Fluorescent Carbon- and Oxygen-Doped Hexagonal Boron Nitride Powders as Printing Ink for Anticounterfeit Applications

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Abstract
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Keywords: boron nitride, fluorescent, printing, ink, anti-counterfeit

Increasing demands for optical anti-counterfeiting technology require the development of versatile luminescent materials with tunable photoluminescence properties. Herein, a number of fluorescent carbon and oxygen doped hexagonal boron nitride (denoted as BCNO) phosphors are found to offer a such high-tech anti-counterfeiting solution. These multicolor BCNO powders, developed in a two-step process with controlled annealing and oxidation, feature rod-
like particle shape, with varied luminescence properties. Studies of the optical properties of BCNO, along with other characterization, provide insight into this underexplored material. Anti-counterfeiting applications are demonstrated with printed patterns which are indistinguishable to the naked eye under visible light but become highly discernible under UV irradiation. The fabricated patterns are demonstrated to be both chemically stable in corrosive environments and physically robust in mechanical bending testing. These properties render BCNO as promising and versatile anti-counterfeiting material a wide variety of environments.

1. Introduction

Hexagonal boron nitride (h-BN), also known as ‘white graphene’, has the same honeycomb structure as graphene, but with very different electronic and chemical properties. h-BN has attracted substantial attention recently due to its high chemical and thermal stability, excellent thermal conductivity, and intense ultraviolet (UV)-emission.[1] To adjust the electronic and optical properties of h-BN, carbon and oxygen co-doped h-BN (denoted as BCNO) has been investigated.[2] A wide range of BCNO materials, in the forms of nanocrystals,[3] nanoparticles,[4] and atomically thin sheets,[5] have been fabricated by pyrolysis or chemical vapor deposition (CVD). CVD is typically used to obtain specific planar heterostructures and usually provides a low yield. In contrast, pyrolysis enables efficient preparation of large quantities of BCNO, with readily tunable composition and high yield. For pyrolysis reactions, BCNO is often produced from three precursors, such as boric acid, urea, and polyethylene glycol (PEG).[3, 7] as the B, N, and C sources, respectively.[4, 6] The amount of C is primarily controlled by varying the weight ratio of the carbon source,[8] however it is difficult to precisely control the B:C:N:O ratios due to elemental overlap between O, C and N in precursors typically used in these syntheses. For example, nitrogen sources such as urea also contain C; O typically exists in two or all of the three commonly used precursor compounds such as boric acid and PEG, making it quite challenging to control the O content in the final BCNO product. As a
result, it is difficult to tune and/or distinguish the impact of C and O on the photoluminescence property of BCNO. Thus, a simpler method to tune BCNO emission properties is to control two rather than three precursors.

Meanwhile, anti-counterfeit technology plays an indispensable role in protecting high value merchandise, legal documents, identity cards, pharmaceuticals and currency. The two key features for anti-counterfeiting applications are 1) the optical properties of the constituting materials, primarily originating from the chemical components used in the ink, and 2) the complexity of the coded patterns. Security inks have been fabricated using inorganic semiconductor nanocrystals, organic dyes, metal nanoclusters and complexes, carbon dots, rare-earth doped complexes and up-conversion nanoparticles. It is still challenging to prepare luminescent materials with well controlled emission properties. Moreover, toxic elements used for fabrication of many anti-counterfeit applications, such as lead and cadmium, as well as the high cost associated with rare-earth elements have hindered their applications. It is therefore necessary to develop environmentally friendly, low cost and easily accessible luminescent materials with tunable excitations/emissions. BCNO materials are well suited for anti-counterfeiting applications, as they show low toxicity, can be produced at low cost, and provide tunable emission properties. Furthermore, BCNO features high thermal and chemical stabilities, which could allow for applications in harsh conditions.

In this study, we first report facile synthesis of rod-shaped BCN and multicolor emitting BCNO powders. Anti-counterfeiting applications were then demonstrated by developing inks made of BCNO, cellulose, and a polyurethane (PU) binder. The inks were utilized to print patterns indistinguishable under visible light, but readily discernible under UV radiation. Various techniques have been employed to characterize the BCNO materials and demonstrate the potential of BCNO as an emerging anti-counterfeiting material.
2. Results and Discussion

The scheme for synthesizing BCN and multicolored BCNO is illustrated in Figure 1a. First, black BCN powders are obtained by heating a mixture of melamine and boric acid at 1000 °C under Ar. The obtained BCN is then converted to BCNO by annealing in air. For comparison, white h-BN is also obtained using melamine and boric acid as the precursors (details in the Experimental and Supporting Information). In sample nomenclature BCNO-X-Y, X notes temperature and Y represents dwell time. Figure 1b and Figure S1 display the XRD patterns of BCN and BCNO samples. BCN shows two broad peaks centered at 24.8° and 43°, characteristic of diffraction from the (002) and (100) planes of h-BN (PDF no. 00-034-0421), respectively. BCNO samples show progressively better crystallinity with the increasing temperature and time held at elevated temperatures as compared to BCN. The peaks corresponding to spacing of the (002) planes of BCNO shifted to a slightly higher 2θ values, in line with the decrease in interplanar distances from 0.352 nm to 0.334 nm. In addition, the color of powders changes from black for BCN to nearly white for BCNO-850-1h (Figure 1a). h-BN is typically white, while BCN is black due to C doping, rather than a physical mixing of carbon with h-BN. This was confirmed in a control experiment (experimental details in the Supporting Information) where physically mixed carbon black and h-BN were heat treated using the same parameters at 650 °C for 3 hours. There is only a slight change in color (Figure S2) with no discernible photoluminescence under 365 nm UV light.

Figure 1c shows thermogravimetric analysis for BCN and h-BN powders heated to 1000 °C in air (more information in Figure S3). During the preparation of h-BN, H₂ was used to ensure full nitridation and removal of C atoms, leading to white BN products. h-BN is seen to be more thermally stable than BCN, with a loss of only 5.44% of its initial weight upon heating to 850 °C which is ascribed to the loss of hydroxyl or amine groups. In contrast a 21.69% weight loss
is observed for the BCN sample. Upon further heating, the h-BN sample experiences a slow mass gain while the BCN sample continued to lose weight, before a rapid mass gain, which was ascribed to oxidation producing B$_2$O$_3$.[21] Carbon dioxide (CO$_2$) was observed when the BCN sample was heated in O$_2$/He (Figure 1d). Extracted ion chromatographs (EIC) were employed to monitor the abundance of particular ions in the gas phase, with respect to the temperature within the furnace of the TGA instrument. It shows a maximum abundance of m/z 44, ie. CO$_2$, at 650 ℃. In addition to carbon loss, oxidation of BCN also occurred, as evidenced by the formation of boron oxides (Figure S4). When the temperature was increased to 850 ℃ and the dwell time was greater than one hour, the powders were observed to start to agglomerate. A glassy coating formed when the temperature was further increased to 950 ℃ (See Figure S5).

Figure 1. a) Schematic illustration of the synthesis of BCN and BCNO, with insets of digital images of the powders; b) XRD patterns of BCN and BCNO prepared at different temperatures; c) TG curves of BN and BCN in dry air and CO$_2$ evolution from BCN heated in air to 800 ℃; d) CO$_2$ evolution based upon extracted ion chromatogram and TG curves of BCN heated up to 650 ℃ and held for 8 h.
The BCN particles are rod-like in shape, with diameters of approximately 400 nm, and 2-8 μm in length (Figure 2a and 2d, and Figure S6a). The majority of BCNO particles retained this rod-like structure after treatment in air (Figure 2e and 2f, and Figure S6b-g), however some rods fused together and formed larger structures. This was more pronounced in samples produced with higher processing temperatures and longer dwell time (Figure 2b and Figure S6f), and is particularly notable in the case of BCNO-650-12h (Figure 2c and Figure S6h). Figure 2g shows an electron diffraction (ED) pattern of BCNO-650-3h. The ED rings indicate the polycrystalline nature of the material, which can be indexed to the (002) and (100) reflections of h-BN, consistent with XRD results.[2c, 3a] High-resolution TEM (HRTEM) images of BCNO-650-3h and BCNO-850-1h are displayed in Figure 2h and Figure S7c. Here it can be seen that higher treatment temperature resulted in better crystallized BCNO nanocrystals. The measured (002) interlayer spacing of BCNO-650-3h is 0.34 Å, slightly larger than the 0.33 Å value of crystalline h-BN, indicating the formation of turbostratic boron nitride (t-BN) nanocrystals.[22] Electron energy loss spectra (EELS) (Figure 2i and Figure S7d) show characteristic K-edge absorptions of B, C, N and O at 188, 284, 401, and 532 eV, respectively. Both the B and N core edges exhibit π* and σ* peaks, characteristic of sp²-hybridized h-BN.[23] Meanwhile, the doublet π* and σ* peaks at 286 eV and 294 eV in C-K edge indicate sp²-bonding characteristic of carbon, with energy loss being slightly higher in compared to the C-K edge peaks of graphite (π* at 285 eV and σ* at 291 eV).[24] Moreover, the broadness of the σ* peak indicates a contribution from the C–N configurations.[24-25] Similarly, oxygen atoms show doublet π* and σ* peaks at 538 eV and 546 eV, respectively.[8, 24] Combined, this shows definitively that B, C, N and O are in an sp²-hybridized, 2D-conjugated electron system, rather than a physical mixture.[26]
Figure 2. SEM images of a) BCN, b) BCNO-750-3h, and c) BCNO-650-12h; high angle annular dark field STEM images of d) BCN, e) BCNO-650-3h and f) BCNO-850-1h; g) ED of BCNO-650-3h; h) High-resolution bright field STEM image of BCNO-650-3h; i) EELS spectra of BCN, BCNO-650-3h and BCNO-850-1h.

The structure of BCN and BCNO was further characterized with FTIR (Figure 3a and Figure S8). All samples display two strong bands at around 773 cm\(^{-1}\) and 1384 cm\(^{-1}\), which are ascribed to in-plane B-N-B stretching and out-of-plane B-N bending vibrations, respectively.\(^{[20a]}\) The small band at 1124 cm\(^{-1}\) can be attributed to C-N bonds.\(^{[6b, 27]}\) Oxidation of BCN occurred during
the heat treatment, evidenced by two small shoulders appearing at 934 cm$^{-1}$ and 1039 cm$^{-1}$, which can be attributed to N-B-O and B-O-B interactions.\[28\] The broad band between 1615-1660 cm$^{-1}$ can be attributed to the C=O bond.\[2b\] The existence of C and O containing bands indicates that C, O atoms are chemically incorporated into BCNO skeleton.

XPS results (Figure 3b) confirm that all samples are composed of B, C, N and O atoms, consistent with EELS results. The typical XPS spectra of B1s, N1s, C1s and O1s (Figure 3c-f) are around 190.8, 398.4, 284.8 and 532.3 – 532.9 eV, respectively. The main B1s peak, at 190.6 eV, is attributed to B atoms surrounded by N atoms, with the two subpeaks at 191.5 and 192.5 eV are due to O–B–N$_2$ (here the 2 is indicative of two B-N bonds) and O$_2$–B–N or O$_2$–B–C bonds, respectively.\[22b\] The N1s for N–B and N–C bands are observed at 398.3 and 399.5 eV, respectively. The small shoulder at 400.5 eV reflects N–H bonds, presumably residual from the amino terminal groups in melamine.\[26\] C1s spectra have a prominent peak at 284.8 eV, attributed to graphitic C–C species, along with four smaller components.\[29\] The two peaks at 285.7 and 286.5 eV are due to B–C–N$_2$ and C–N$_3$, respectively.\[19a, 22b\] Another two components with higher binding energy at 287.8 eV and 288.9 – 289.2 eV are likely from C–O and O–C=O bonds, respectively.\[24, 30\] In the O1s spectrum, the most significant contribution at 532.6 eV is associated with O–B bonds, along with a shoulder at 513.6 eV resulting from O–C bonding.\[5\] Meanwhile, there is a slight blue shift of the O1s peak for samples treated at elevated temperatures from 532.3 eV to 532.9 eV (Figure S9). This is probably related to the decrease of carbonyl/carboxyl groups and an increase in O-B bonds. The contents of C and O (in at%) are displayed in Figure 3 (e) and (f) (more see Table S1), respectively. Higher temperature treatment removed more C content from the matrix with the C content decreasing from 13.83 at% in BCN to 4.73 at% in BCNO-850-1h. The same trend was observed for the O content, which decreased from 18.29 at% to 14.28 at%. Based upon Figure 3 (e), a significant amount
of carbonyl/carboxyl groups in the BCN structure were removed during heat treatment. Meanwhile, the O-B component became more dominant than O-C (Figure 3f).

![Figure 3](image)

**Figure 3.** a) FTIR spectra of BCN and BCNO at different temperature; b) XPS survey scan, and c-f) XPS B1s, N1s, C1s and O1s fine scans of BCN, BCNO-650-3h, and BCNO-850-1h.

The optical properties of the BCNO samples were characterized, firstly using reflectance spectrophotometry, with all samples shown to absorb strongly in the UV and blue parts of the spectrum (See Figure 4a). Significant absorption is also seen beyond this range, the degree of which being negatively correlated with annealing temperature and time. This can be attributed to defect states, in line with previous reports.\[^7\] Here, it is seen that temperature plays a more
important role than dwell time with respect to the absorption properties of these materials. The broad absorption around 420 nm are ascribed to carbon and oxygen related defects.\cite{7,8} There is a clear blueshift of these absorption peaks, owing to reduced defects on the surface of the material with increasing temperature. The long absorption tails in the visible range indicates the presence of carbon cluster/carbon quantum dots (CQDs),\cite{31} and intra-band impurity mediated transitions, which may be located at the surface, i.e., surface states.\cite{26} In addition to this, a further feature is found in the red/NIR portion of the spectrum, seen as a distinct peak for the BCNO-850-1h sample and as a shoulder for others. In conjunction with photoluminescence spectra below, this is assumed to be evidence of carbon quantum dots, which have been predicted to form in BCNO by Wang et al.\cite{32}

Photoluminescence (PL) measurements were carried out with both emission and excitation spectra collected (Figure 4b-i). It was noted that a number of these materials displayed wavelength dependent emission spectra, in line with our understanding of there being substantial concentrations of defects, which appear to be in poor electronic communication with one another (i.e., not able to thermalize to the lowest energy prior to emission occurring). Samples heat treated at 650 °C, with dwell times varying from 3 to 12 hours, all showed similar PL properties (Figure 4c and Figure S10), with photoexcitation from wavelengths below 450 nm yielding emission centered around ~540 nm, and lower energy excitation giving rise to a significantly shifted emission peak (~580 nm), convoluted with the aforementioned one (Figure 4d and Figure S10). A similar competition between excitation-emission pathways was also seen, but less distinct, for the 750 °C treated sample. Here the peak emission from high energy excitation is ~520 nm and from low energy to ~540 nm, both blue shifted relative to what was seen for BCNO-650-Y materials (Figure 4e). Emission was further blue-shifted for BCNO-850-1h, with emission at ~430 nm. In this case, low energy excitation did not provide distinctly different shapes, but instead the tail of the peak was observed from 350 nm excitation. From
these emission spectra (Fig. 4b and 4c), it can be seen that long-term heat treatments can affect the emission properties of BCNO, however the impact is not as substantial as using different temperatures. It should be noted that emission spectra are normalized to aid visual comparison. In each case, except BCNO-850-1h, the emission intensity is similar (See Figure S11). Meanwhile, visible light emission from the 550 °C treated sample was quite low (Figure S11 and S12).

The excitation-emission wavelength dependence (Figure 4d-f, Figure S10a-g) was further investigated with specific focus on emission at 525 nm and 575 nm, for the 650 °C and 750 °C treated samples (Figure 4g and 4h). On account of the significant blue shift, 425 nm and 500 nm were used for analyzing the 850 °C treated material. A similar but less distinct phenomenon is observed for the 750 °C sample, while there is a marginal difference for the material prepared at 850 °C. All BCNO samples displayed two excitation peaks that are related to defects induced by carbon and oxygen. In accordance with the excitation and emission spectra, the shift of the excitation peak (470-530 nm) position for the materials synthesized at higher temperature originated from a decrease in carbon related impurities. One of the key findings from Figures 4 is that different dwell times at 650 °C result in similar photoluminescence properties, indicating that temperature control is the key parameter which must be controlled in order to change the C, O-related defects.

Photoexcitation at longer wavelengths was also performed (675 nm, Figure 4i), with the aim to probe the low energy absorption feature mentioned above. All BCNO samples show NIR emission resulting from such an excitation, with 650-850 °C treated samples emitting around 910 nm. This may be explained by different sized CQDs embedded in the BN lattice. BCNO-550-1h shows a substantially red-shifted emission by comparison (~960 nm), which is also broader and more intense. Notably, this was in contrast to its weak emission in the visible
region. It seems that 550 °C is insufficient to effectively change the content and defects related to C and O, making it distinct from the other BCNO samples. The carbon content of BCNO-550-3h (13.37%) is similar to that of BCN (13.83%, see Table S1). Excitation in the range of 500 to 700 nm shows consistent NIR emission spectral shape (Figure S13), which suggests that here excitation energy within the material ‘funnels’ to these low energy states. This fits quite well with the previous suggestion of carbon quantum dot formation within a BN matrix.\cite{31b, 32}

**Figure 4.** a) UV-vis-NIR absorption spectra for BCNO; Normalized emission spectra excited at 350 nm of BCNO b) synthesized at different temperatures and c) synthesized at 650 °C with different dwell time; PL spectra of BCNO d) 650-3h, e) 750-3h, f) 850-1h. Insets are the digital images of BCNO phosphors under 365 nm UV light. Excitation spectra of BCNO collected for emission at g) 525 nm and h) 575 nm. i) NIR emission of BCNO excited at 675 nm.
To demonstrate the suitability of BCNO for anti-counterfeit purposes, a series of security inks were prepared for extrusion printing of patterns which appeared as close to the same color under visible light but revealed themselves under UV illumination. The inks were prepared by mixing BCNO with cellulose microfibers, ethanol, water and a polyurethane (PU) binder. Examples of printed patterns, on either polyethylene terephthalate (PET) or black cardboard are shown in Figure 5a and 5b, respectively (more can be found in Figure S14). The loading of BCNO in the ink was kept low, resulting in prints with nearly the same appearance under visible light, ostensibly that of cellulose. This approach can be easily adapted to create any desired pattern. Upon illumination with a UV light source (365 nm), the printed features emitted differently depending on the type of BCNO used in the ink preparation, revealing the hidden patterns (Figure 5a, b). It was noted that the weak blue emission from cellulose is the likely cause of the slight difference in color between neat BCNO (Figure 4d-f) and the BCNO embedded in the patterns. Since the BCNO is highly stable in both acidic and basic environment, the printed sensors remained active in strong acid (0.8 M HCl) or base (30% NH₃) aqueous solutions (Figure 5c, d, respectively). TG results show that BCNO/cellulose composite has slightly better thermal stability than bare cellulose structures (Figure S15). In general, the printed items have the texture and appearance of a cellulosic substance such as cellulose filter papers. The printed structures are highly flexible and can be easily bent and twisted (Figure 5e). The photoluminescence quantum yield (PLQY) was calculated based on decreased signal from prompt scatter and increase emission for the three printed materials. We observed PLQY of less than 10% for all the samples. Although these values are not particularly high, the illumination intensity required to clearly observe patterns is reasonable. Stability in high and low pH conditions, as well as under UV irradiation make this a very promising material.
Figure 5. Digital images of printed patterns taken under room light and 365 nm UV light illumination. BCNO-650-3h, BCNO-750-3h and BCNO-850-1h powders were mixed with cellulose. Scale bars are 2 cm in a), b), and e) and 1 cm in c) and d).

3. Conclusion

In summary, by controlling the annealing temperature and dwell time, BCNO powders were prepared with tunable composition, corresponding to different color photoluminescence. Various characterizations have confirmed that the content and chemical state of B, N, C and O can be effectively adjusted by annealing BCN in air and the optical properties of BCNO are strongly correlated with carbon and oxygen contents, defects related to these elements, and the presence of carbon quantum dots within the BN matrix. Security inks developed by combining BCNO with cellulose and a PU binder show discernable pattern under UV illumination. This printed pattern also features unique chemical stability and flexibility, which make it highly promising for anti-counterfeiting applications.

4. Experimental Section

Synthesis of BCN nanorods: Boric acid (H₃BO₃, Sigma-Aldrich) was used as a boron source,
while melamine (C₃N₆H₆, Sigma-Aldrich) was employed as the source of nitrogen and carbon.

Firstly, 3.72 g boric acid was dissolved in 250 mL deionized water to form a clear solution. 3.78 g melamine was then added into this solution and heated to 90 ℃. Following vigorous stirring for 12 hours, water was subsequently evaporated, leaving a white precursor precipitate. This dried precursor was further heated in a vacuum oven at 70 ℃ for 12 hours before being finely ground and then placed into a quartz tube. The powders were then heated to 1000 ℃ at 2 ℃ min⁻¹, with a 2 hour dwell time under Argon (Ar) flow at 150 sccm, to produce a black boron carbon nitride powder, denoted as BCN. For comparison, white BN powder was prepared by heating white precursor precipitate in Ar/H₂ (5 vol% H₂) gas flow at 1000 ℃ for 2 h, the same synthetic procedure used for producing BCN except for carrier gas.

**Synthesis of BCNO multicolor phosphors:** BCN was further heated at different temperatures (550, 650, 750, 850 ℃) with various dwell time (1, 3, 5, 8 and 12 hours) under dry air (moisture ≤ 15 ppm) with a gas flow of 150 sccm. Ambient air affords similar results but with a slightly lower yield, which is likely due to reactions between moisture and BCN, forming boron oxide.

The obtained powders were washed with excessive deionized (DI) water to remove any B₂O₃/H₃BO₃. The insoluble colorful powders are denoted by BCNO-X-Y, where X is the temperature and Y is the duration of the heat treatment. According to different sintering temperatures and dwell time, the BCNO samples are separated into two series. For the first series, BCN samples are treated in air at 550, 650 and 750 ℃ with a dwell time of 3 hours. A shorter dwell time of 1 hour was used for treatment at 850 ℃ to prevent agglomeration. These products are denoted as BCNO-550-3h, BCNO-650-3h, BCNO-750-3h and BCNO-850-1h. For the second series, the sintering temperature was fixed at 650 ℃ and the dwell time was varied between 5 hours to 12 hours. The prepared BCNO are denoted by BCNO-650-5h, BCNO-650-8h and BCNO-650-12h, respectively.

**BCNO anti-counterfeit inks:** To demonstrate the anti-counterfeit applications, a series of inks
were prepared by mixing different BCNO powders with cellulose microfibers (50 µm average length), polyurethane (PU) binder, ethanol and water. Cellulose is highly abundant in nature and the main component of paper.[35] Utilizing cellulose as the matrix in ink fabrication leads to printed constructs with appearance and texture similar to paper. Polyurethane (PU) binder was used to facilitate printing of flexible patterns.[36] Briefly, 10-100 mg of BCNO was added to 2.5 g cellulose microfibers (Sigma-Aldrich) and mixed vigorously for 2 hours at room temperature. Separately, a hydrophilic polyether-based PU (HydroMed D3, AdvanSource Biomaterials, USA) was dissolved in ethanol and water (95:5, volume ratio) to obtain a 10% (wt/vol) solution. To prepare the printing inks, this PU solution was added to the mixture of cellulose and BCNO and stirred at room temperature for two days until a homogeneous dispersion was achieved. The amount of cellulose in the inks strongly influences printability and after multiple optimization iterations, the ratio of cellulose in the ink formulations was fixed at 35% (wt/wt) in order to achieve the best printing resolution. The amount of BCNO in the ink formulation was optimized to closely match the appearance under visible light for all inks, while having different emission colors under UV irradiation. The inks could be printed on a variety of surfaces such as paper, cardboard, glass and plastic using a gel extruder printer (EnvisionTEC Bioplotter Manufacturing Series, Germany). Printing was performed at room temperature with a 1 mm nozzle and 1 bar pressure.

Materials Characterization. X-ray diffraction (XRD) measurement was recorded on a D8 Bruker Discover with Cu Kα (λ = 1.54 Å). Scanning electron microscopy (SEM) was conducted on a Zeiss Supra 55VP to observe the morphology of the powders. Every sample was sputter coated with Au/Pd before imaging. High-resolution imaging, selected area electron diffraction (ED), and electron energy loss spectroscopy (EELS) were carried out using a scanning transmission electron spectrometer (STEM) (JEOL ARM200F at 80 kV). X-ray spectroscopy (XPS) was performed using mono-chromated Al K alpha (energy 1486.68 eV) as the source. The C1s peak at 284.8 eV was set as the reference. Fourier transform infrared (FTIR)
Spectrometry (Nicolet 6700 Spectrometer) was used to determine the chemical bonds. Thermogravimetric (TG) analysis was conducted on a TA-SDT Q600 instrument. The technique of thermogravimetry-gas chromatography-mass spectrometry (TG-GC-MS: NETZSCH, STA 449 F5; Agilent Technologies 7890B GC System; Agilent Technologies 5977B MSD) was used to determine the mass loss and identity of gaseous compounds released. The UV-visible absorption spectra were obtained using Shimadzu UV-3600 plus spectrophotometer. Photoluminescence data were collected using a Jobin Hvon Flurolog 3 from Horiba, with a Xenon arc lamp as a light source and either PMT or InGaAs detector for visible and NIR collection, respectively. All emissions were normalized against excitation beam intensity and the slit widths were kept constant for each individual sample. Optical images were collected using a digital camera (Nikon D3500), with excitation from a Spectroline CM-10A model ultraviolet (UV) lamp (365 nm excitation) in a dark lab.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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References


A facile method has been developed to produce multicolor BCNO powders with tunable compositions and emissions. When used for anti-counterfeit applications, the BCNO embedded patterns display highly visible patterns under UV illumination, even in harsh environment and in mechanic testing.

Keywords: boron nitride, fluorescent, printing, ink, anti-counterfeit

Fluorescent BCNO powders as printing ink for anti-counterfeit applications