Carbon-doped BN nanosheets for metal-free photoredox catalysis

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The generation of sustainable and stable semiconductors for solar energy conversion by photoredox catalysis, for example, light-induced water splitting and carbon dioxide reduction, is a key challenge of modern materials chemistry. Here we present a simple synthesis of a ternary semiconductor, boron carbon nitride, and show that it can catalyse hydrogen or oxygen evolution from water as well as carbon dioxide reduction under visible light illumination. The ternary B–C–N alloy features a delocalized two-dimensional electron system with sp² carbon incorporated in the h-BN lattice where the bandgap can be adjusted by the amount of incorporated carbon to produce unique functions. Such sustainable photocatalysts made of lightweight elements facilitate the innovative construction of photoredox cascades to utilize solar energy for chemical conversion.

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The use of abundant sunlight to split water into H₂ and O₂ has been considered as the simplest pathway to make clean fuels that can be converted to electricity, for example, in H₂–O₂ fuel cells. Since the report on photocatalytic water splitting in 1972 (ref. 3), a quantum yield of ~56% has been achieved for NiO/NaTaO₃-La at 270 nm for overall water splitting, while for visible light systems a highest quantum yield of ~5% at 420 nm was reported for RhCrO/ZnGaON₂. These studies promise solar fuel production by photocatalysis.

Further progress, however, relies on breakthroughs in the development of stable photocatalysts and co-catalysts, classically based on metals⁶,⁷ (for example, metal oxides, (oxy)nitride and (oxy)sulfides) for light harvesting, together with noble metal co-catalysts (for example, Pt and RuO₂) for driving the two half reactions, water reduction and water oxidation. The two half reactions can be later combined to construct two-photon (Z-scheme) photocatalytic systems to achieve overall water splitting in a cascade fashion⁵, as inspired by the photosynthetic reactions in plants.

Recently, a class of metal-free photocatalysts has been emerged, including elemental boron⁹, sulfur¹⁰ and phosphor¹¹, as well as the binary carbon nitride¹² and boron carbide¹³. These papers indicate that this construction of stable photocatalysts from lightweight and abundant elements is possible and opens up new opportunities for photochemistry. The two-dimensional (2D) character of their electron systems gives further access to partly ‘exotic’ physical properties, as described for graphene¹⁴ and layered hexagonal BN (h-BN)¹⁵–¹⁷. Graphene, the single atomic layer of carbons expresses a zero bandgap, whereas the h-BN possesses a wide bandgap (~5.5 eV). Both materials are therefore, as photocatalyst, not suitable, but intermediates of these layered materials (called ternary BCN compounds) could constitute the desired medium-bandgap semiconductors where bandgap and absolute energy levels can be adjusted by chemical variations¹⁸,¹⁹.

Here we present a facile synthesis method to produce a ternary structure of BCN nanosheets that has a functionality to catalyse hydrogen and oxygen evolution from water as well as CO₂ reduction under visible light illumination.

Results

Theoretical calculations. From density functional theory (DFT) calculations, pure h-BN possesses an indirect bandgap of 4.56 eV (Fig. 1a–c), consistent with the previous theoretical values⁹⁰. This is about 1.00 eV smaller than the experimental value⁷³, due to the well-known limitation of the DFT within GGA method. As shown in Fig. 1g for a ‘B₁₁C₁₂N₉’-compound, the gap is significantly reduced from 4.56 to 2.00 eV. Different from that of pure h-BN (Fig. 1c), the partial density of states indicates that the valence band and conduction band edges of B₁₁C₁₂N₉ are mainly composed of the C 2p orbits (Fig. 1i). Contrary to the localized valence band top of pure h-BN, the valence band top states of B₁₁C₁₂N₉ are more delocalized as displayed in Fig. 1h. Calculation results on the B–C–N alloy with a different composition of ‘B₁₃C₈N₁₁’ are displayed in Fig. 1e,f, and their computational optical absorption was displayed in Supplementary Fig. 1. Similar results on band structure were attained, but with an enlarged gap of 2.90 eV due to the reduced carbon content in h-BN. Clearly, the doping of aromatic carbon into the h-BN lattice narrows its bandgap, making it possible to induce visible light catalysis²⁰,²².

Preparation of BCN-x samples. Doping of graphene with boron and nitrogen is generally performed to open up its bandgap²³, but it is still challenging to keep this process sufficiently controlled.

The adjustment of the carbon doping within h-BN¹⁸ seems to us the more easy access to BCN-based materials with high yield in a controllable manner. Herein, we develop such a carbon-doping
strategy by using a pyrolysis method. In brief, different amounts of glucose were mixed with boron oxide and urea. The mixture was put into a tube furnace in an ammonia atmosphere for 5 h at 1,250 °C (see Methods section for details). The obtained samples were named as BCN-χ, where χ is the glucose weight in per cent of boron oxide.

**Characterization of BCN-χ samples.** Figure 2a shows the X-ray diffraction (XRD) patterns of the prepared samples with different amounts of glucose. Without glucose, the synthesis yielded h-BN showing two characteristic XRD peaks at ~26° and ~43°, attributable to the (002) and (100) planes of the graphitic structure of h-BN, respectively. With glucose, all samples featured XRD peaks similar to those of h-BN, while increasing amounts of glucose broadens the peaks, accompanied by a slight shift of the peak to lower angles. This indicates the doping of carbon in the h-BN lattice, forming ternary B–C–N alloys.

The chemical structure was further characterized with Fourier transform infrared (FT-IR; Supplementary Fig. 2). Two bands observed at 1,380 and 780 cm⁻¹ correspond to the in-plan B–N transverse stretching vibration and the out-of-plan B–N–B bending vibration, respectively. We failed to detect the C–N bonds, which typically overlap with B–N bands around 1,100–1,300 cm⁻¹. 13C solid-state NMR was therefore performed to show the presence of carbon (Fig. 2b). Interestingly, the resonance appears around 125 p.p.m., similar to that of reduced graphene oxide/graphite, which corresponds to sp² carbons with an electron density very similar to graphite. This means that in this BCN alloy the influence of the electronegativity of N and electropositivity of B balance each other out, with the carbon as such being only slightly more electron rich than in graphite. The incorporation of carbon in the h-BN layers smears out Raman signals of h-BN due to the distortion of the layer symmetry. Supplementary Fig. 3 is the X-ray photoelectron spectroscopic (XPS) spectra of the BCN product. The main peak of B1s at 190.4 eV is attributed to B atoms surrounded by N atoms. The subpeaks at 189.9 and 192.3 eV are due to the B–C bond and unreacted B–O, the latter potentially being a surface impurity. The C1s signal at 284.6 eV is due to the graphitic carbon (C=C), while the peaks at 285.7 and 283.5 eV are assigned to C–N bonds and B–C bonds, respectively. The corresponding N-signals for N–B or N–C bands are also observed and located at 397.9 and 398.6 eV (ref. 29). The small subpeak at 400.5 eV reflects N–H bonds, again presumably needed for edge termination and reflecting the reductive ammonia atmosphere. Elemental analysis by XPS (Supplementary Table 1) revealed that the carbon content is gradually increasing with increasing amounts of glucose. Thus, XPS analysis very clearly supports the incorporation of carbon in the h-BN.

Figure 2d displays the electron energy loss spectroscopy (EELS) of the h-BN samples, showing the K-edges of B, C and N. The B- and N-signals of BCN coincide with those of h-BN, reflecting a similar incorporation in layered sp² domains. The sharp doublet C–K (π*) and C–K (σ*) evidence a rather perfect sp²-bonding environment also for the carbon positions. In addition, the carbon doping actually commutatively affects the corresponding B–K, N–K and C–K energies. All data indicate that B, C and N are in a commonly sp²-hybridized, 2D-conjugated electron system, rather than a physical mixture.

Figure 3 depicts transmission electron microscopy (TEM) and STEM images of the BCN-30, and the scanning electron microscopy and energy-dispersive X-ray spectroscopy analyses were presented in Supplementary Fig. 4. A flake-like morphology similar to few-layer-graphene gives evidence that folded BCN layers constitute the structure. High-resolution TEM (inset of Fig. 3a) allows the observation of an interlayer crystal lattice spacing of 3.40 Å. The nanosheets are composed of ~10 stacked layers and have 3–4 nm overall thickness. Such 2D systems with thicknesses below 10 nm are particularly interesting for optoelectrics as the exciton and charge diffusion length is generally in that size range. The selected-area electron diffraction (inset of Supplementary Fig. 5) also suggests that the in-planar order of the sample is polycrystalline, which might reflect that the carbon forms a solid solution or constitutes grain boundaries of BN nanodomains. Element mapping of BCN-30 (Fig. 3b) gave a uniform distribution of B, C and N throughout the whole selected area, proving homogeneity of the ternary BN alloys. This is also proven by the STEM image that clearly displays homogeneous...
The optical absorption of the samples is shown in Fig. 2e. Carbon-free h-BN made as such is a typical insulator with a bandgap of about 5.6 eV (refs 16,21). As shown in Fig. 2f, the optical absorption edge of BCN alloys gradually red-shifts as the amount of carbon increased. From the plot of the transformed Kubelka–Munk function versus light energy, a bandgap of 2.72 eV was estimated for BCN-30. The long absorption tails in the visible however indicates the presence of intraband impurity transitions, potentially located at the surface. Further optimization of the synthesis of high-quality h-BCN alloys is certainly a valuable option. Nevertheless, for a proof-of-concept advance, the optical properties are sufficient to generate electron–hole pairs on h-BCN as confirmed by photoelectrochemical (Supplementary Fig. 7) and electron paramagnetic resonance characterizations (Supplementary Fig. 8a,b). The band positions of the h-BCN is estimated to straddle the water redox potentials, which are however tuneable by the amount of carbon doped (Supplementary Fig. 9). Therefore, we could apply these new semiconductors for the first time for visible light photocatalysis.

Discussion

The photocatalytic performance of BCN samples was assessed by a H₂ evolution assay. H₂ evolution under light was found, while in dark the samples are inactive. The best sample is BCN-30, while hydrogen evolution rate gradually decreases as the carbon content further increases (Supplementary Fig. 10). Excessive amounts of carbon presumably diminish the size of ordered domains and weaken the semiconductor properties, as confirmed by the decrease in the charge-carrier lifetime with excessive carbon doped (Supplementary Fig. 11). It is however a remarkable observation that the BCN alloys could photocatalyse hydrogen generation even without using noble metals as a cocatalyst and even with visible light. Under those conditions, the samples present a quite stable activity (Fig. 4a), but a deactivation was observed when the materials was illuminated with ultraviolet light (Supplementary Fig. 12a).

We also modified BCN with Pt for H₂ evolution, but observed only comparable H₂ production in the range of 0.5–3 wt % Pt (Supplementary Fig. 13). This indicates that the surface of BCN alloys are already rather active, and one can speculate about a pro forma hydride elimination from the boron sites (corresponds to a reversible hydrogenation of a –N≡B-bond) in the catalytic cycle. However, the stability of BCN under strong ultraviolet irradiation is remarkably increased by adding Pt (Supplementary Fig. 12b). We can speculate that the Pt is avoiding the over-reduction of the –N≡B-structure and the consecutive reductive disintegration of the material. The overall production of hydrogen gas amounts to 4,570 μmol in these two-cycle reactions, exceeding the amount of h-BCN (1,342 μmol) and Pt (5.12 μmol). After the reaction, the structure of BCN-30 was stable as reflected by the XRD, FTIR and TEM examinations of the used photocatalyst (Supplementary Fig. 14). The apparent quantum efficiency of BCN-30 was calculated to be 0.54% at 405 nm (Supplementary Table 2) by using equation (1). We also compared the performance of BCN-30 with other photocatalysts, and results show that the activity of BCN-30 is higher than that of TiO₂ (P25) and g-C₃N₄ under visible light (Supplementary Table 3). It is noted that there is not clear relationship between the specific surface area and hydrogen evolution rate of BCN samples (Supplementary Table 4). This is due to the fact that in most solid–liquid phase photocatalysis the reaction rate is basically limited by charge separation instead of mass transfer.

The H₂ generation from water is pleasing, but it constitutes only the minor half of the problem of water splitting. The other half-reaction, the oxygen evolution reaction, is particularly
visible light, and with ultraviolet light the experiment gave 35 μmol O₂ (Supplementary Fig. 16).

These results indicate that the band positions of h-BCN are correctly positioned for water splitting, that is, the Ni-Co LDH is able to take up the photogenerated holes and evolves O₂. The decrease in activity with reaction time is primarily due to the deposition of metallic silver at the catalyst surface, which blocks light absorption and obstructs active sites. Further optimization of the O₂ evolution system is thus certainly needed as the found activity is only moderate.

Having a very reductive photoelectron however allows to address the direct photochemical conversion of CO₂ (ref. 32). We therefore expanded in a last experiment the application of h-BCN to the photocatalytic reduction of CO₂ to CO (Fig. 4e) using visible light (λ > 420 nm). On irradiation for 2 h, the system evolved CO (9.3 μmol) and H₂ (2.9 μmol). A prolonged operation of the photochemical system gave a gradual increase in both CO and H₂ evolutions in a linear fashion. Isotopic experiments confirmed the carbon source of the produced ¹³CO is ¹³CO₂ (Supplementary Fig. 17).

In summary, we introduced here a novel and simple way of carbon doping of h-BN nanosheets to generate ternary BCN alloys as sustainable and stable visible light photocatalysts. Water splitting in the elements as well as CO₂ reduction was proven to be possible. This new photocatalyst features a 2D electron system and tuneable bulk and surface properties, and further structural optimizations can be expected that may facilitate innovations and applications in the fields from artificial photosynthesis to graphene-like semiconductors, as well as organocatalysis.

**Methods**

**Synthesis of BCN-x.** Typically, boron oxide (2 g), urea (4 g) and a certain amount of glucose were grinded fully with an agate mortar. After that, mixed precursor was put into a horizontal tube furnace. Before heating up, it costs nearly 30 min to expel the whole oxygen in the tube and the sample was then heated to 1,250 °C for 5 h. The obtained products were washed with 0.1 M HCl in hot water. The resulting final sample was denoted as BCN-x, where x (20, 30, 40, 70) is the percentage weight content of glucose to boron oxide. When the glucose was omitted, the synthesized sample was named h-BN.

**Synthesis of Ni-Co LDHs/BCN-30.** Co(NO₃)₂·6H₂O (0.2 g), Ni(NO₃)₂·6H₂O (0.1 g) and NH₄NO₃ (0.04 g) were dissolved in H₂O (3.5 ml) and 30 wt% ammonia (1.5 ml) to form clear solution, named as Ni-Co LDHs. 200 mg BCN-30 powder was dispersed in water (20 ml), which was then subject to ultrasonic treatment for 10 min to promote the dispersion of BCN-30 in the solution. A certain amount of the Ni-Co LDHs solution (400 μl) was added to the mixture. After stirring for 3 h, the mixture was washed by filtering with distilled water and dried at 343 K to obtain Ni-Co LDHs/BCN-30.

**Characterization.** Powder XRD patterns were collected on Bruker D8 Advance diffractometer with Cu-Kα radiation (λ = 1.5406 Å). Data were collected with a rate of 0.02°·s⁻¹ in the range of 10 to 60°. The FT-IR spectra were obtained on a Nicolet 670 FT-IR spectrometer with KBr as the diluents. To get smooth spectra, the final results were registered after accumulation of 108 scans and a resolution of 4 cm⁻¹. XP spectra were accomplished on an ESCALAB 250 (Thermo Scientific, USA) by using a monochromatized Al Kα line source (200 W). Solid-state ¹³C MAS NMR experiments were conducted on a spectrometer (Bruker Avance III-400WB) equipped with a 4-mm ZrO₂ rotor probe at a 5 kHz spinning rate for ¹³C nuclei. The direct ¹³C-polarization spectrum was acquired with a 90° pulse of 5 μs for a pulse repetition delay of 2 s for 2,048 scans. The ¹³C spectrum was referenced to tetramethylsilane at 0 p.p.m. using adamantane as an external reference. Raman spectroscopic measurements were performed on a Renishaw in Via Raman System 1000 with a 532 nm Nd:YAG excitation source at room temperature. The UV/Vis picture was recorded on a Cary 500 Scan Spectrophotometer (Varian, USA).

Here BaSO₄ was used as a reflectance standard in the ultraviolet–visible diffuse reflectance experiment. Nitrogen adsorption–desorption isotherms were collected at 77 K using a Micromeritics ASAP 2020 surface area and porosity analyser. Thermogravimetric analysis was performed on TG209 (NETZSCH Co.). Photoluminescence spectra were recorded on an Edinburgh FI/FST/CSPC 920 spectrophotometer. The morphology of the sample and energy-dispersive X-ray spectroscopy were investigated by Hitachi S4800 field emission scanning electron microscopy. TEM was operated by Tecnai20 FEG microscope. The elemental
mapping, and selected-area electron diffraction were also collected on the TEM. In the synthetic section, it possessed 5 h to reaction under high temperature. Maybe in the early reaction section, the C, B, N can group freely, but in the compound. In our synthetic section, it possessed 5 h to reaction under high temperature. At present, there is a great controversy of the BCN structure. Some argue the possible structure of the BCN was constructed based on our experimental results.

Photocatalytic reaction for water reduction and oxidation. Reactions were experimented with a Pyrex top irradiation reactor connected to a glass closed gas-circulation system. Photoreduction to H2 and photocatalysis to O2 were performed separately in aqueous solutions containing triethanolamine or silver nitrate as sacrificial reagents, respectively. To study the H2 production ability, 50 mg catalyst was dispersed into 100 ml aqueous containing triethanolamine solution (10 vol%). In the cell, a Pt cathode (0.5 cm) was employed to the anode, whereas for electronic properties calculations, the Brillouin zone was sampled by 9 × 9 × 1 k-points. In addition, to avoid the interlayer interactions, a vacuum spacing in the z direction was set to be 14 Å. Here the possible structure of the BCN was constructed based on our experimental section. At present, there is a great controversy of the BCN structure. Some argue that the BN and C present independent just like a carbon island or BN island while other think the C is a part of the BN, which means that there is a C–B or C–N bond in the compound. In our synthetic section, it possessed 5 h to reaction under high temperature. Maybe in the early reaction section, the C, B, N can group freely, but in the compound. It’s already testified that the bonding energies of C–C and B–N bonds is comparatively higher than that of other hetero bonds present in the ternary system, consequently, the hybrid systems will be domain-separated into two different regions, one with C-rich domain and other with BN-enriched domain, to gain thermodynamic stability. Fortunately, our results are coincided with this common sense. So, we build the possible structures like above.

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Author contributions
X.W. conceived and designed the experiments. C.H., C.C. and M.Z. synthesized the experimental samples and carried out the experiments of XRD, NMR, XPS, BET, FT-IR, EPR, Raman, DRS, SEM, EDX, TEM, SAED, TG, photo-current and photocatalytic hydrogen production. M.Z. performed photocatalytic oxygen production experiments. C.C. carried out CO2 reduction experiments. L.L. conducted the experiment of electrochemical analyses and the measurement of the quantum yield of the samples. C.H. and L.L. carried out Pl. experiment. X.W. and C.H. performed EELS and STEM experiments. S.L. and X.Y. worked on all theoretical calculations. M. A. participated in the scientific discussion on the experimental results. All the authors discussed the results and wrote the manuscript.

Additional information
Supplementary Information accompanies this paper at http://www.nature.com/naturecommunications

Competing financial interests: The authors declare no competing financial interests.

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