

Supporting Information

Crystalline borophene quantum dots and their derivative boron nanospheres

Huiqi Wang, *^a Duo An,^a Mei Wang,^a Liwen Sun,^a Ying Li,^a Hairu Li,^a Ning Li,^a Shengliang

Hu, *^a Yan-Bing He *^b

^a *School of Energy and Power Engineering & School of Materials Science and Engineering, North University of China, Taiyuan 030051, P. R. China*

^b *Shenzhen Geim Graphene Center, Tsinghua Shenzhen International Graduate School, Tsinghua University, Shenzhen, 518055, P. R. China*

**corresponding author:*

E-mail: hqiwang@nuc.edu.cn (H. Wang);

hshiang@yeah.net (S. Hu);

he.yanbing@sz.tsinghua.edu.cn

Samples preparation

All of the chemicals were used without purification. First, 50 mg bulk boron powder (99.99 %) was dissolved into 30 mL isopropyl alcohol (IPA) by an ultrasonic concussion to form a clear solution. Then, 20 mg H₃BO₃ powder (99.998 %) was added into the solution and stirred for 10 h until completely dissolved. Next, 2 mL H₂O₂ (30 %) solution was dropwise added in the above solution. The resultant solution was vigorously stirred for 5 h at ambient condition. The product was ultrasonically dispersed in 50 mL IPA solution using a high-power probe-type ultrasonic crusher (900 W, 4 s ultrasonication and 6 s pause), and the temperature was always kept at about 5 °C. After 5 h ultrasonication, the product was centrifugated at a speed of 2000 rpm for 1 h and the supernatant was dialyzed. The obtained powder was denoted B-QDs. 5 mg B-QDs powder was ultrasonically dispersed in 30 mL IPA solution, and then different volumes of hydrazine hydrate (HHA) were added into the resultant solution and continued to stir for 5

h. The product was centrifugated at a speed of 10000 rpm for 30 min and the precipitate was washed for three times and dried in a vacuum. Finally, the derivative boron nanospheres (DBS) were prepared. Further, the obtained DBS was calcined at 500 °C for 1 h under argon atmosphere.

Characterizations

TEM and HRTEM images were obtained on a JEM-2010F transmission electron microscopy at an accelerating voltage of 200 kV, along with EDX mapping. SEM images were taken using a JSM-7900F field-emission scanning electron microscopy (FE-SEM). The XRD patterns was obtained on a Bruker AXS D8X-ray diffractometer. Raman spectra were recorded on inVia (Renishaw) instrument with a 532 nm Ar-ion laser. XPS measurements were performed on Thermo Fisher Scientific spectrometer using an Al-K α radiation. Fourier transform infrared (FT-IR) spectra were determined on a Nicolet 6700 FTIR spectrophotometer. The ^{11}B MAS spectra were detected on a Bruker AVANCE NEO 400 WB spectrometer equipped with a 4 mm standard bore CP MAS probe head whose X channel was tuned to 128.39 MHz for ^{11}B , using a magnetic field of 9.39T at 297 K. The dried and finely powdered samples were packed in the ZrO $_2$ rotor closed with Kel-F cap which were spun at 12 kHz rate. A total of 1000 scans were recorded with 2 s recycle delay for each sample. All ^{11}B MAS chemical shifts are referenced to the resonances of boron nitride (BN), 99.5% (metals basis) standard ($\delta=0.00$). Fluorescence spectroscopy were collected on a Hitachi F4500 fluorescence spectrophotometer. The absorbance was carried out on a Shimadzu UV-2550 UV-vis spectrometer.

Supplementary Figures:

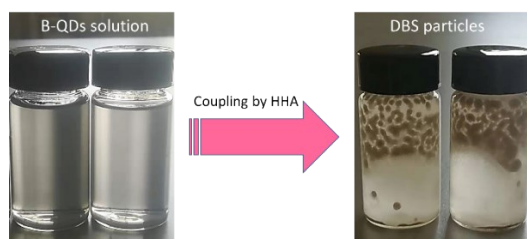


Fig. S1 A state change of B-QDs solution observed after adding the HHA.

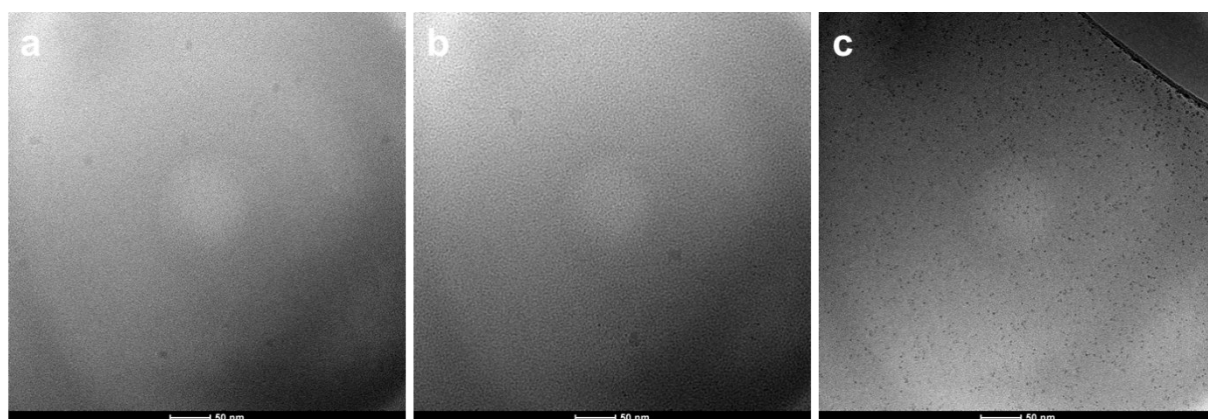


Fig. S2 TEM images of as-fabricated samples in a similar method (a) except boron powder, (b) except boric acid, and (c) including boron powder and boric acid.

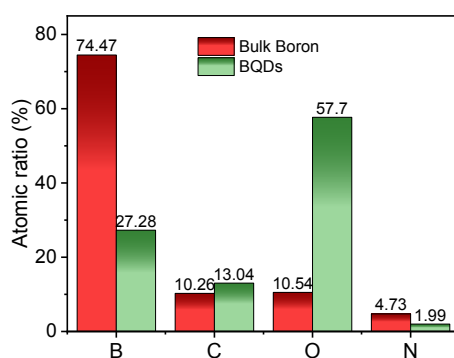


Fig. S3 The corresponding atomic ratios according to the binding energy shown in Fig. 2g.

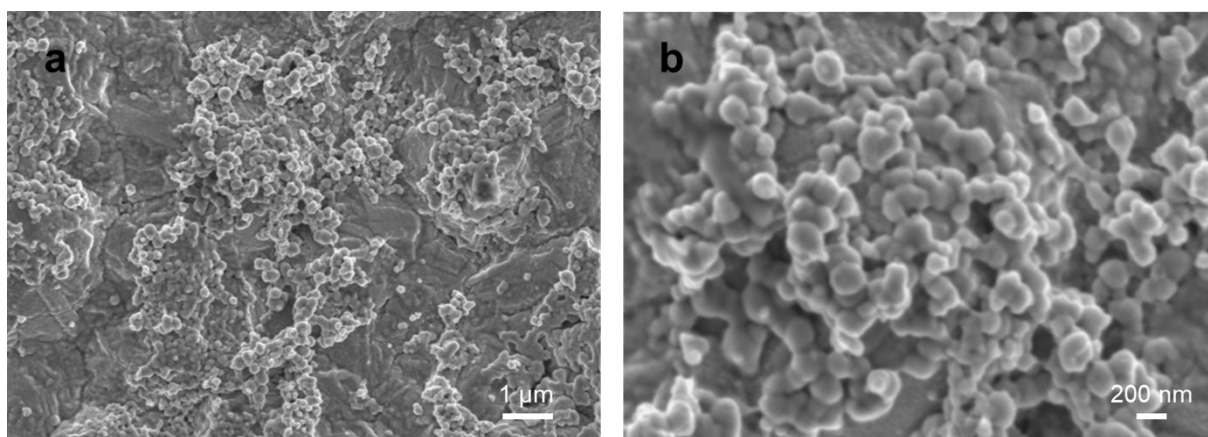


Fig. S4 SEM images with different magnifications of the obtained DBS particles.

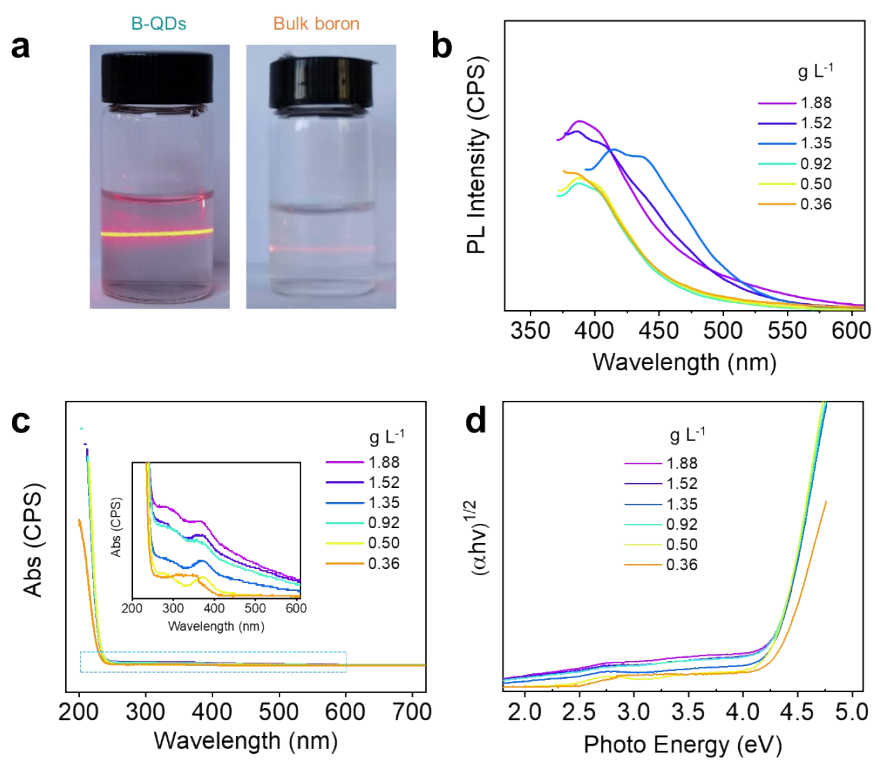


Fig. S5 (a) Photograph of B-QDs dispersed in IPA solution under ambient light irradiation after 60 days. (b) B-QDs concentration-dependant PL spectra excited by a 325 nm laser. (c) UV-vis spectra of B-QDs with different concentrations. (d) $(\alpha h\nu)^2$ as a function of $h\nu$ for band gap determination.

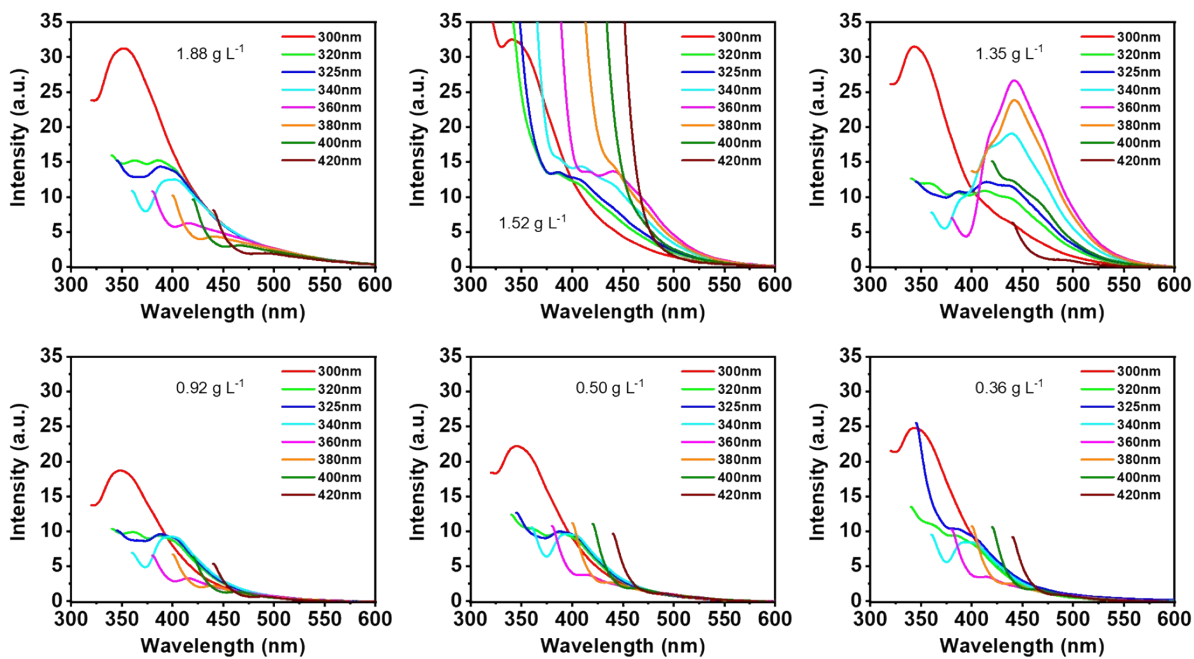


Fig. S6 PL spectra of the B-QDs with different concentrations excited at various wavelengths.