

Fig. 5a is the XPS spectra of the two samples, showing the B 1s, C 1s, N 1s and O 1s peaks at about 190.6, 284.8, 398.2, and 532.2 eV, respectively. The peaks at about 932.4 and 978 eV are attributed to Cu $2p_{3/2}$ and C (KLL), respectively.³² The atomic concentrations of B, N, C and O elements resulting from the XPS analysis are summarized in Table 1. From this table one can see that the ratios of B to N atoms are about 1.13 and 1.11 for both the samples, thus approaching the atom ratios specific to B to N atoms in the h-BN nanostructures. In addition, Table 1 shows that sample B has higher concentrations of boron and nitrogen atoms than sample A, which indicate that sample B has more h-BN phases compared to sample A.

The results of the XPS characterization described below also confirmed the presence of binding states of B, N, C and O elements in the synthesized samples.

According to the above analyses, the nanoflakes are made up of h-BN nanoflakes with carbon and oxygen admixtures, *i.e.*, the films are composed of 2D BNCO nanoflakes.

3.2. PL properties and composition of 2D BNCO films

Fig. 5b are the PL spectra of the two samples taken at the room temperature. The PL spectra show strong green PL bands in a range of ~ 515 – 569 nm, which are usually observed in BNCO phosphors.^{12,13,17} The above discussed XPS results indicate that the main component of the 2D BNCO film is h-BN, while the bandgap of h-BN is about 5.9 eV,¹⁸ thus the PL bands of 2D BNCO films are related to the defects present in the 2D BNCO nanostructures. For the green PL emission of BNCO materials, it is proposed to be related to the defects formed by carbon and boron oxide.^{12,13,17}

To confirm the binding states of B, N, C and O elements, the B 1s, N 1s, C 1s and O 1s peaks are fitted using the standard XPS fitting software after Shirley background subtraction and the results are shown in Fig. 6 and 7. The fitted XPS peak positions

Fig. 3 (a and b) FESEM images of the two samples with successfully synthesized two-dimensional BNCO nanostructures (the insets are the high-resolution FESEM images). The growth durations were 15 and 20 min for samples A and B, respectively. (c and d) HR FESEM and FESEM images of the sample grown for 20 min. Nanoflakes have a thickness in the range of 5–6 nm.

Fig. 4 XRD and Raman characterization of two samples grown for 15 and 20 min. (a) XRD diffraction patterns of samples A and B, showing two XRD peaks at about 43.4° and 50.5° , respectively. (b) Raman spectra of the same samples. Each Raman spectrum shows the main peak at about 1369 cm^{-1} of h-BN, thus evidencing that the main component is h-BN phase.

are summarized in Table 2. In Fig. 6, the B1 and B2 peaks are attributed to the B–N and B–N–O bonds,^{32,33} the N1 and N2 peaks result from the B–N and C=N bonds.³² In Fig. 7, the C1, C2, C3 and C4 peaks originate from the C=B, C=C, C=N bonds and the $\text{NH}_2\text{--CO}$ groups,^{32,34} and the O1 and O2 peaks are attributed to the Cu_2O and carbon oxide, respectively.^{32,33} The formation of the C=N, C=B and C–O bonds implies that carbon and oxygen atoms are incorporated into the BN

nanoflakes, which are further evidenced by the FTIR results shown in Fig. 8. In Fig. 8, the two peaks at about 1378 and 812 cm^{-1} are attributed to the transverse stretching vibration of in-plane B–N and the bending vibration of out-of-plane B–N–B plane, respectively.^{35,36} The peak at about 1605 cm^{-1} results from the C=C bonds.³⁷ The two peaks at about 993 and 1233 cm^{-1} are related to the N–B–O bonds and the C=N bonds, respectively.^{38,39} The origination of the peak at about 663 cm^{-1} is

Fig. 5 XPS and photoluminescence spectra of the two samples. (a) XPS spectra of the two samples, showing the B 1s, C 1s, N s and O 1s peaks at about 190.6, 284.8, 398.2, and 532.2 eV, respectively. (b) Photoluminescence spectra of the two samples.

Table 1 Atomic concentrations of B, N, C, and O elements

Sample	B (at.%)	N (at.%)	C (at.%)	O (at.%)
A	36.25	31.96	13.39	14.85
B	38.75	34.62	13.04	11.2

not completely clear. It may be related to B–O bonds, since the FTIR peaks of B–O bonds are observed at about 550–885 cm^{-1} .³⁸ The FTIR results further evidence that carbon and oxygen incorporated into the BN nanoflakes. Comparing the two spectra, one can see that the FTIR spectrum of sample B shows strong peaks related to h-BN and a weak peak related to C=C bonds as compared to sample A, and absence of the peaks

relevant to the N–B–O bonds and C=N bonds. This indicates that sample B contains more h-BN phases and less carbon and oxygen than sample A, consistent with the XPS results. The amount of N–B–O and C=N may be too small to be detected by FTIR technique, and this results in the absence of the peaks relevant to N–B–O bonds and C=N bonds in the FTIR spectrum of sample B.

From Fig. 6(a) and (b) we have obtained the integral intensities of B1 and B2 peaks. According to the integrals, the ratios of the BNO component to the total B amount are about 0.37 and 0.36 for the two samples grown for 15 and 20 min, respectively, which implies that the content of boron oxide in the BNCO films is very low. In other words, the generation of PL bands of BNCO films primarily relates to the defects formed by carbon. In ref. 12 Zhang *et al.* studied the electronic structure of BNCO and the

Fig. 6 B 1s and N 1s XPS peaks of the two samples. The ratios of the BNO component to the total B amount are about 0.37 and 0.36 for the two samples grown for 15 and 20 min. The B1 and B2 peaks are attributed to the B–N and B–N–O bonds, the N1 and N2 peaks result from the B–N and C=N bonds, respectively.

Fig. 7 C 1s and O 1s XPS peaks of the two samples grown for 15 and 20 min. The C1, C2, C3 and C4 peaks originate from the C=B, C=C, C=N bonds and the NH₂-CO groups and the O1 and O2 peaks are attributed to the Cu₂O and carbon oxide, respectively.

Table 2 Positions of fitted XPS peaks in Fig. 5

Sample	B1 (eV)	B2 (eV)	N1 (eV)	N2 (eV)	C1 (eV)	C2 (eV)	C3 (eV)	C4 (eV)	O1 (eV)	O2 (eV)
A	190.4	191.1	397.9	398.4	283.9	284.8	286.0	288.2	530.7	532.5
B	190.5	191.1	397.9	398.5	283.7	284.8	286.1	288.4	530.9	532.6

Fig. 8 FTIR spectra of samples A and B. The FTIR spectrum of sample B shows strong peaks related to h-BN and a weak peak related to C=C bonds as compared to sample A, and absence of the peaks relevant to the N-B-O bonds and C=N bonds.

results indicate that the nitrogen vacancies produce two levels named as three boron centre (V_{N3}) and one boron centre (V_{N1}) below the conduction band about 1.0 and 0.7 eV, respectively. On the other hand, the defects related to the carbon and oxygen

impurities produce the levels below the conduction band of about 4.1 and 4.5 eV, respectively. However, the level related to the carbon impurity changes from ~ 2 –3 eV depending on the concentration of carbon.^{12,13} Considering the change of the defect level caused by the carbon concentration, the green PL bands originate from the transition between the nitrogen vacancy level and the carbon impurity level.

From ref. 12 and 13 it follows that the BNCO materials generate single PL band under each excitation. However our sample B grown for 20 min simultaneously generate two strong PL bands at about 520 and 569 nm under the excitation of 325 nm line of He-Cd laser which implies that the PL bands are also generated by some other mechanism. It should be noted that the aggregation of carbon atoms is not considered in ref. 12 when the electronic structure of BNCO was studied. In fact, the deposition and diffusion of carbon atoms in the structure are random, thus it is inevitable that some carbon atoms meet at the edges of the BNCO nanoflakes. Hence, when these carbon atoms bond to the edges of the BNCO nanoflakes, they exist in the BNCO structure in the form of carbon clusters. Due to the non-uniformity of carbon clusters, they exhibit different bandgaps.^{40,41} According to the PL mechanism in the C-N nanomaterials, the green PL bands may be related to the transition between π^* and π bands of these carbon clusters.⁴⁰

According to the above analyses, the green PL emission of BNCO films originates from the transition between the nitrogen vacancy level and the carbon impurity level and the transition between π^* and π bands of the carbon clusters.

The PL spectra show that the BNCO films generate the green PL bands, which are different from the ultraviolet PL bands of h-BN⁴² and red PL bands of graphene treated by oxygen plasma.⁴³ These differences in the PL properties indicate that the change in the components affects the electronic structure of h-BN and graphene.

3.3. Formation of 2D BNCO nanomaterials

The above discussed results indicate that the 2D BNCO nanomaterials can be grown at low temperature on copper foils by the PEHFCVD technique using B₄C precursor, in contrast to the growth of similar nanostructures and BN sheets using BH₃-NH₃ precursor at high temperature.^{8,9,18} In this section, the formation of 2D BNCO nanomaterials on the copper foils is analysed, and the plausible growth mechanism is proposed to explain the found regularities and experimental facts.

During the substrate heating, high temperature of hot filaments ($\sim 1800^\circ\text{C}$) ensures the reaction of residual oxygen with hydrogen in the gas environment to form H₂O(g) molecules. As a result, these H₂O(g) molecules react with the surfaces of B₄C sheets to form B₂O₃ molecules *via* the following reaction:²⁷

Due to the significantly lower temperature ($\sim 880^\circ\text{C}$) of the copper foil compared to the filaments, a great temperature gradient between the filaments and copper foil is present which prompts the B₂O₃ molecules to move toward the copper foil. While the surface of copper foil is in general smooth, there still are many micro-valleys on its surface.^{44,45} After deposition of the B₂O₃ molecules onto the copper foil surface they diffuse toward the micro-valleys along the copper surface and aggregate in the micro-valleys.⁴⁶ In addition, a small number of CO molecules also deposits onto the surface of copper foil due to their low mass and hence, higher thermal velocity.

After plasma ignition, N₂ and H₂ gases are ionized to form various ions such as N⁺, H⁺, NH₂⁺, and NH₃⁺, *etc.*²⁹ These ions fast move to the surface of copper foil under the action of the electric field formed by plasma.^{47–49} Among these ions, the NH₃⁺ ions react with the B₂O₃ molecules in the micro-valleys to form BN molecules:²⁸

The BN molecules formed in the micro-valleys participate in the nucleation of BN nanoflakes. Other ions such as N⁺ and H⁺ bombard the B₄C sheets and sputtering them, thus the B and C atoms are supplied to the gas environment, deposit on the surface of copper foil and eventually diffuse toward the BN nuclei. Since copper foil is connected to the cathode of the DC power supply, the N⁺ ions deposited on the surface of copper foil easily form N atoms⁵⁰

As a result of the N⁺ ions deposition, the N atoms also diffuse toward the BN nuclei. When the N and B atoms move to the edges of the BN nuclei, they incorporate into the nuclei structure and form the BN nanoflakes. Simultaneously, the carbon atoms and CO molecules move to the edges of the BN nuclei and incorporate into the BN nanoflakes to form the BNCO structure. The residual oxygen is ionized into oxygen ions by the plasma, thus the B₂O₃ is formed in the gas environment:

According to (2), the B₂O₃ molecules react with the NH₃⁺ ions in the gas environment to form the BN molecules; then, the BN molecules deposit onto the edges of BNCO nanoflakes and bond to the edges of BNCO nanoflakes to promote their growth. Furthermore, it is possible that these oxygen ions can directly incorporate into the BN nanoflakes.

In the process of nucleation and growth of the 2D BNCO nanomaterial, O₂ is not supplied from the external environment to the CVD chamber, *i.e.*, the oxygen in the 2D BNCO nanomaterials originates from the residual oxygen in the CVD chamber. However the content of the residual oxygen in the CVD chamber is limited, thus the oxygen content in the BNCO nanoflakes is low, as evidenced by the XPS results. On the other hand, the ratio of B to C atoms in B₄C molecule is 4 : 1, which indicates that lower amount of the carbon atoms is formed by the sputtering. As a result, there are a small number of carbon atoms to be incorporated into the BN sheets, as confirmed by the XPS results.

The growth times of samples A and B were 15 and 20 min, respectively. A long growth time implies that more BN phases were formed according to reactions (1) and (2). In other words, the sample with a long growth time has a better crystalline structure, which is confirmed by the XRD and FTIR results. Fig. S2 in ESI† shows the section FESEM images of samples A and B. From Fig. S2† we have obtained average thicknesses of the films, which reached 172 and 284 nm for samples A and B, respectively. According to the film thicknesses and growth times, the growth rates are about 11.5 and 14.2 nm min^{−1}. These data indicate that the nanomaterials grow in a non-linear mode, and the growth is accelerated with time. However, the ion bombardment of the formed nanomaterials can result in the sputtering, which lowers the growth rate. Simultaneously, the amount of B₄C is limited and the exhaustion of B₄C further reduces the growth rate. Considering the ion bombardment and exhaustion of B₄C, the growth rate will have a maximum value, and then it will reduce. Finally, the growth stops.

To compare, the BNCO sheets were synthesized in ref. 8 by CVD technique at high temperature (1015 °C) using the BH₃-NH₃ as the boron and nitrogen sources. In ref. 9 it is also noted that the formation of BN from BH₃-NH₃ in a CVD system is carried out under high temperature (1000 °C). However, the formation of 2D BNCO nanoflakes in our experiment depends on the reactions of B₄C, O₂, H₂ and NH₃⁺ ions and the diffusion of C and B atoms formed by ion sputtering and N⁺ produced by

the plasma. These reaction and diffusion processes can occur under relatively low temperature ($<900\text{ }^{\circ}\text{C}$), thus the 2D BNCO nanomaterials can be formed at a relatively low temperature in our experiment.

4. Conclusions

In summary, the BNCO structures composed of 2D BNCO nanoflakes were synthesized on copper foils in $\text{N}_2\text{-H}_2$ plasma by the PEHFCVD method using B_4C compound as a precursor. According to the characterization results by FESEM, FTIR, XPS, XRD and micro-Raman spectroscopy, the formation mechanism of BNCO films relates to the reactions of B_4C , O_2 , H_2 and NH_3^+ ions, and diffusion of C and B atoms formed by ion sputtering and N^+ formed by the plasma. In particular, the results indicate that the NH_3^+ ions formed by the plasma play an important role in the initial formation of BNCO nanostructures. The photoluminescence properties of the BNCO nanostructures were studied by the Raman system, and the PL results indicate that the BNCO films can generate strong green PL bands in a range of 515–569 nm. The generation of these PL bands is related to the defect level and the arrogation of carbon atoms in the BNCO films. These achievements provide us a novel method for fabrication of the BN-based nanomaterials using cheap precursors, and contribute to the design of functional BN-based nanomaterials for the applications in various BN-based optoelectronic and other devices, including biomedical applications.⁵¹

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