Electronic Supplementary Information

Molten Salt Assisted Assembly Growth of Atomically Thin Boron Carbon Nitride Nanosheets for Photocatalytic H_2 Evolution

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Experimental Section

Synthesis of BCNNS: Boron oxide, melamine and glucose (1:2:7 by weight) were firstly ground with hybrid salts NaCl/KCl (45:55 by weight) to obtain a fine powder mixture. Subsequently, the mixture was annealed at 1250 °C for 5 h under an ammonia flow (250 $mL \cdot min^{-1}$) to fabricate the BCNNS. Before heating up, it costs nearly 30 min to expel the air in the tube by ammonia flow. The fluffy product can be used for characterizations and performance tests without any post-treatment. Three samples were prepared using this method with different weight ratios of hybrid salts to B_2O_3 ($Salts/B_2O_3 = x$), and denoted as BCNNS-x (x = 10, 20, 100).

Synthesis of bulk BCN: For comparison, bulk BCN sample was synthesized under the same condition, but without adding the hybrid salts.

Synthesis of BNNS: Boric acid (0.1 g) was firstly ground with hybrid salts NaCl/KCl (45:55 by weight, 10 g) until a fine powder was obtained. Subsequently, the mixture was annealed at 1250 °C for 5 h under an ammonia flow (250 $mL \cdot min^{-1}$), producing the boron nitride nanosheets (BNNS).

Synthesis of G: Glucose (0.1 g) was firstly ground with hybrid salts NaCl/KCl (45:55 by weight, 10 g) until a fine powder was achieved. Afterward, the mixture was annealed at 1250 °C for 5 h under a nitrogen flow (250 mL·min^{-1}), yielding the graphene (G) nanosheets.

Characterization: The morphology of the samples was studied using field emission scanning electron microscopy (SEM, JSM-6700F), transmission electron microscopy (TEM, Tecnai G2F20), atomic force microscopy (AFM, Agilent 5500). X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance diffractometer with Cu K_{a1} radiation (λ = 1.5406 Å). The Fourier transformed infrared (FT-IR) spectra were acquired on a Nicolet 670 FT-IR spectrometer with KBr as the diluents. X-ray photoelectron spectroscopy (XPS) data were obtained on Thermo Scientific Escalab 250 instrument with a monochromatic Al Kα source. The UV/Vis diffuse reflectance spectra (DRS) were collected on a Varian Cary 500 Scan UV/Vis system. Room temperature photoluminescence (PL) spectra were conducted on an Edinburgh FI/FSTCSPC 920 spectrophotometer. Photocurrent response tests were taken on A BAS Epsilon Electrochemical System and performed on a traditional three-electrode system. Fluorine-tin oxide (FTO) glass was used as the conductive substrate to prepare the working electrode. Typically, the as-obtained product (5 mg) was dispersed in 1mL DMF by sonication. Then, the slurry (10 µL) was dropped onto the FTO glass with an area of ~ 0.25 cm^2. The transient photocurrent response spectra were collected in Na_2SO_4 aqueous solution (0.2 M) under the irradiation with a 300 W xenon lamp ($\lambda \geq$ 420 nm), and the applied bias potential was -0.4 V vs Ag/AgCl (pH = 6.8).

Photocatalytic tests: Reactions were carried out in a Pyrex top-irradiation reaction vessel connected to a closed glass gas system. H_2 production was performed by dispersing catalyst powders (50 mg) in an aqueous solution (100 mL) containing triethanolamine (10 vol. %) as sacrificial electron donor. Co-catalyst Pt nanoparticles were deposited on photocatalysts by an in-situ photodeposition method, where 1wt. % (respect to Pt atoms) $H_2PtCl_6 \cdot 6H_2O$ was added and well distributed in the reaction solution. The reaction solution was evacuated several times to remove air completely prior to irradiation under a 300 W Xeon-lamp with a water filter. The wavelength of incident light was controlled by applying appropriate long-pass cut-off filters. The temperature of the reaction solution was maintained at 10 °C by a flow of cooling water during the reaction. The evolved gases were analyzed by an online gas chromatography equipped with a thermal conductive detector (TCD) and a 5Å molecular sieve column, using Argon as the carrier gas.

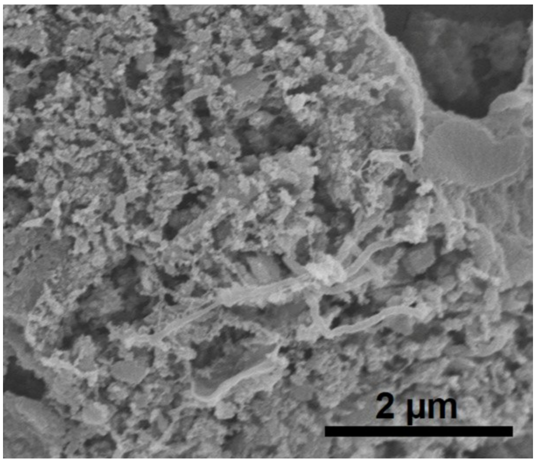

Fig. S1. SEM image of BCN nanoparticles exfoliated from bulk BCN through a liquid phase exfoliation method. In a typical synthesis, 20 mg of as-prepared bulk BCN powders and 10 mL of water were added into a flask (30 mL in capacity). The sealed flask was sonicated for 6 h, and then mixture was centrifuged at 3000 rpm for 10 min to get the products.

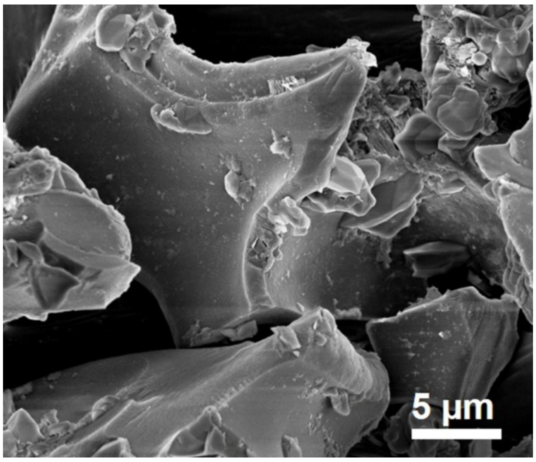

Fig. S2. SEM image of bulk BCN.

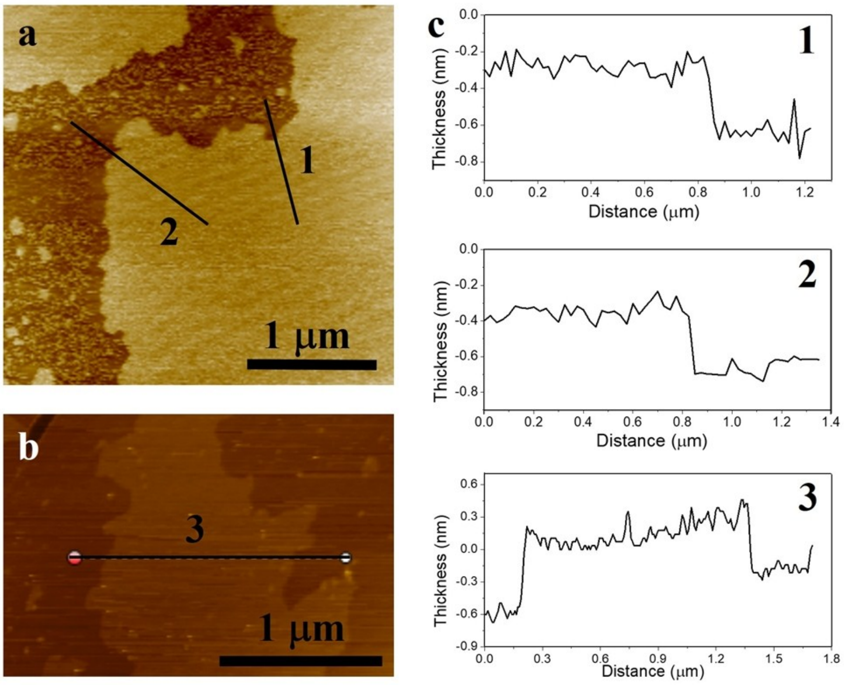

Fig. S3. AFM images of BCNNS-100 in different areas and the corresponding height profile. The numbers of 1, 2 and 3 in (c) correspond to the numbers from 1, 2 and 3 in (a) and (b). AFM images clearly show a smooth sheet with a similar thickness of approximately 0.4 nm.

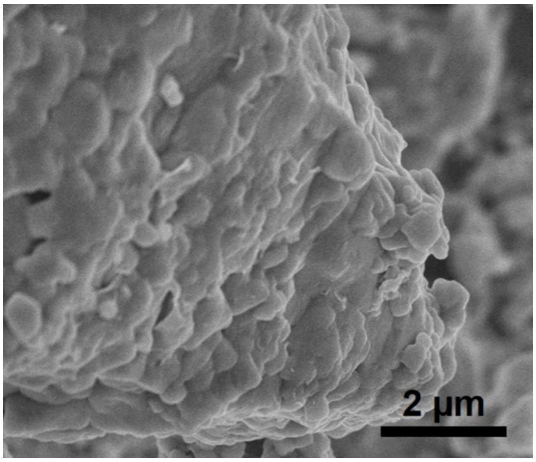

Fig. S4. SEM image of BCNNS/Salts mixture. Boron oxide, melamine and glucose (1:2:7 by weight) were firstly ground with hybrid salts NaCl/KCl (45:55 by weight) until a fine powder was obtained. The salts-to-boron oxide ratio is 100. Then, the mixture was annealed at 950 ^{o}C for 5 hours under an ammonia flow (250 mL·min^{-1}) to produce the BCNNS/Salts mixture. The low temperature (< 1000 ^{o}C) is to prevent the drastic volatilization of the salts.

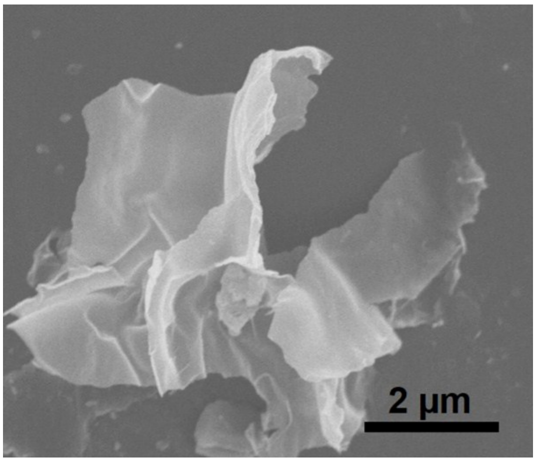

Fig. S5. SEM images of BCNNS after washing the BCNNS/Salts mixture by water to remove the salts.

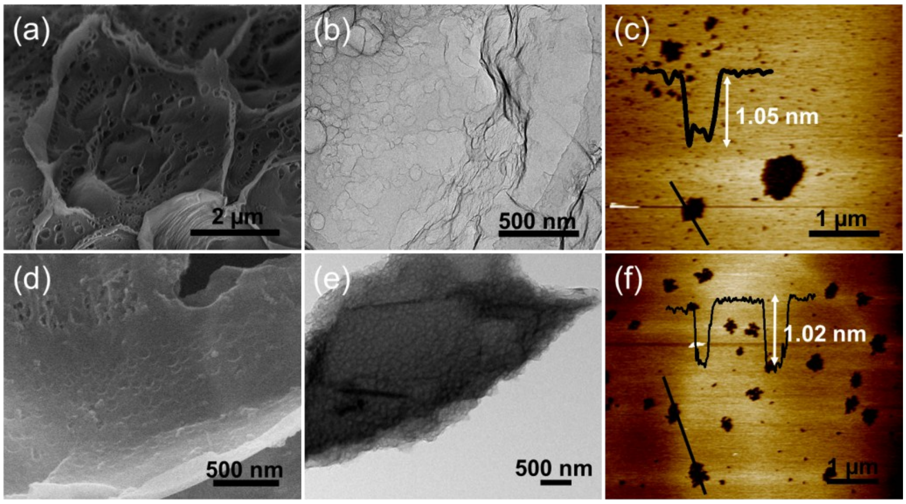

Fig. S6. (a,d) Typical SEM images, (b,e) TEM images and (c,f) AFM images of (a-c) BCNNS-20 and (d-f) BCNNS-10. The insets in AFM images are the corresponding thickness curves determined along the lines.

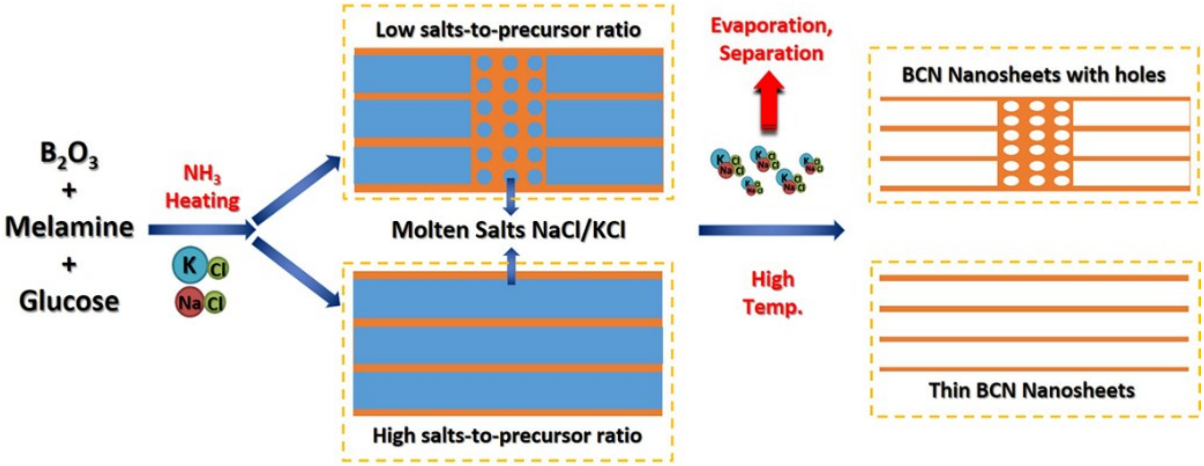

Fig. S7. Synthetic procedures for BCN nanosheets in a eutectic NaCl/KCl salt melt medium with low salts-to-precursor ratio.

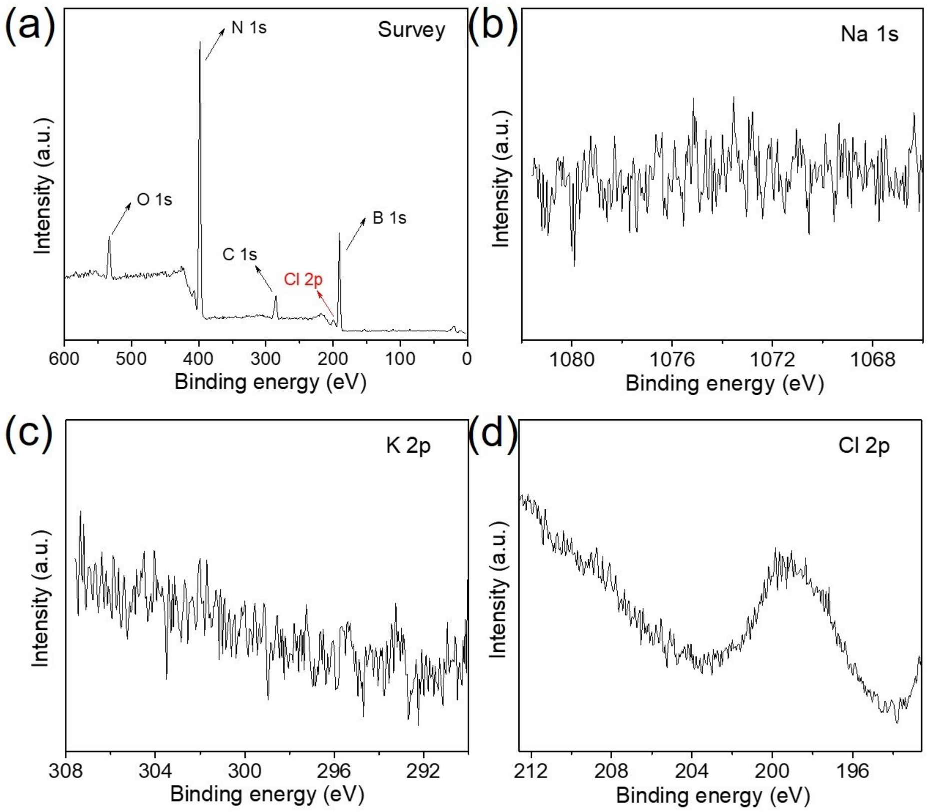

Fig. S8. XPS spectra of (a) the survey spectrum and (b) Na 1s, (c) K 2p, and (d) Cl 2p peaks for BCNNS-100.

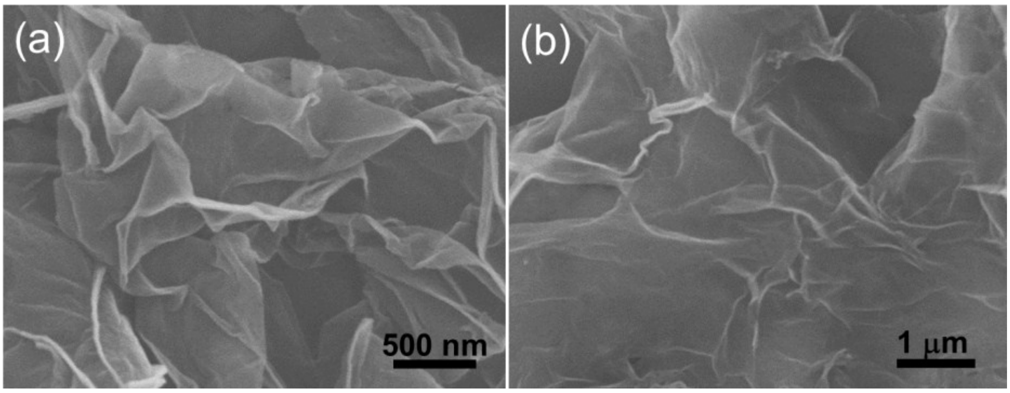

Fig. S9. Typical SEM images of (a) BNNS and (b) G.

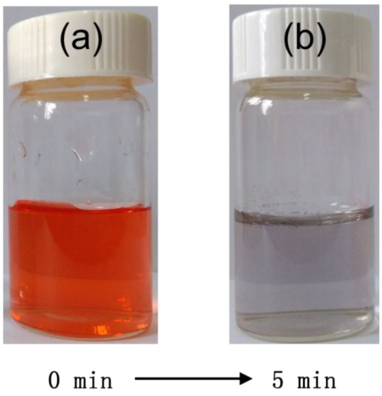

Fig. S10. The adsorption of Congo red (CR) on graphene powder. In a typical adsorption of CR experiment, 1 mg of G powder was added to 10 mL CR aqueous solution (10 mg·L^{-1}) under stirring. The photographs of CR aqueous solution (a) before and (b) after adsorption by G for about 5 min.

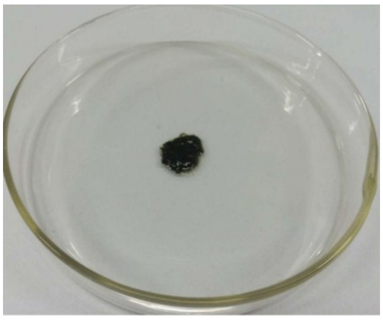

Fig. S11. The photograph of pump oil-saturated G. 1 mg G powder can absorb about 6.5 g pump oil.

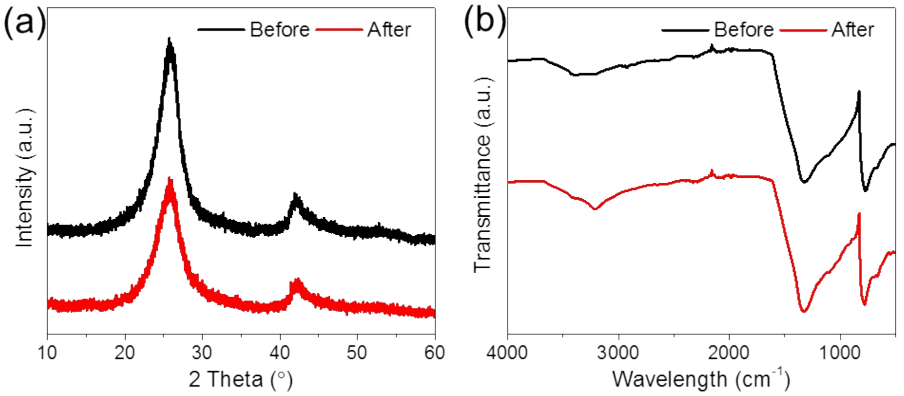

Fig. S12. (a) Powder XRD patterns and (b) FT-IR spectra of BCNNS-20 sample before and after the photocatalytic H_2 evolution reactions.