

Supporting information

Synthesis of monolayer hexagonal boron nitride on Cu foil using chemical vapor deposition

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Method

***h*-BN growth procedure.** The borazane powder is contained in a ZrO₂ boat inside a small quartz tube to prevent it from flowing away during vacuum pumping. In a typical growth, the first heating zone is ramped up to $T_1 = 60 \sim 90$ °C with a heating belt to produce the BN precursor. The on-off valve between the first and second heating zone is closed most of the time, except during the CVD, to prevent undesired growth. The second heating zone is heated up to $T_2 = 1000$ °C for typically 10 ~ 90 min under 10 sccm hydrogen atmosphere with a pressure of 350 mTorr after mounting the copper foil. Copper foil (25 μ m, Alfa Aesar) was used as the metal catalyst substrate. Before growth of *h*-BN, the copper foil was annealed at 1000 °C for 20 min under 10 sccm H₂ to grow the copper grain and to obtain a smooth surface.

Graphene growth procedure. Graphene was synthesized by low pressure chemical vapor deposition using a copper foil (25 μ m, Alfa Aesar) as a catalytic metal substrate. Before graphene growth, the copper foil was annealed at 1000 °C for 30 min under a 10 sccm hydrogen atmosphere (~ 330 mTorr) to increase the grain size and to ensure the growth of a smooth surface, followed by synthesizing graphene under 15 sccm and 50 sccm of methane and hydrogen atmospheres for 40 min (~1.5 Torr) while maintaining the same temperature. During cooling the chamber, 10 sccm of hydrogen was flowed until room temperature was reached.

Transfer. After the growth, both *h*-BN and graphene were transferred with the same method. Poly(methyl methacrylate) (PMMA) (4.5 % in anisole) was spun on the sample with 2,500 rpm for 1 min, followed by etching copper with copper etchant (CE-100, Transene). The film of PMMA/*h*-BN was washed by DI water to remove the residual copper etchant. To remove the residual iron particles which came from the copper etchant (FeCl₃), the film was floated on 10 % HCl for 20 min, followed by neutralizing with deionized water. After the PMMA/*h*-BN film was transferred onto either SiO₂/Si or quantifoil TEM grid (2.5 μ m hole, Tel Pella), PMMA was removed by acetone vapor and thermal annealing at 450 °C for 2 hrs under an H₂/Ar atmosphere.

Characterization. A TEM (JEOL 2010) instrument equipped with electron energy loss spectroscopy (EELS) and selective area electron diffraction (SAED) was used to characterize the structure and chemical properties of *h*-BN. The surface morphology of the copper foil and *h*-BN was examined by atomic force microscopy (Dimension 3100, Veeco). X-ray photoelectron spectroscopy (XPS) characterized the chemical composition of the boron and nitrogen constituents of *h*-BN. To observe the surface morphology, high resolution field emission scanning electron microscopy (HRSEM, SUPRA™ 40, Zeiss) was used. Optical absorption spectra of the samples were obtained by using a Varian Cary 500i instrument.

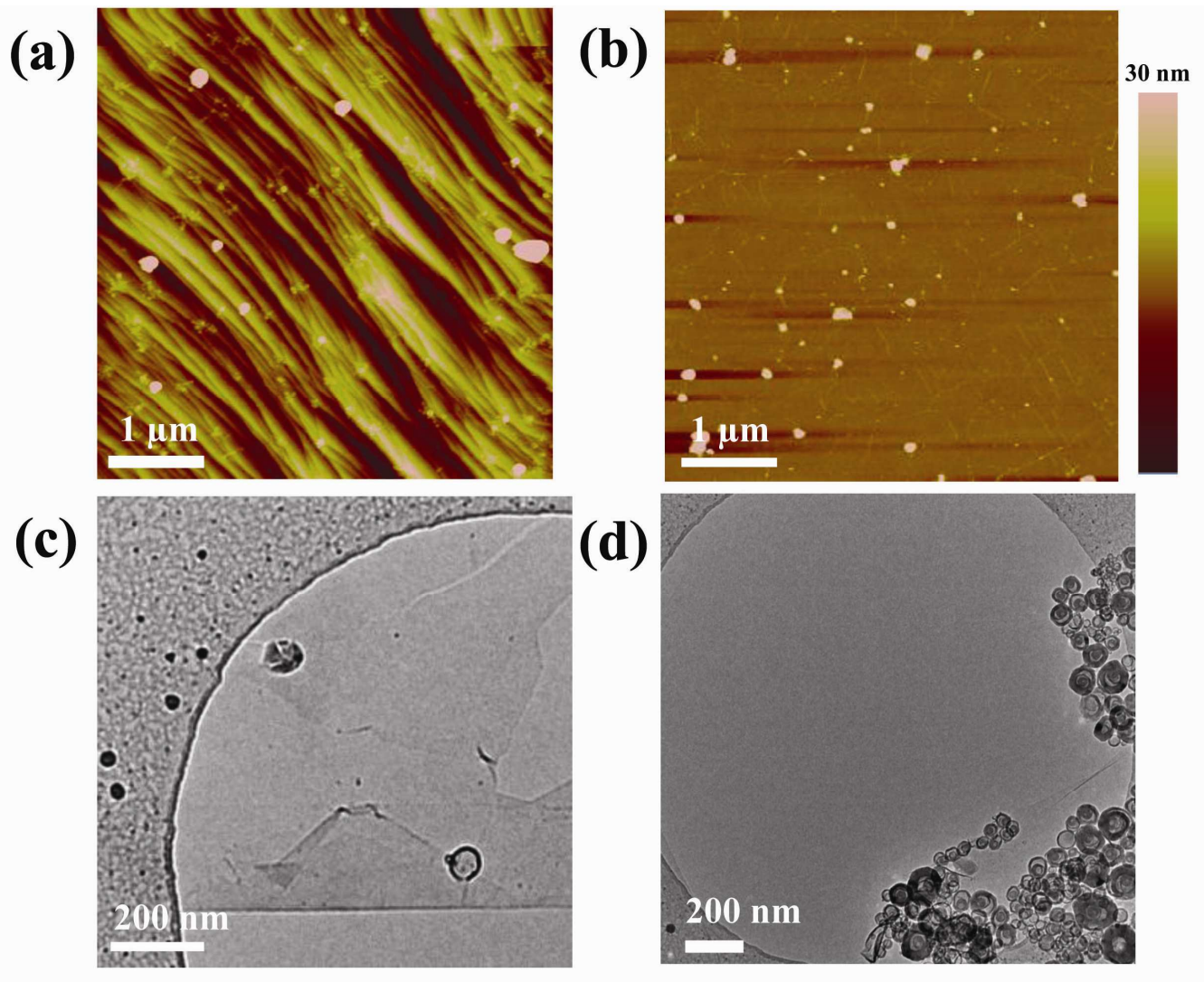


Figure S1. AFM images of (a) as grown *h*-BN and (b) transferred *h*-BN on SiO_2/Si with a carrier gas flowing through T_1 zone. (c) and (d) TEM images of these *h*-BN films with hollow BN nanospheres.

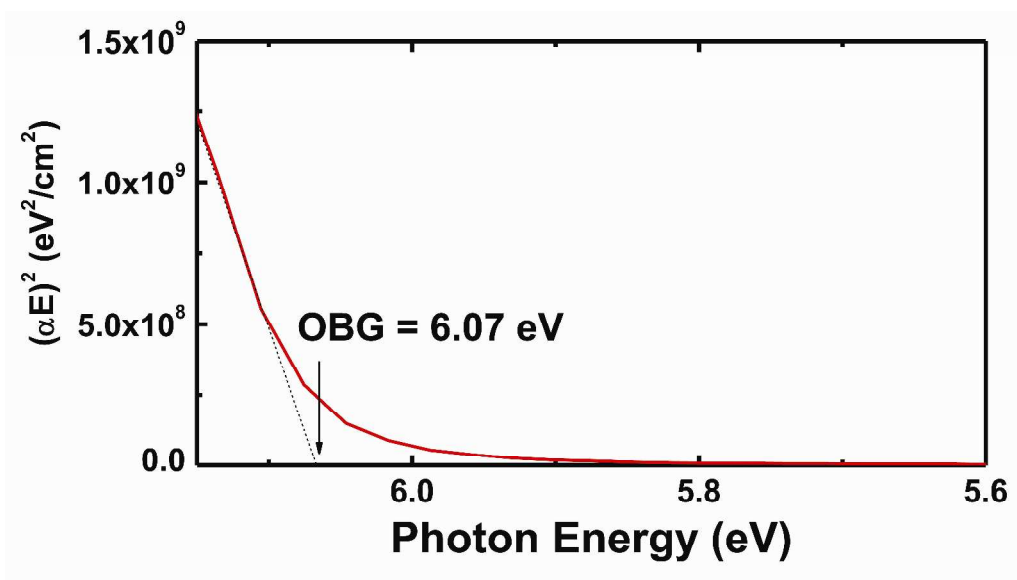


Figure S2. Optical bandgap (OBG) of monolayer *h*-BN derived from the absorption spectra.

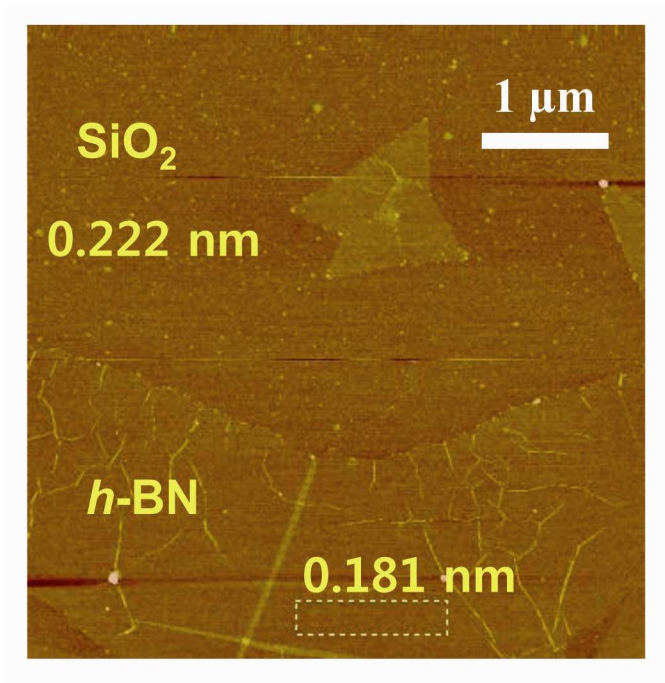


Figure S3. Surface roughness comparison of *h*-BN on a SiO_2/Si , and the SiO_2/Si substrate.

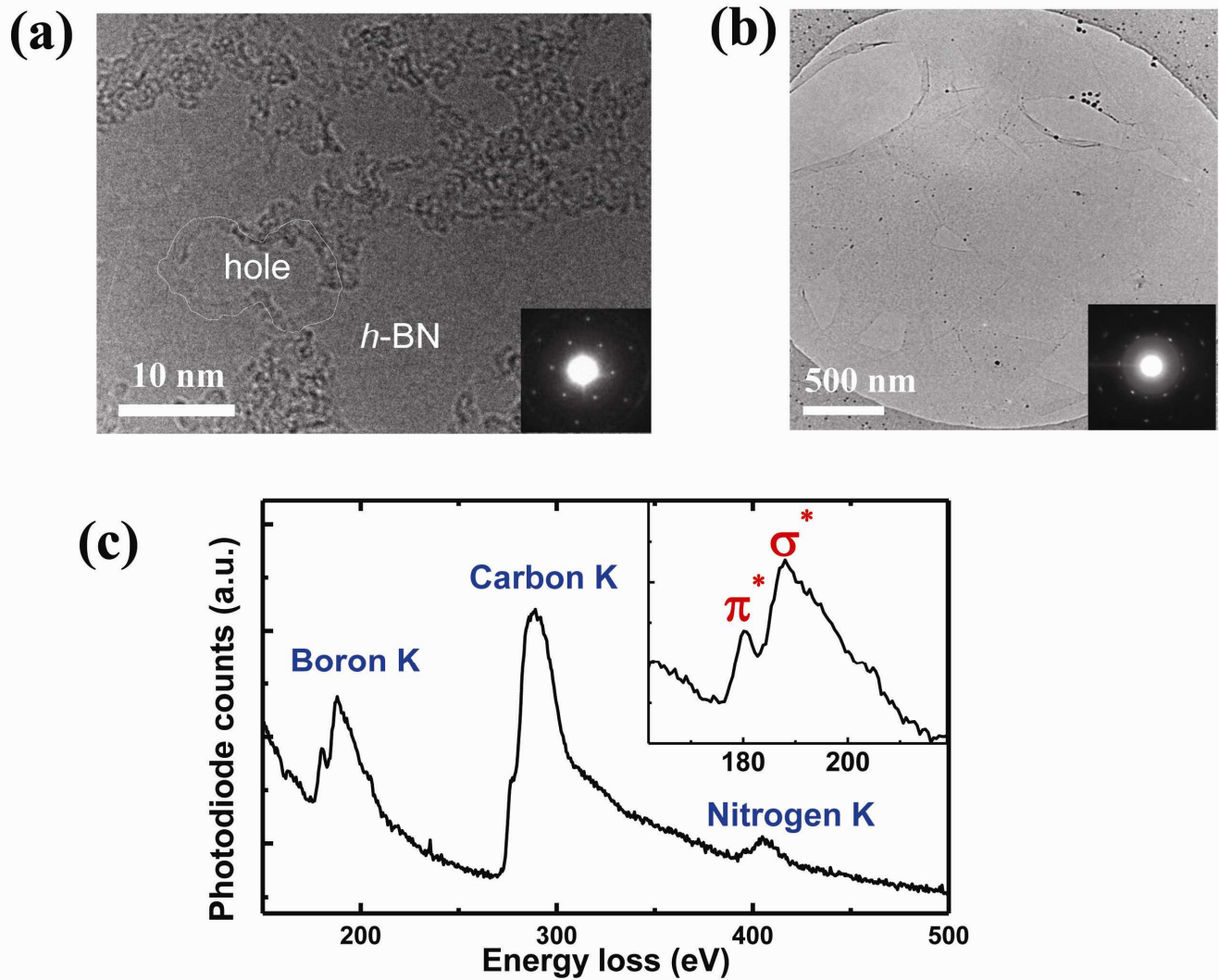


Figure S4. TEM images of *h*-BN with (a) small (1600nm^2) and (b) large ($4\mu\text{m}^2$) regions. The insets in (a) and (b) are the SAED within each area. From the edges of the hole in (a), we can see that the *h*-BN film is monolayer (as shown in Fig 2c). (c) The core-loss spectra of the *h*-BN film from EELS measurement, which has three distinct visible peaks of 180, 280, and 390 eV, corresponding to the characteristic K-shell edges of B, C, and N, respectively. Inset shows the enlargement of the boron core level spectra, indicating that *h*-BN has sp^2 hybridization bonding.

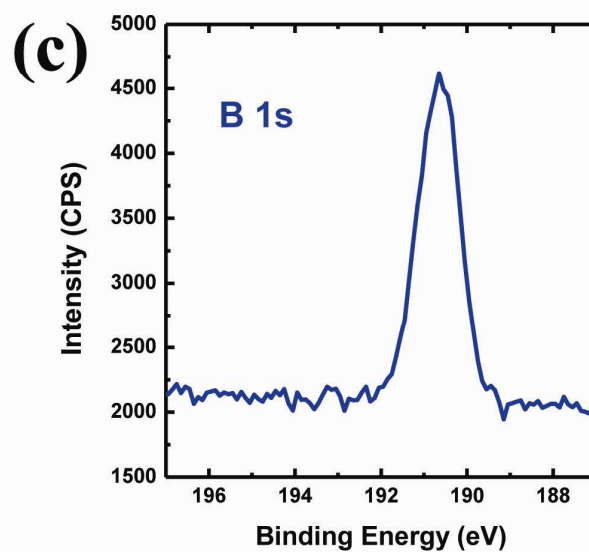
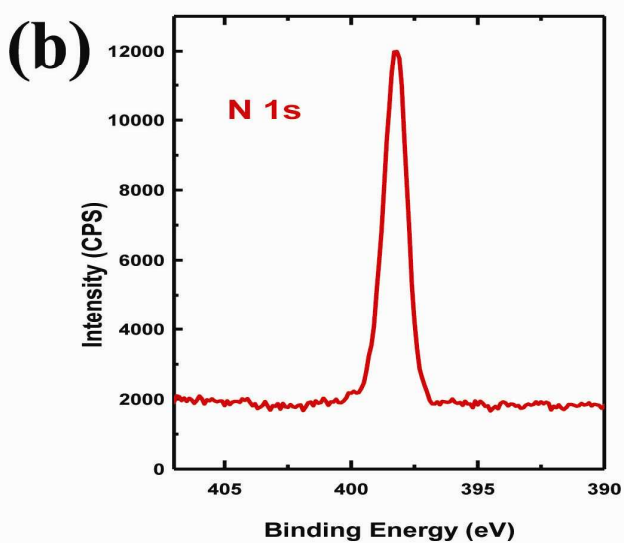
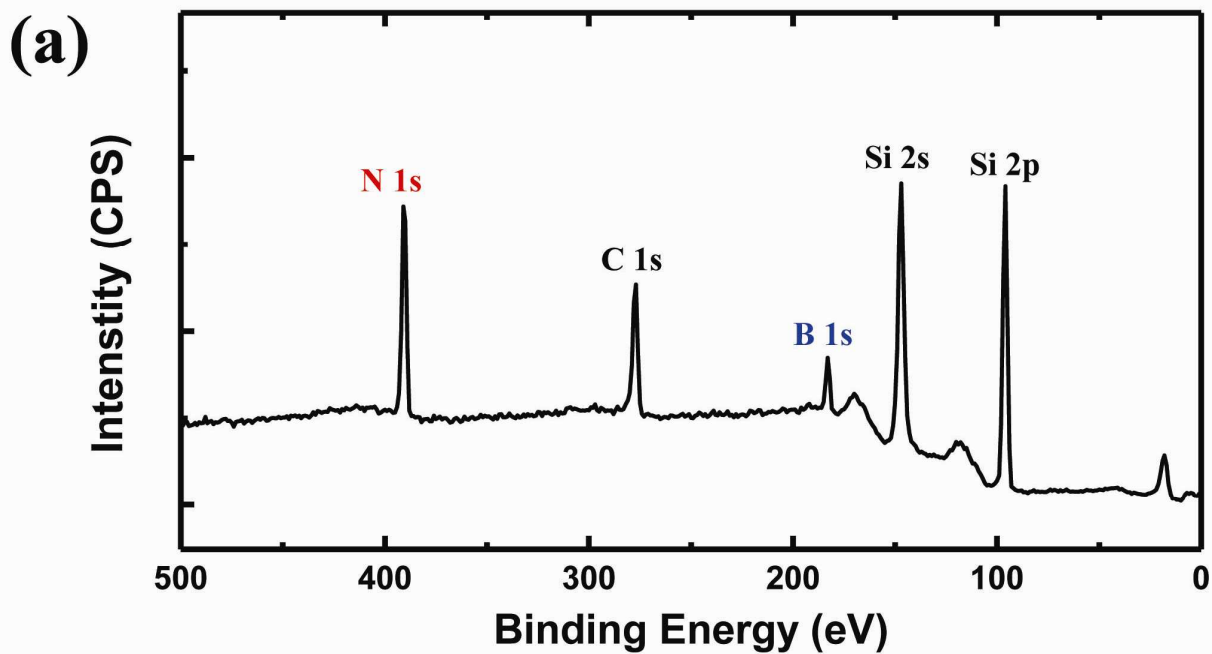


Figure S5. XPS spectra of *h*-BN on a SiO₂/Si substrate. (a) Survey spectra, (b) N1s spectra, and (c) B1s spectra of the *h*-BN sample.

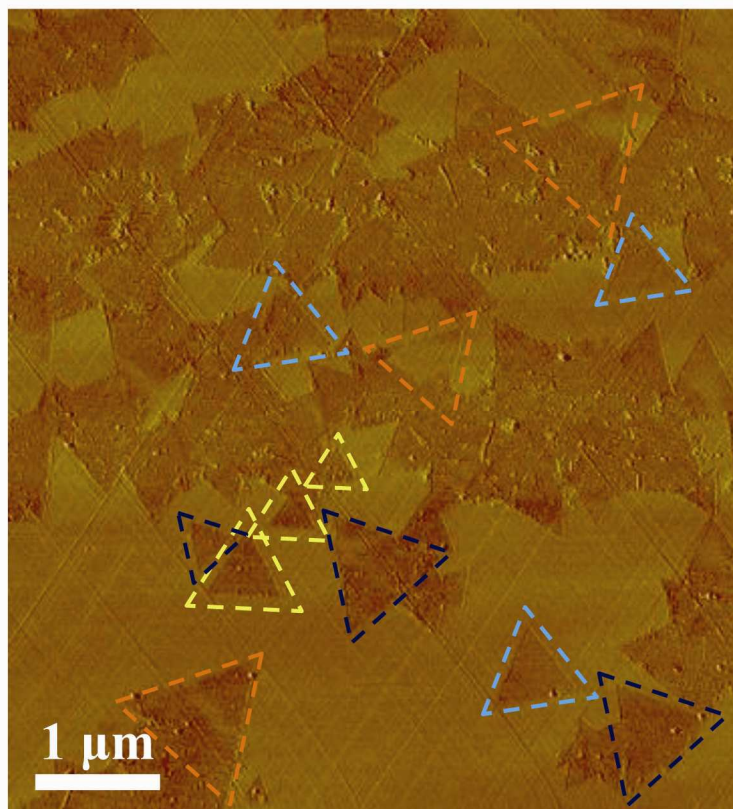


Figure S6. Orientation of *h*-BN triangular islands on copper surface. Some islands have similar orientations, and are outlined by the triangles with the same color.

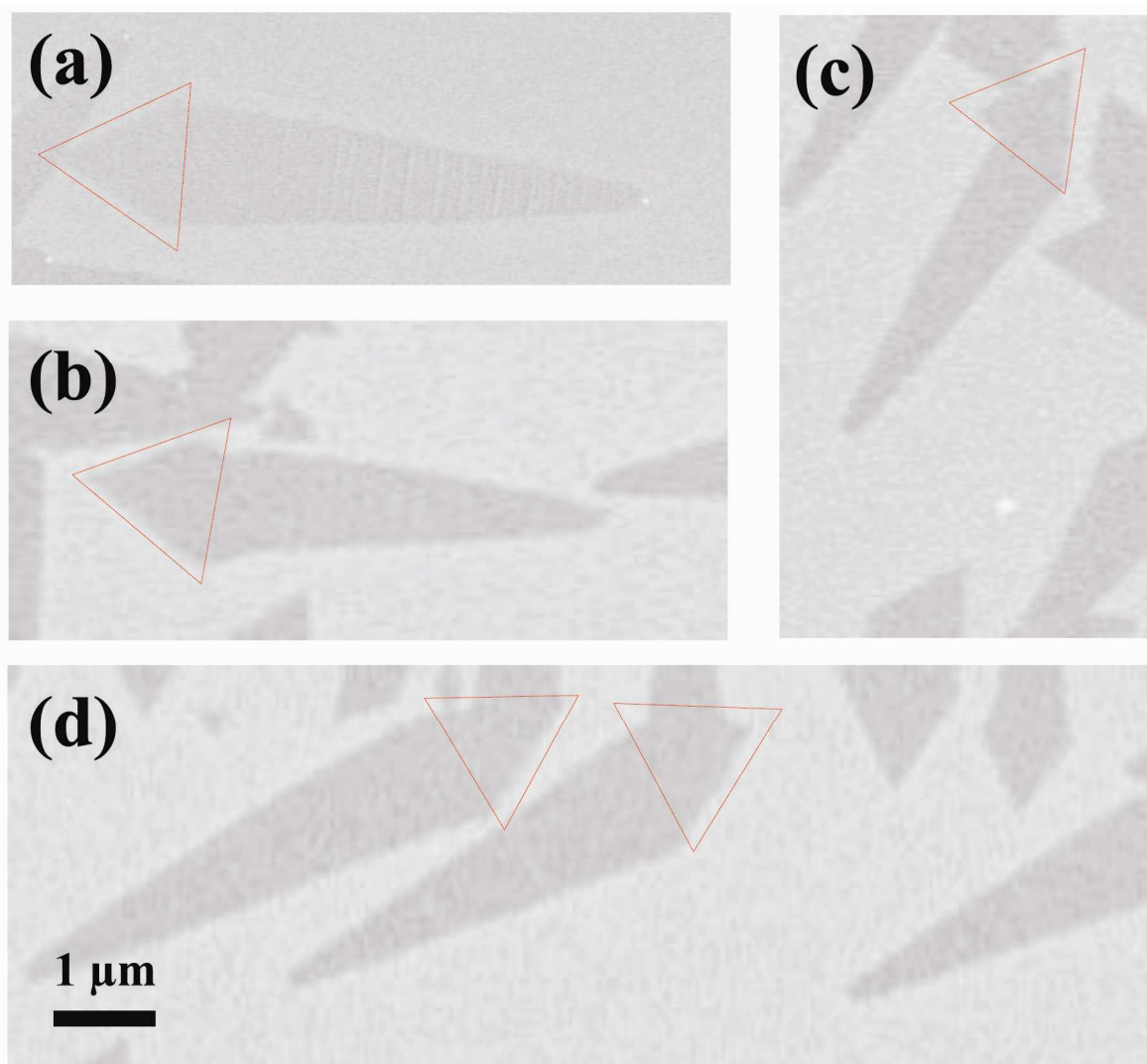


Figure S7. (a-d) Representative asymmetric diamond shapes for individual *h*-BN region.