

## Supporting Information

### **Black Phosphorus with Near-Superhydrophobic Properties and Long-Term Stability in Aqueous Media**

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#### **Materials**

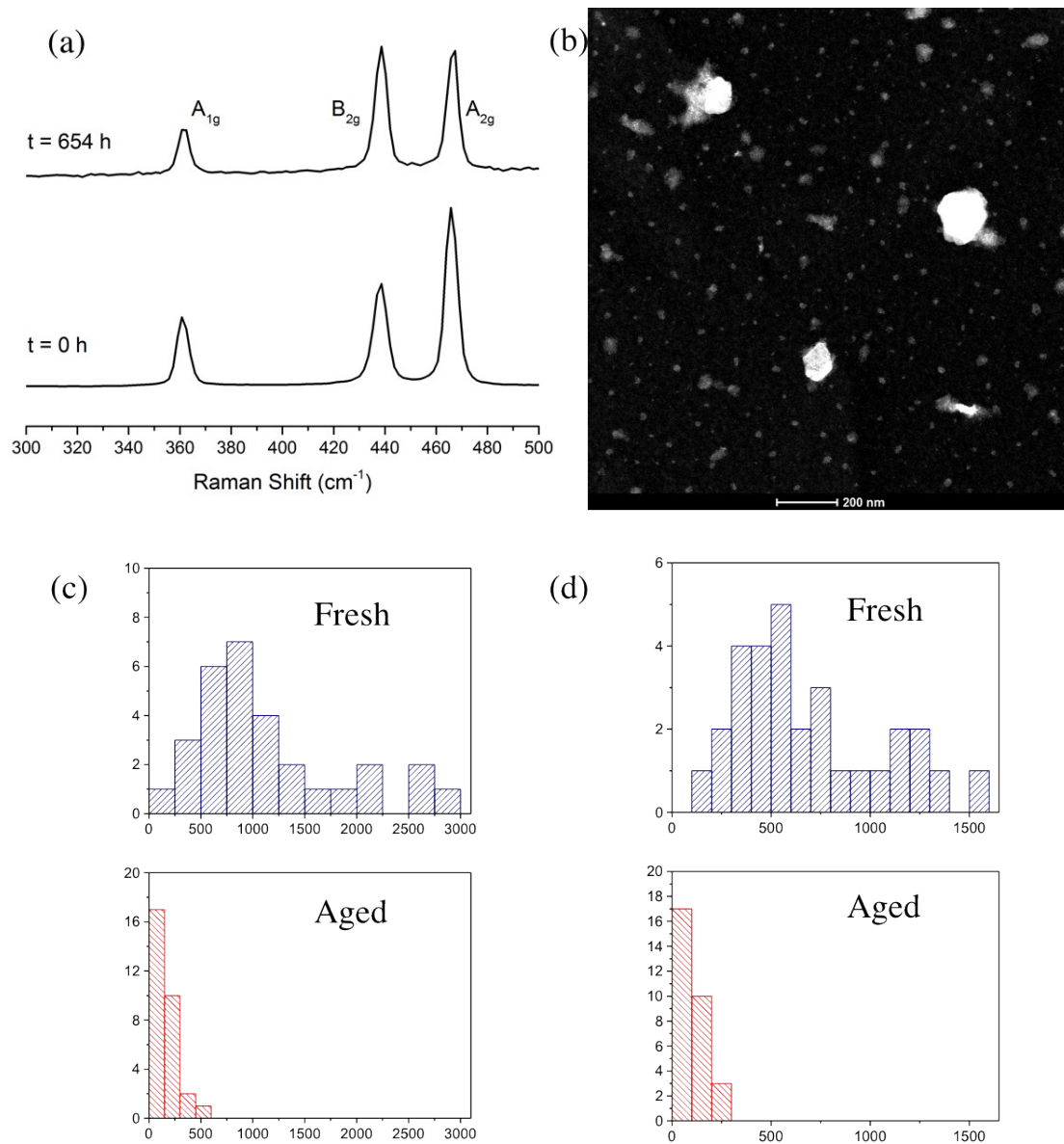
Black phosphorus (BP) was purchased from Smart Elements (Austria).

#### **Instrumentation**

Optical absorption measurements were performed with a Shimadzu UV 1800 instrument. Raman spectra were collected on a Renishaw System 1000 Raman Spectrometer. STEM imaging and energy dispersive X-ray (EDX) spectroscopic analysis was performed in a probe-side aberration corrected FEI Titan G2 80-200 ChemiSTEM microscope operated at 200 kV equipped with Super-X EDX silicon drift detectors with a total collection solid angle of  $\sim 0.7$  srad. For high angle annular dark-field (HAADF) imaging a convergence angle of 26 mrad and a detector inner angle of 48 mrad were used. EDX spectrum images were acquired with the sample at  $0^\circ$  tilt and with all four of the ChemiSTEM's Super-X SDD detectors turned on. STEM images were recorded in FEI TIA software and EDX data was recorded and analysed using Bruker Esprit. Atomic force microscopy (AFM) was performed using a Bruker Multimode 8 instrument equipped with a silicon nitride cantilever tip. Samples for AFM were deposited on a Si substrate and washed to remove as much surfactant as possible. Due to the large amount of surfactant residue the size distribution was obtained manually using Nanoscope (version 1.5) software. We had already minimised the amount of surfactant residue by rinsing samples after deposition and included only those features which could unambiguously be considered nanoflakes, based on defined shapes and edges characteristic of inorganic particles rather than non-crystalline organics. This may have led to a slight overestimate of the average size as it is more difficult to identify extremely small particles.

#### **Synthesis of FL-BP**

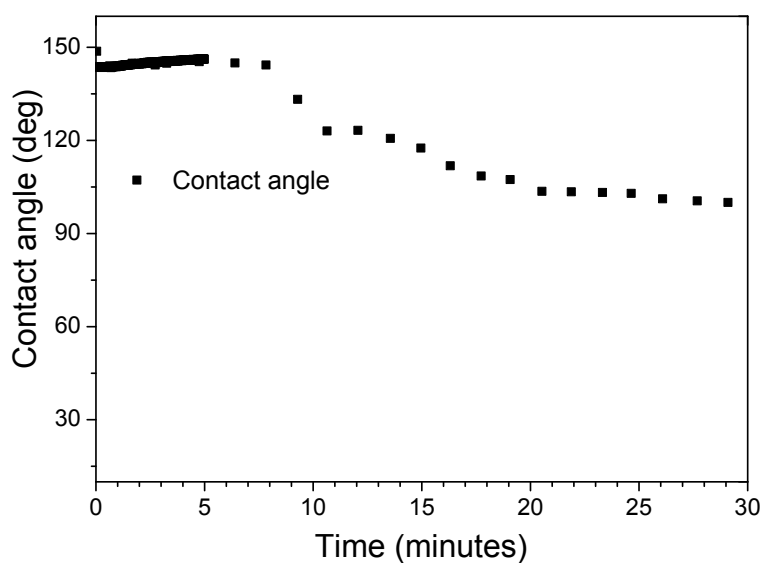
100 mg of black phosphorus was added to a vial of a degassed aqueous surfactant solution (15 ml, 1% w/v of Zonyl 7950 in deionised water). The suspension was sonicated in an Elmasonic P 70 H bench-top ultrasonic bath (820 W across four horns) operating at 37 kHz and 30% power. The temperature of the bath was maintained at  $25^\circ\text{C}$  throughout via the use of a home-made cooling coil. After 36 h the dispersions were centrifuged at 3000 rpm for 30 min and the top 10 mL of the suspension was removed.



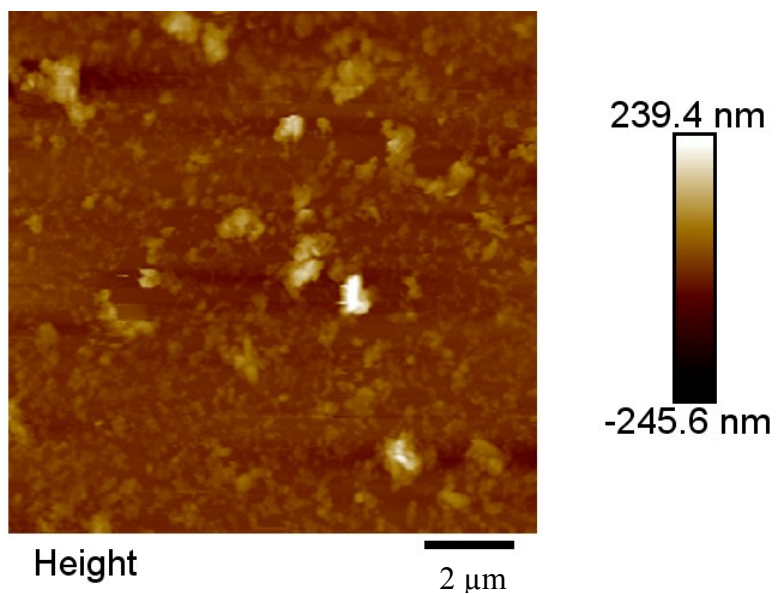
**Figure S1.** (a) The Raman spectra of fresh and aged flakes, (b) HAADF STEM image of aged flakes, (c) flake height and (d) flake width analysis of fresh and aged samples from HAADF STEM.

### Contact angle (CA) measurement

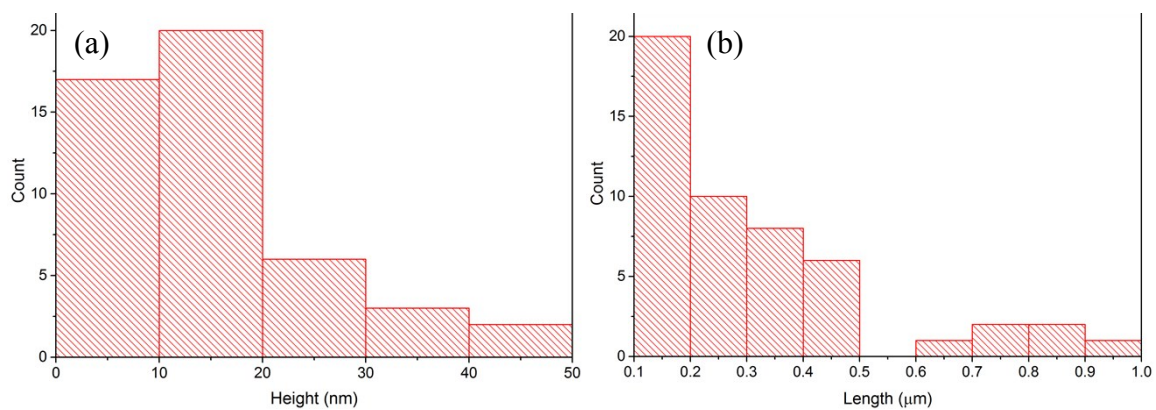
A Theta Optical Tensiometer (Biolin Scientific, Finland) was used for measurement of contact angle values in conjunction with OneAttension software (version 2.3) in the sessile mode to control the liquid droplets and contact angle values. Contact angle (WCA) was measured by placing ultra-pure water droplets on the surface of phosphorene supported by PVDF membrane ( $\theta_{\text{liquid|phosphorene membranes}}$ ). For the static CA measurements, liquid droplets in three different areas were controlled to a volume of  $\sim 6 \mu\text{L}$ , for consistency a high humidity vessel was used to reduce drop evaporation. The static CAs were determined within 5 minutes of contacting the droplet on the phosphorene membrane using a camera to capture the droplet images during experiments (1.9 FPS). The CA was calculated using OneAttension software based on the Young-Laplace equation.<sup>1,2</sup>



**Figure S2:** Longer Contact angle test showing delamination occurring at  $t > 10$  min.



**Figure S3:** Additional AFM image of flakes deposited on a Si substrate.



**Figure S4:** Histogram showing (a) height and (b) length distributions of the flakes as determined from AFM imaging.

### References for SI

- (1) Stalder, A. F.; Melchior, T.; Müller, M.; Sage, D.; Blu, T.; Unser, M. *Colloids Surfaces A Physicochem. Eng. Asp.* **2010**, *364*, 72–81.
- (2) Tao, L.; Duan, X.; Wang, C.; Duan, X.; Wang, S. *Chem. Commun.* **2015**, *51*, 7470–7473.