

Supporting information

p-Phosphonic acid calix[8]arene assisted exfoliation and stabilization of 2D materials in water

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S1 Experimental methods

(a) Materials

Pristine graphite flakes (043480, 7-10 μm , 99%) from Alfa Aesar, and boron nitride (255475, ~ 1 μm , 98%), molybdenum disulfide (234842, < 2 μm , 99%), and tungsten disulfide (243639, ~ 2 μm , 99%) from Sigma Aldrich were used as received. *p*-Phosphonic acid calix[8]arene (*p*-H₂O₃P-calix[8]arene) was synthesized following the literature method.¹ Milli-Q water was used for preparing the 10 mL aqueous suspensions of graphite (2 mg mL⁻¹), BN (2 mg mL⁻¹), and MoS₂ (5 mg mL⁻¹) and WS₂ (5 mg mL⁻¹). Solid *p*-H₂O₃P-calix[8]arene was added into each of the suspensions in targeting a 1 mg mL⁻¹ concentration. The suspensions were probe sonicated continuously for 2 hours at ambient conditions (150W at 70% amplitude, Sonifier cell disruptor, Model SLPt, Branson Ultrasonics Corporation). After 5 minutes for the solution to cool to room temperature, the suspensions were transferred into 15 mL centrifuge vials and centrifugated for 30 min at 3000 rpm (Centrifuge 5810, Eppendorf). Thereafter, the supernatant was decanted and kept in a glass vial, as shown in Figure 1a. The yields of the exfoliated materials were evaluated by weighting the dried slurry, which was generated from repeated centrifugation, under the same conditions, to ensure that all of the material stabilized by the calixarene had been collected, i.e. cleaning until the supernatant was clear.

(b) Characterization

The zeta potential analysis of the as-synthesized dispersions was measured using a Malvern Zetasizer Nano-ZS analyser. Samples were injected into clear disposable zeta cells, and the data for each sample as an average of 10 measurements. The pH of the dispersions was adjusted by addition of aqueous 1M HCl or 1M NaOH.

For further characterizations, the dispersions were processed to remove excessive *p*-H₂O₃P-calix[8]arene using high speed centrifuge (Centrifuge 5418, Eppendorf). For each of the dispersions, 1 mL was pipetted into a 1.5 mL vial and centrifuged for 30 min at 14,000 rpm. The resulting supernatants were removed and Milli-Q water was then added to the vials. Gentle sonication for 1 minute using a sonic bath (Ultrasonic cleaner, Unisonics) re-dispersed the slurries into water, and this was followed by another round of high speed centrifugation.

The cleaning process was repeated 5 times in order to remove the solvated *p*-H₂O₃P-calix[8]arene. The resulting dispersions (shown in Figure S3i) were used for subsequent characterizations.

Raman spectra were collected with a Dilor Labram spectrometer utilizing a diode (783.8 nm) laser. For Raman analysis the centrifugation-washed graphene slurry was dried with a light flow of argon gas. XPS data was acquired using a VG ESCALAB220i-XL X-ray Photoelectron Spectrometer equipped with a hemispherical analyser. The incident radiation was monochromatic Al K α X-rays (1486.6 eV) at 220 W (22 mA and 10kV). Survey (wide) and high resolution (narrow) scans were taken at analyser pass energies of 100 eV and 20 eV, respectively. Survey scans were carried out over 1200-0 eV binding energy range with 1.0 eV step size and 100 ms dwell time. Narrow high resolution scans were run over 20 eV binding energy range with 0.05 eV step size and 250 ms dwell time. Base pressure in the analysis chamber was 7.0×10^{-9} mbar. The flood gun was not used considering that the samples were conductive due to graphene. XPS data were processed using the CasaXPS software. All high resolution spectra were calibrated to C 1s (C-C) at 285.0 eV.

The as-treated dispersions were dropped onto 200 mesh holey carbon copper grids for TEM characterizations. A JEOL 2100 LaB₆ TEM equipped with a Gatan Orius charged-coupled device camera and Tridiem energy filter operating at 120 kV was used for TEM and EFTEM images and data acquisition which was processed using Image J software. For SEM studies, the samples were dropped onto 12 mm carbon tabs covered aluminum specimen mounts (SPI supplies), and then coated with 5 nm Pt films after drying. A Zeiss 1555 VP-FESEM was used for characterization. A NanoMan AFM system (Veeco Instruments Inc.) was used for AFM characterization. The system is a combination of several components which includes the Dimension 3000 Scanning Probe Microscope (SPM) in providing basic imaging platform, with the Dimension Closed Loop XY Scanning Head for precise lateral positioning, and the NanoMan User interface available within a NanoScope controller. Tapping mode AFM was used for size and height profile measurements of the exfoliated 2D materials. Samples were prepared by drop casting dispersions in water onto freshly cleaved mica with the water evaporated under a gentle flow of nitrogen gas. The raw data was processed by using the Gwyddion software.

S2 Formation of stable dispersions

In order to investigate the role of the p -H₂O₃P-calix[8]arene and the application of sonication in forming stable dispersions, comparative experiments were undertaken on graphite, Figure S1, as an example of the four laminar materials featured in the study. Figure S1a shows a dispersion of stabilized graphene in water after centrifugation, which was produced by sonicating an aqueous suspension of graphite flakes in the presence of p -H₂O₃P-calix[8]arene. The second sample was prepared with the same concentration of graphite and p -H₂O₃P-calix[8]arene in water, but the suspension was stirred for 2 hours. The resulting solution after centrifugation is shown in Figure S1b. The third centrifuged sample (Figure S1c) was sonicated for 2 hours but without the addition of the calixarene. In absence of p -H₂O₃P-calix[8]arene or sonication dispersion of the material is not evident.

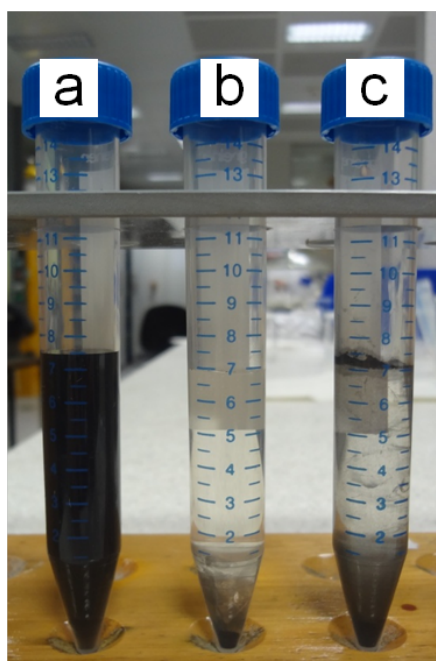


Figure S1 Photograph of the centrifuged graphite samples.

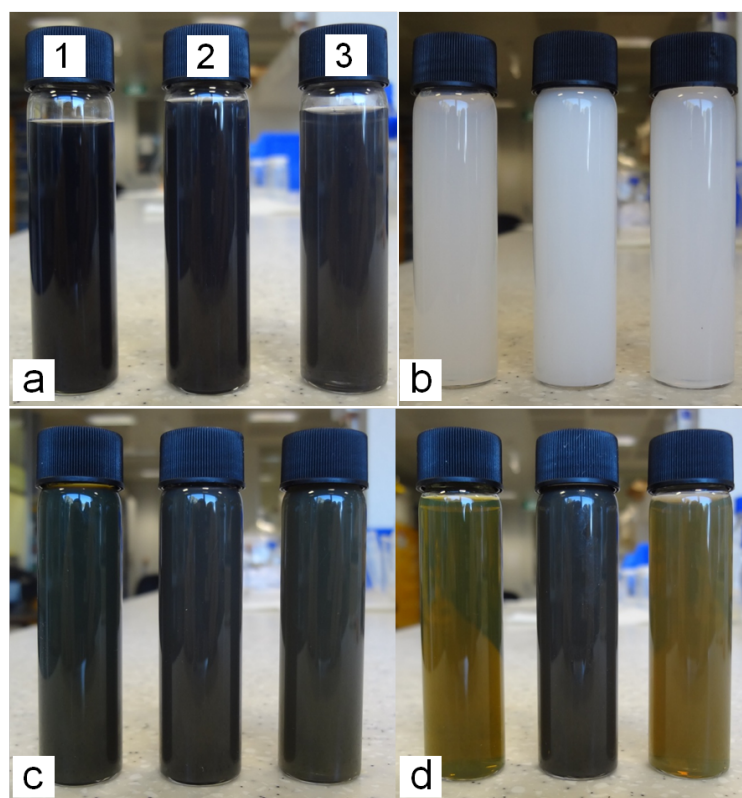


Figure S2 Photographs of dispersions of the 2D materials after the first round (1) and second round (3) of centrifugation followed by re-dispersing in water (2).

S3 Dispersibility investigations

The slurry formed after centrifugation can be re-dispersed in water. Figure S2a shows the dispersion of graphene taken after the first round of centrifugation (3,000 rpm, 30 min) (a1), the re-dispersed suspension (a2) and the dispersion after the second round centrifugation with the same parameters (a3). The dispersions with the same conditions for BN, MoS₂ and WS₂ are shown in Figure S2b, S2c and S2d, respectively. The first-round dispersions share a similar appearance as the second-round dispersion, indicating a similar concentration of the material. For increasing number of centrifugations, the supernatants gradually become clear. About 150 mL Milli-Q water was used to isolate the stabilized products, as clear solutions.

The first-round dispersions were used to investigate the change of concentrations with different centrifugal speeds ranging from 3,000 rpm to 14,000 rpm, as shown in Figure S3, with 1, 2, 3 and 4 corresponding to graphene, BN, MoS₂ and WS₂, respectively. The concentrations of the 2D materials dispersions became lower with an increase in centrifugal speed. It is worth noting that the colors of the dispersions persist even after 14,000 rpm centrifugation, which highlights the stability of the exfoliated materials in aqueous solutions. This is indicative of the presence of mono- and few-layered exfoliated materials in the supernatant liquids.

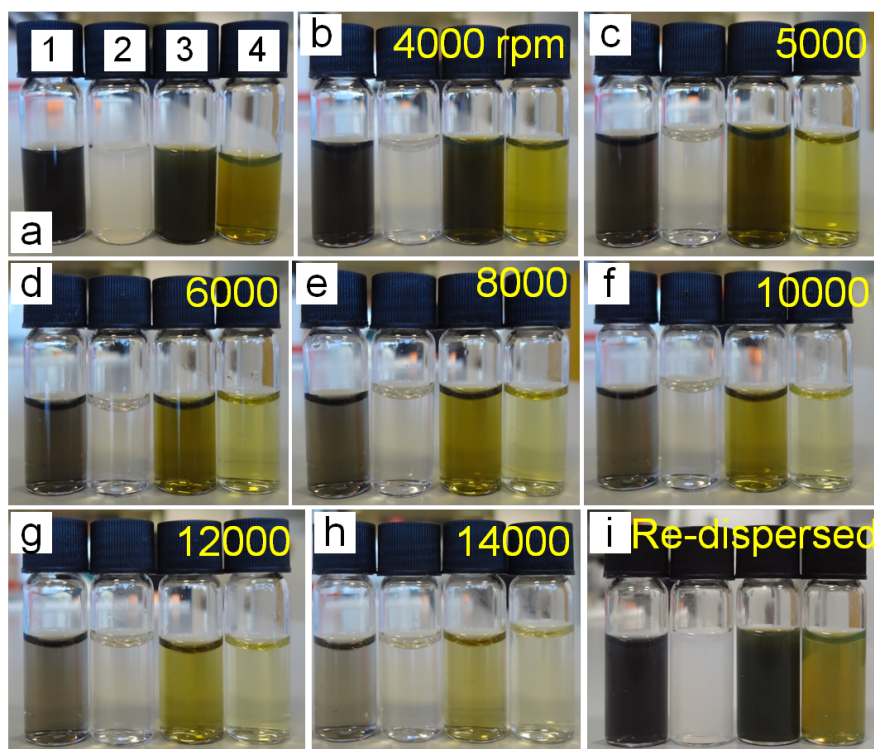


Figure S3 Photographs of the 2D materials dispersions with different centrifugal speeds and the re-dispersed solutions after cleaning 5 times.

S4 Zeta potential of *p*-H₂O₃P-calix[8]arene

The zeta potential of the *p*-H₂O₃P-calix[8]arene (1 mg mL⁻¹) was measured as shown in Figure S4. It decreases with an increase in pH, in a similar way to the change in zeta potential of the as-synthesized 2D dispersions, which is expected given the presence of excess *p*-H₂O₃P-calix[8]arene.

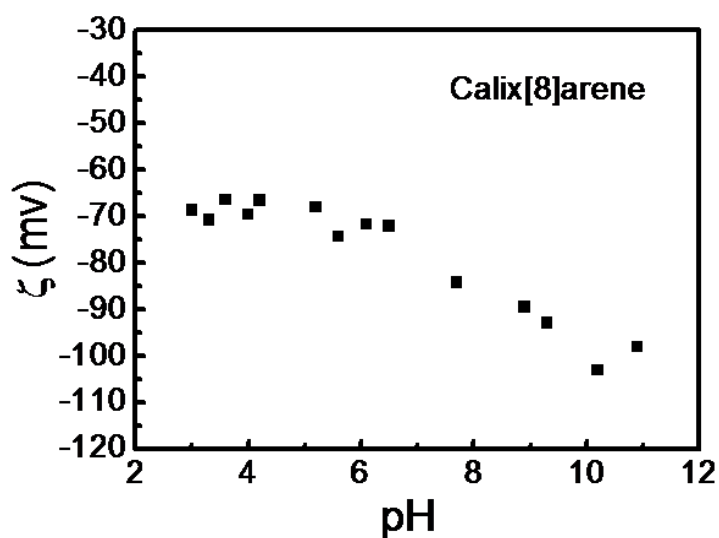


Figure S4 Zeta potentials of *p*-H₂O₃P-calix[8]arene as a function of pH.

S5 pH titration of *p*-H₂O₃P-calix[8]arene

Change in pH of a 1 mg mL⁻¹ solution *p*-H₂O₃P-calix[8]arene was measured as a function of volume of added base. A 5 mL *p*-H₂O₃P-calix[8]arene aqueous solution was pipette into a 50 mL conical with a narrow base and a stirrer bar. The pH of the calixarene solution was adjusted by the addition of 1 M HCl to approximately 3. NaOH (5 mM) solution in a burette was added in increments of 0.1 mL with the change in pH recorded using a Mettler Toledo SevenMulti pH meter. The apparent lack of influence that the pK_a of the calix[8]arene exerts on the zeta potential for MoS₂ and WS₂ strongly suggests a different binding-induced stabilization of the calixarene over graphene and BN. These results are consistent with the higher percentage yield of exfoliated and stabilized material, Figure 1 (b). As indicated in Figure 2, the higher yield of graphene and BN may result from the intercalation of the calixarene between the sheets associated with π - π calixarene to sheet interactions, with the phosphonic acid groups still exposed to water. The absence of the discontinuity in the zeta potential for MoS₂ and WS₂ suggests a different mode of stabilization by the calixarene.

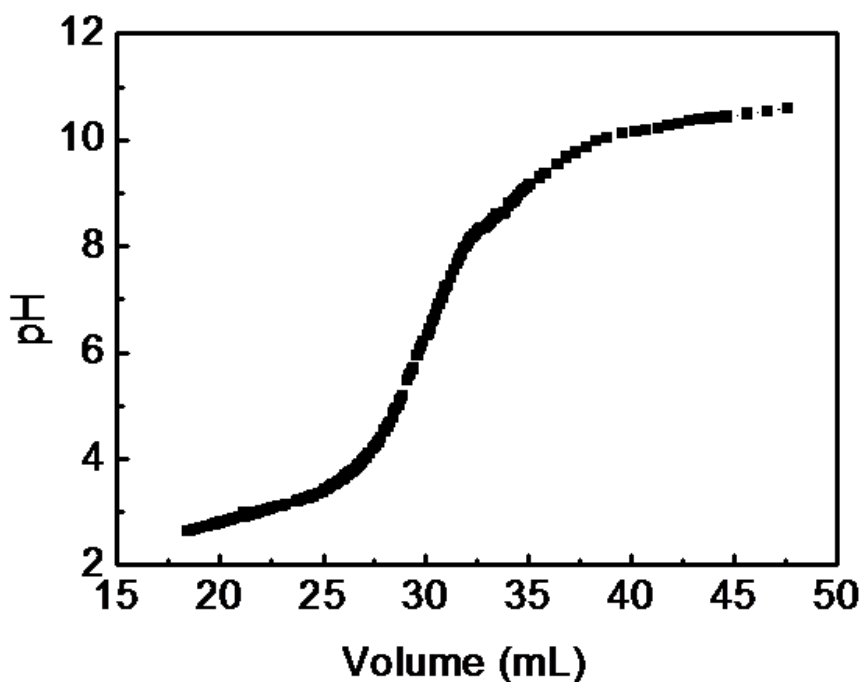


Figure S5 pH titration of 1 mg mL⁻¹ aqueous *p*-H₂O₃P-calix[8]arene against 5 mM NaOH.

S6 Removing excess p -H₂O₃P-calix[8]arene

The as-synthesized graphene/calix[8]arene (Figure S6a) and boron nitride/calix[8]arene (Figure S6b) dispersions used for the TEM samples revealed a large amount of the foreign material, presumably excess calixarene, which obscured the 2D material. After 5 washings with water (above), the re-dispersed material showed little foreign material in the TEM images, Figure S6c and S6d. The same process was used for preparing samples for AFM and SEM.

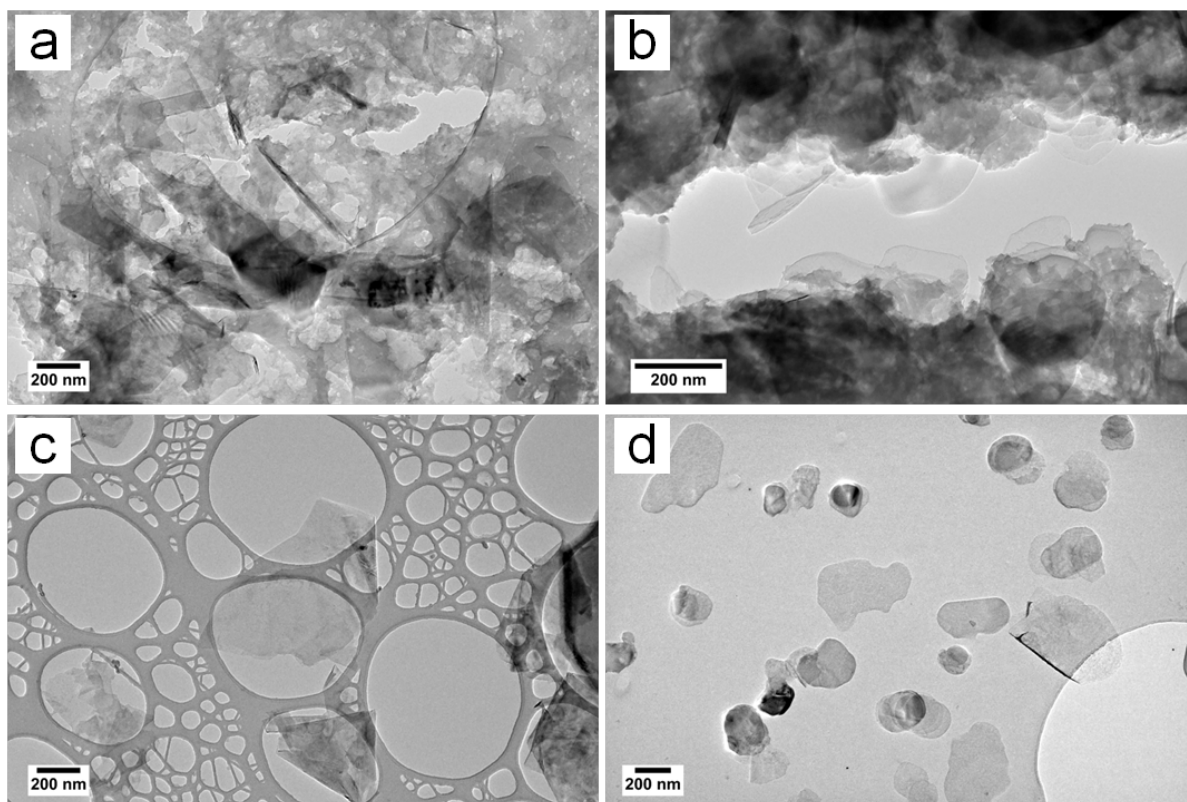


Figure S6 TEM images of the exfoliated graphene (a) and BN sheets (b) without removing excess p -H₂O₃P-calix[8]arene, and the graphene sheets (c) and BN sheets (d) after the cleaning.

S7 AFM size and topographical height distributions of exfoliated 2D structures

The size and height of exfoliated 2D structures were measured using AFM, Figure S7. The size of exfoliated sheets ranges from 50 to 300 nm. The size of graphene, MoS₂ and WS₂ sheets are less than that of the BN sheets. From the height distributions, most of the graphene sheets are ~2 nm height. For BN, the sheets tend to aggregate, giving some heights > 10 nm, although with a large percentage approximately 5 nm in height. The analysis also shows the height of MoS₂ and WS₂ sheets, which are down to ~10 nm and ~5-8 nm, respectively.

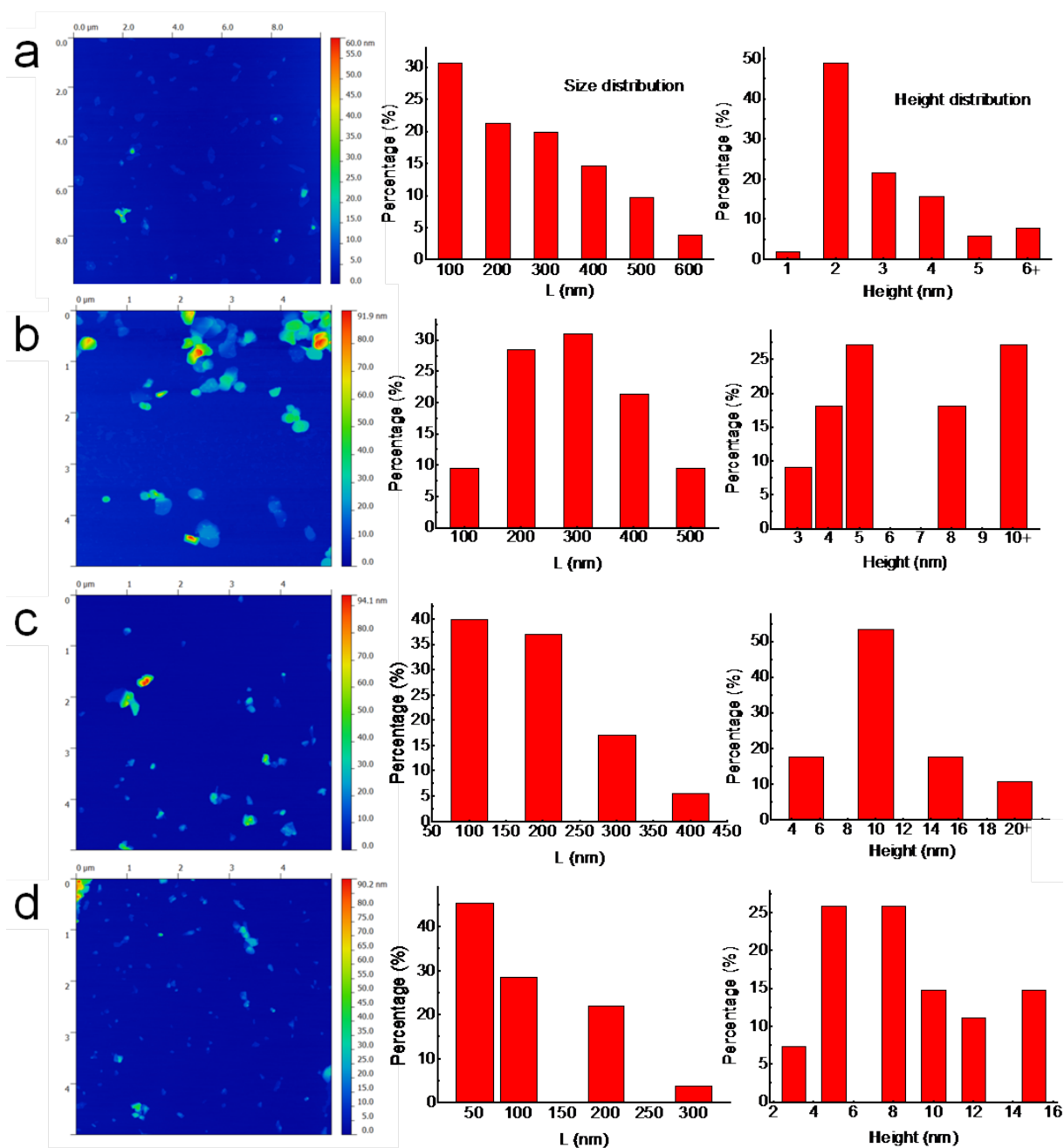


Figure S7 AFM images, and the corresponding size and topographic height distributions of the graphene sheets (a), and sheets of BN (b), MoS₂ (c), and WS₂ (d).

Figure 3a, shows well distributed graphene sheets on a mica substrate, with a zoomed-in image showing a height of $\sim 1\text{-}2$ nm. This height corresponds to one or two sheets, as observed by others.² The analogous measurements for BN, MoS₂ and WS₂, as shown in Figure 3b, 3c, and 3d, respectively, reveal that the BN sheet is ~ 4 nm thick, and the MoS₂ and WS₂ sheets are ~ 5 nm thick. The AFM results establish that the average thickness of the MoS₂ and WS₂ sheets is larger than that of the graphene and BN. The difference in thickness may relate to a difference in surface energy between sheets and the higher energy required for exfoliation. Theoretical studies suggest that the surface energy of MoS₂ and WS₂ (> 250 mJ m⁻²) is many times larger than that of graphene² and BN.³ SEM images of the exfoliated graphene sheets, BN, MoS₂ and WS₂ are shown in Figure 4, respectively. These images give a broader view of the morphologies of the exfoliated sheets, clearly showing a significant decrease in thickness of the 2D materials after sonication in the presence of the calixarene.

S8 SEM images of the exfoliated 2D materials

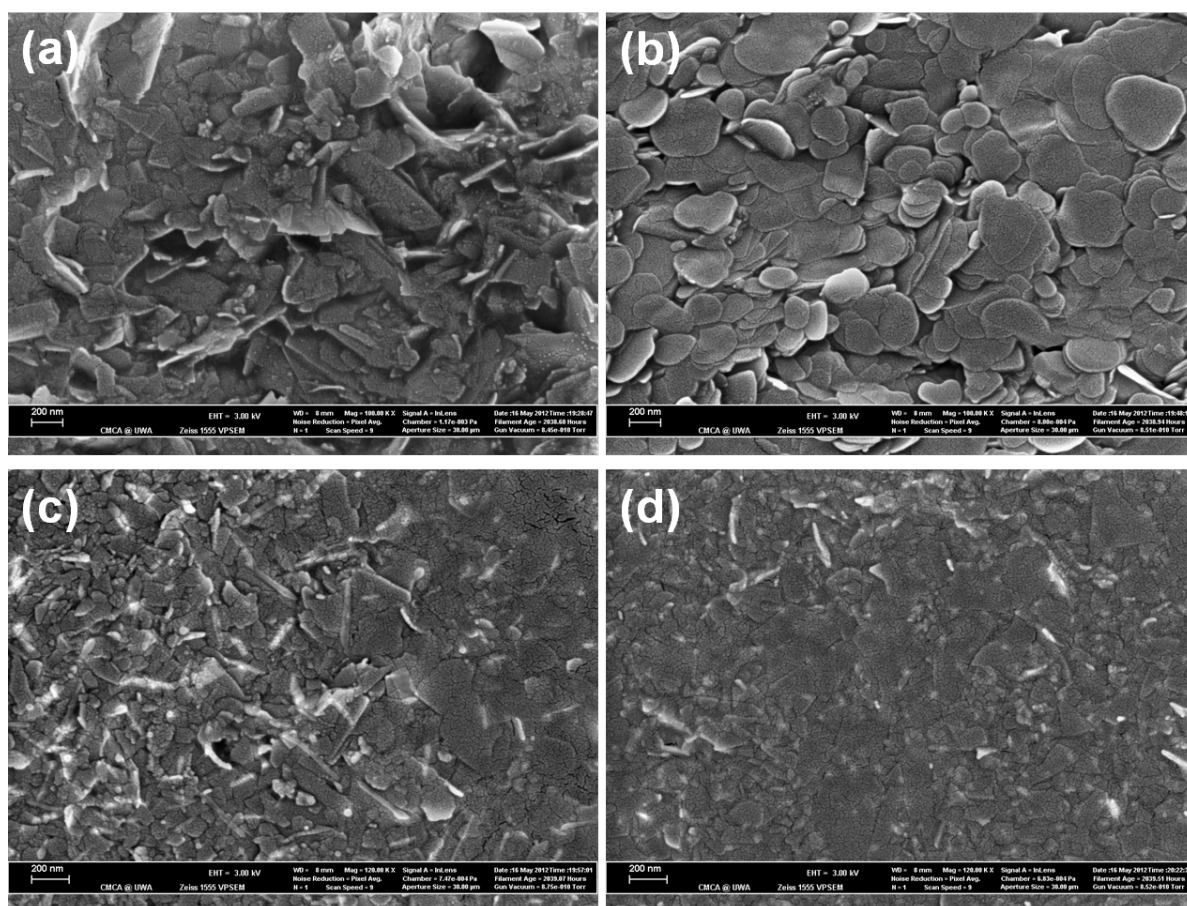


Figure S8 SEM images of the exfoliated (a) graphene, (b) BN, (c) MoS₂ and (d) WS₂.

Reference

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