SUPLEMENTARY INFORMATION

Tuning delamination of layered covalent organic frameworks through structural design

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Materials and Methods

Chloroform, methanol and acetone were purchased from SdS. Toluene was purchased from Carlo Ebra. 2-propanol was purchased from Panreac. 1,3,5-triethynylbenzene was purchased from Alfa Aesar. Cooper(I) iodide was purchased from Riedel-de Haën. Triethylamine, 1,4-diethynylbenzene, 1,4-diiodobenzene, 4,4'-diiodobyphenyl, 1,3,5-tris-(4-iodophenyl)benzene, tetrakis(triphenylhosphine)palladium(0), dichloromethane and calcium hydride were all purchased from Sigma-Aldrich. All products were used as received except dichloromethane that was distilled over calcium hydride under argon atmosphere before use.

Atomic force microscopy (AFM) images were acquired in dynamic mode using a Nanotec Electronic system. Olympus cantilevers were used with a nominal force constant of 0.75 Nm^{-1} and a resonance frequency of 70 kHz. The images were processed using WSxM (freely downloadable scanning probe microscopy software from www.nanotec.es) operating at room temperature in ambient air conditions.

Transmission Electron Microscopy (TEM) images were obtained in a JEOL model JEM 2100 F (field emission) TEM system with an accelerating voltage of 200kV. The microscope has a multiscan charge-coupled device (CCD) camera and Energy-dispersive X-ray spectroscopy (EDXS) microanalysis system.

CMP-0, CMP1, CMP2 and CMP3 were synthesized according to a reported method.[1] In order to characterize the bulk samples of CMP0, CMP1, CMP2 and CMP3, elemental analyses were performed by the Microanalysis Service of the Universidad Autónoma de Madrid on a Perkin-Elemer 240 B microanalyzer. FTIR spectra (KBr pellets) were recorded on a Perkin-Elmer 1650 spectrophotometer. ^{13}C NMR high-resolution solid-state nuclear magnetic resonance (NMR) spectra were recorded at ambient temperature on a Bruker AV-400 spectrometer using a tripe-channel Bruker magic-angle spinning (MAS) probe with 4-mm (outside diameter) zirconia rotors. Cross-polarization (CP) with MAS was used to acquire ^{13}C NMR data at 100.61 MHz. The ^{1}H NMR pulse was 3 μs. The CP contact time was 3.5 ms. High-power two-pulse phase modulation (TPPM) ^{1}H NMR decoupling was applied during data acquisition. The decoupling frequency

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[1] J. X. Jiang, F. Su, A. Trewin, C. D. Wood, H. Niu, J. T. A. Jones, Y. Z. Khimyak and A. I. Cooper, *J Am Chem Soc*, 2008, **130**, 7710-7720.

was 83 kHz. The MAS sample-spinning rate was 10 kHz. Recycle delays were scans 4s. The ^{13}C NMR chemical shifts are given relative to tetramethylsilane as zero ppm, calibrated using the –CH carbon signal of adamantane assigned to 29.50 ppm as a secondary reference.

Full characterization was consistent with previous reported data:[1]

CMP-0:
(Yield: 74.4%). IR (KBr cm^{-1}): 3295 (-C≡C-H), 2206 (-C≡C-).
Elemental (%) Calcd. for $C_{36}H_{18}$: C 95.25, H 4.75; Found: C 84.66, H 3.89.

Solid state ^{13}C NMR (M.A.S.): δ ppm 141.4, 131.7, 127.2, 124.3, 89.8.

CMP-1:
(Yield: 67.5%). IR (KBr cm^{-1}): 3293 (-C≡C-H), 2200 (-C≡C-).
Elemental analysis (%) Calcd. for $C_{21}H_9$: C 96.55, H 3.45; Found: C 86.62, H 3.67.

Solid state ^{13}C NMR (M.A.S.): δ ppm 131.0, 123.7, 90.2.

CMP-2:
(Yield: 62.4%). IR (KBr cm^{-1}): 3286 (-C≡C-H), 2202 (-C≡C-).
Elemental analysis (%) Calcd. for $C_{36}H_{18}$: C 96, H 4; Found: C 90.06, H 4.11.

Solid state ^{13}C NMR (M.A.S.): δ ppm 140.1, 131.8, 126.3, 90.0.

CMP-3:
(Yield: 96%). IR (KBr cm^{-1}): No peak observed from (-C≡C-H), 2206 (-C≡C-).
Elemental analysis (%) Calcd. for $C_{39}H_{21}$: C 95.71, H 4.29; Found: C 86.88, H 4.39.

Solid state ^{13}C NMR (M.A.S.): δ ppm 141.2, 131.5, 126.8, 123.4, 91.4.

Exfoliation Procedure: 5 mg of CMP polymer was dispersed in 5 mL of CH_2Cl_2 previously dried and bidistilled. The suspension was sonicated with an ultrasonication bath (Elma, 37 kHz, 380 W) during 45 min., 75 min., 120 min. or 180 min. Thereafter, the suspension was filtered and centrifuged at 9000 rpm for 5 min. The resulting clear suspension was diluted by adding 100 μL of such solution to 900 μL of pure CH_2Cl_2. 20 μL of the diluted solution was deposited by drop-casting on SiO_2 substrate. The sample was left on air, allowing to the complete evaporation of the solvent and analyzed by AFM.

For each experiment we prepared control samples according to the following procedure: 5 mL of CH_2Cl_2 dried and distilled two times was sonicated with ultrasonication bath (frequency of 37 kHz and 380 W) at different times (45 min, 75 min, 120 min and 180 min). Finally, the solution was filtered and centrifuged at 9000 rpm for 5 min, 100 μL was diluted with 900 µL of additional CH_2Cl_2, and deposited by drop-casting on SiO_2 surface. Control samples did not show laminar structures (Fig. S.I.1.).

Surface preparation: SiO_2 surfaces were sonicated for 15 min in 2-propanol and 15 min in acetone and then dried under a flow of argon.

TEM Sample Preparation: Samples for HR-TEM were prepared from suspensions generated by the same experimental procedure used for AFM experiments. 100 µL of clear suspension were deposited by drop casting on a grid (lacey carbon-coated copper grids, 200 mesh) and dried in air.

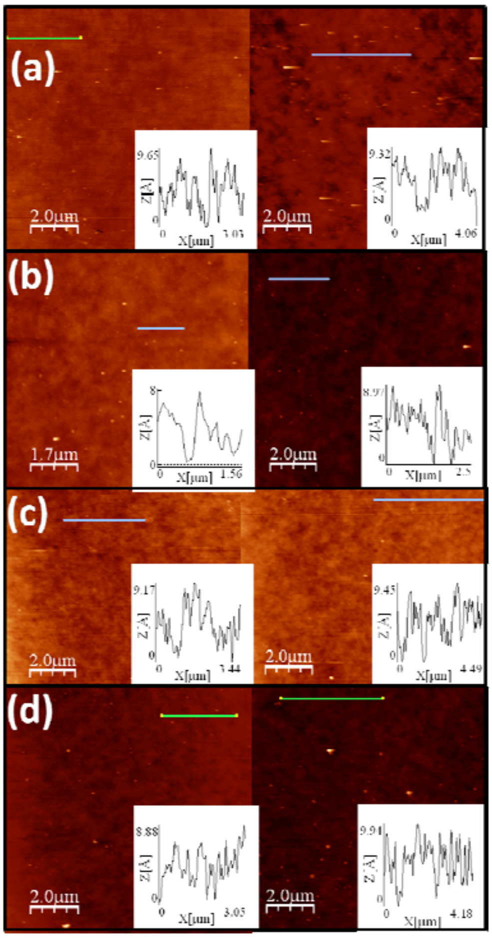

Fig. S.I.1 Control experiments on SiO_2. At (a) 45 min., (b) 75 min., (c) 120 min. and (d) 180 min. of sonication treatments.

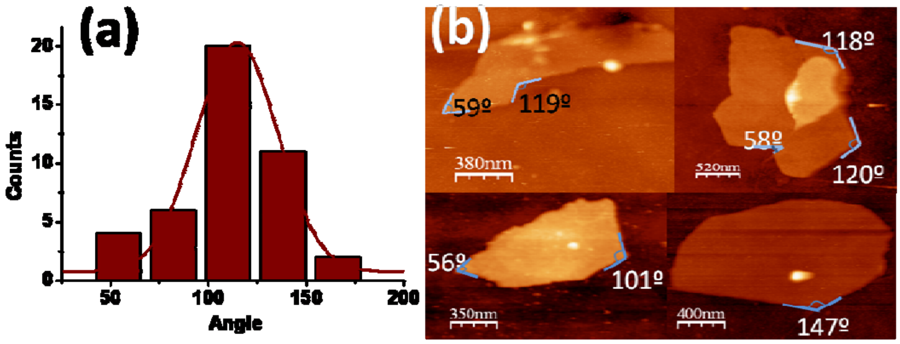

Fig. S.I.2 (a) Histogram corresponding to statistical representation of 50 measured angles found in nanolayers of CMP-0 generated by 45 min. of sonication process. (b) Representative images of angle analysis of nanolayers of CMP-0 generated by 45 min. of sonication process.

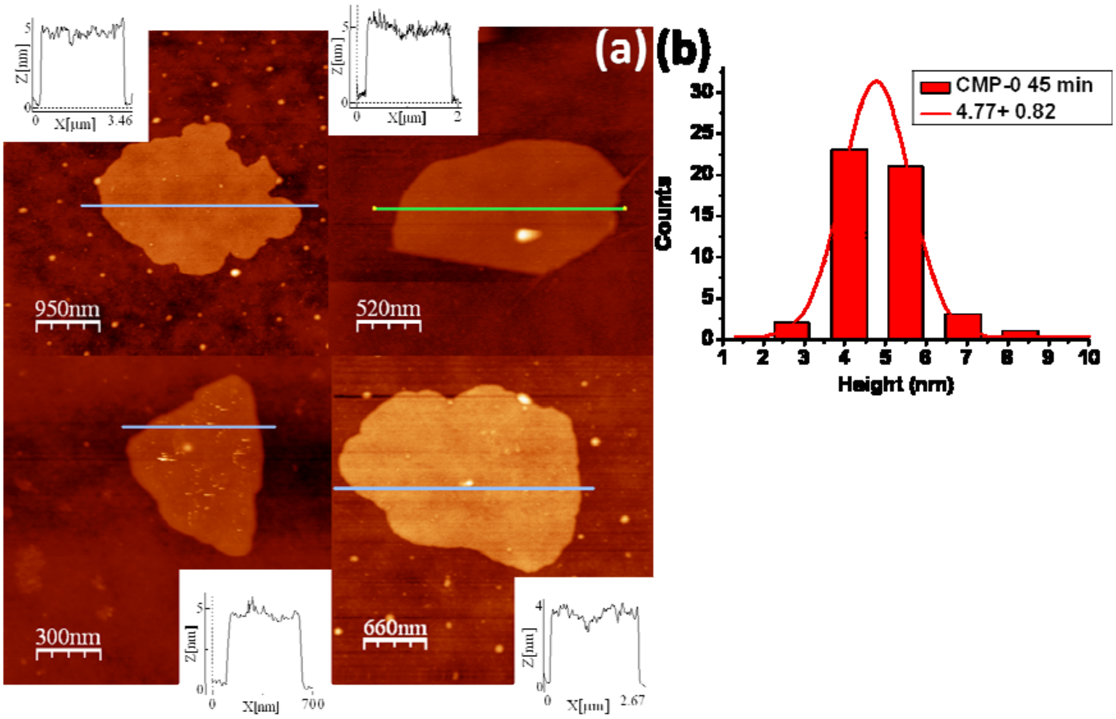

Fig. S.I.3 (a) Representative AFM images found for CMP-0 suspensions generated by 45 min. of sonication. (b) Histogram corresponding to statistical analysis of nanolayers found from solutions resulting from sonication of CMP-0 during 45 min.

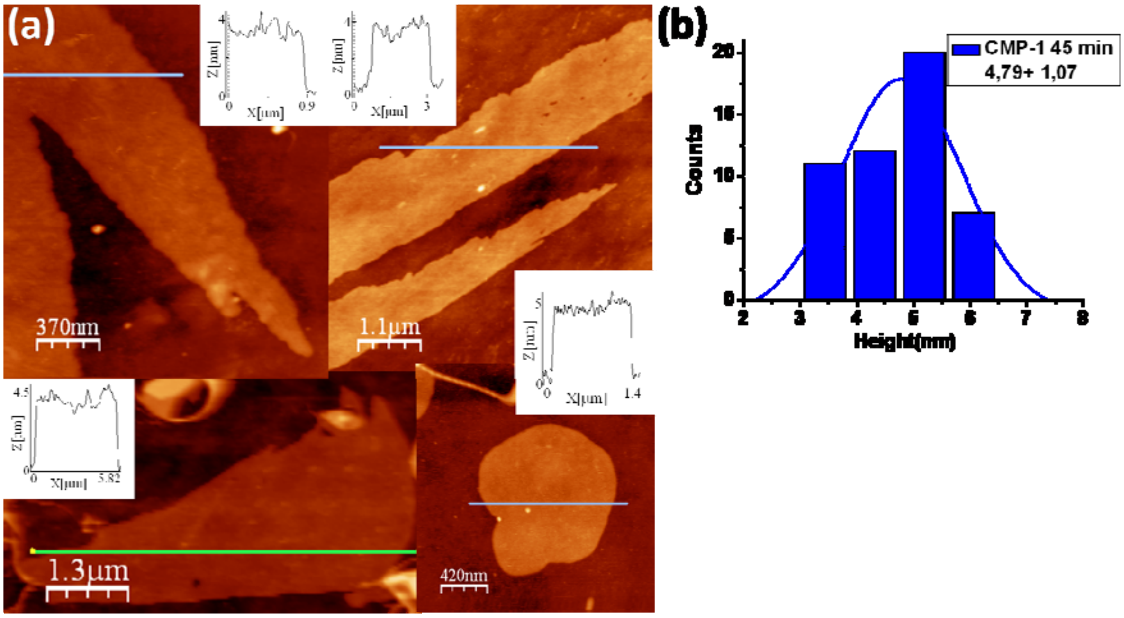

Fig. S.I.4 (a) Representative AFM images found for CMP-1 suspensions generated by 45 min. of sonication. (b) Histogram corresponding to statistical analysis of nanolayers found from solutions resulting from sonication of CMP-1 during 45 min.

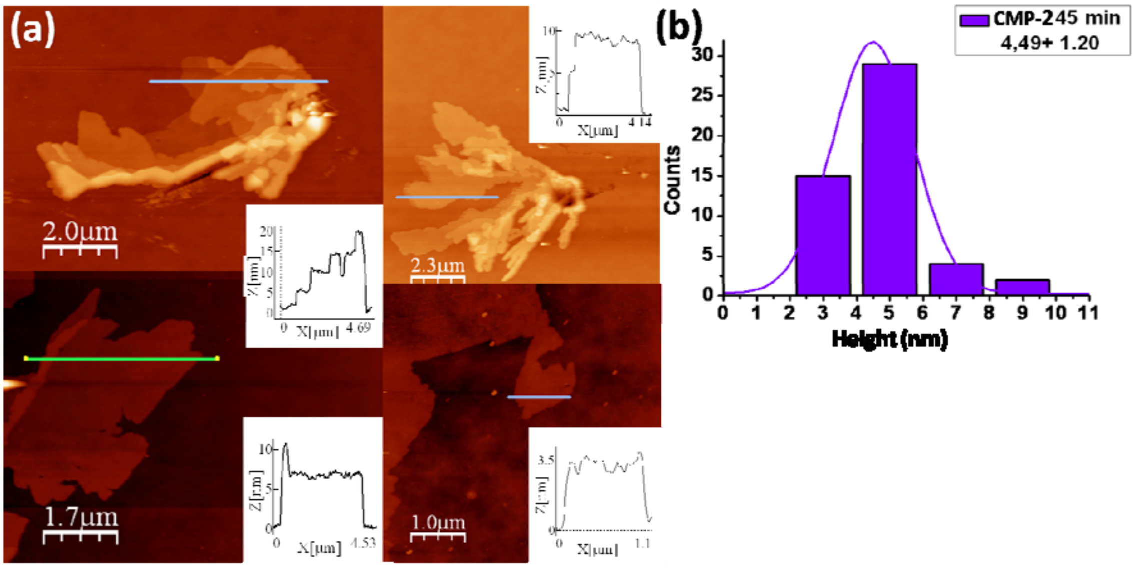

Fig. S.I.5 (a) Representative AFM images found for CMP-2 suspensions generated by 45 min. of sonication. (b) Histogram corresponding to statistical analysis of nanolayers found from solutions resulting from sonication of CMP-2 during 45 min.

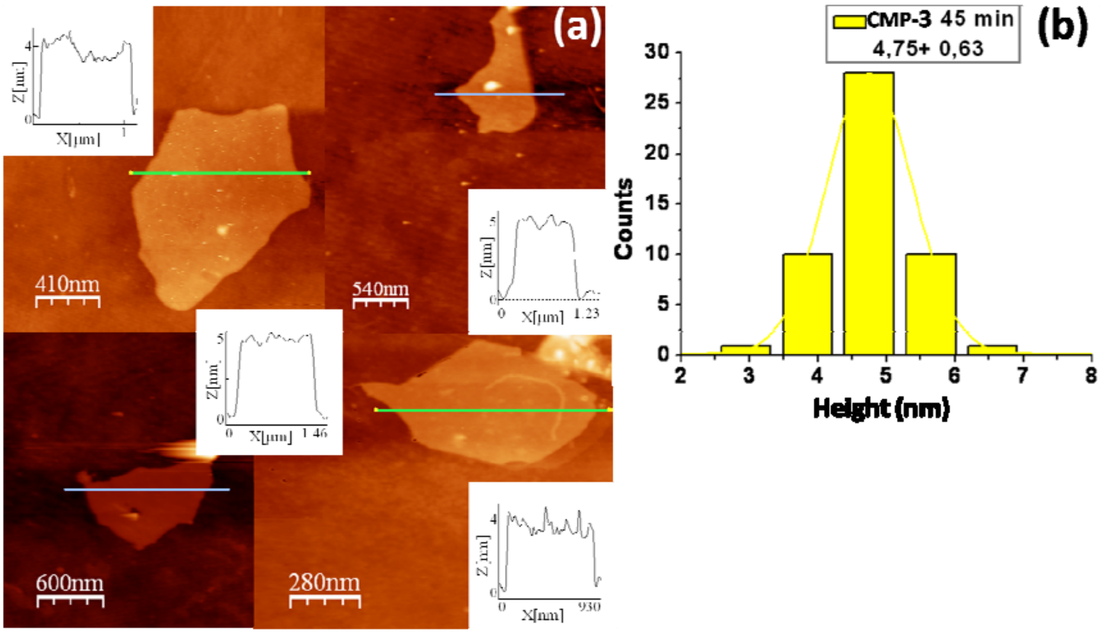

Fig. S.I.6 (a) Representative AFM images found for CMP-3 suspensions generated by 45 min. of sonication. (b) Histogram corresponding to statistical analysis of nanolayers found from solutions resulting from sonication of CMP-3 during 45 min.

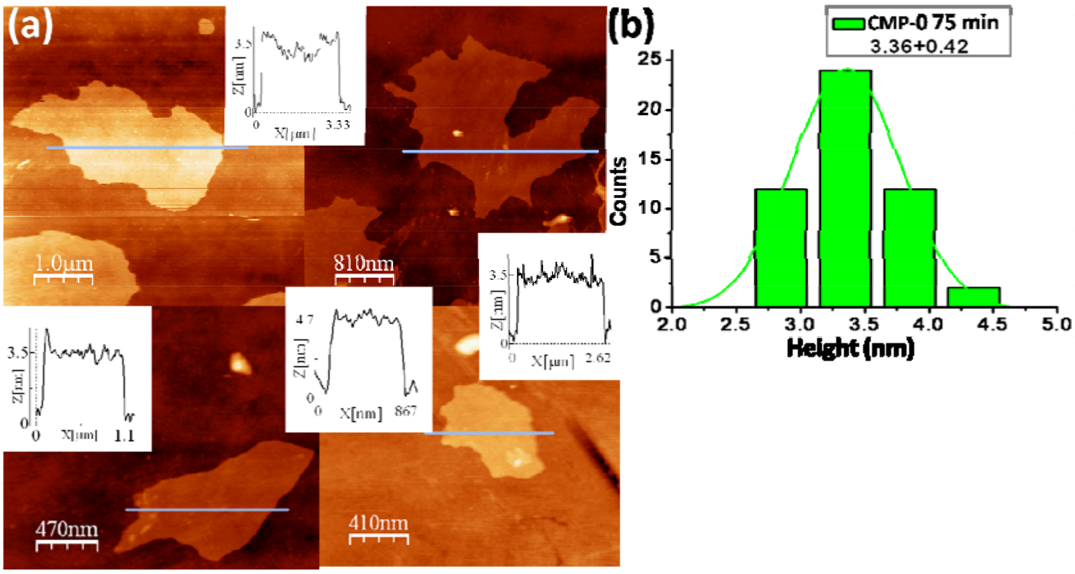

Fig. S.I.7 (a) Representative AFM images found for CMP-0 suspensions generated by 75 min. of sonication. (b) Histogram corresponding to statistical analysis of nanolayers found from solutions resulting from sonication of CMP-0 during 75 min.

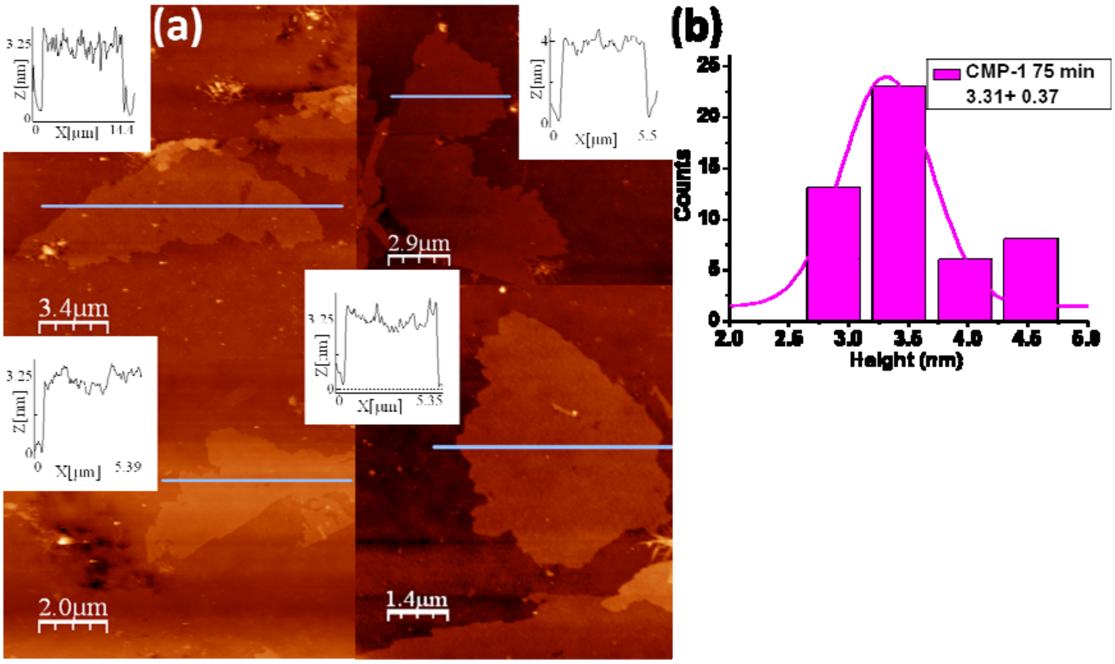

Fig. S.I.8 (a) Representative AFM images found for CMP-1suspensions generated by 75 min. of sonication. (b) Histogram corresponding to statistical analysis of nanolayers found from solutions resulting from sonication of CMP-1 during 75 min.

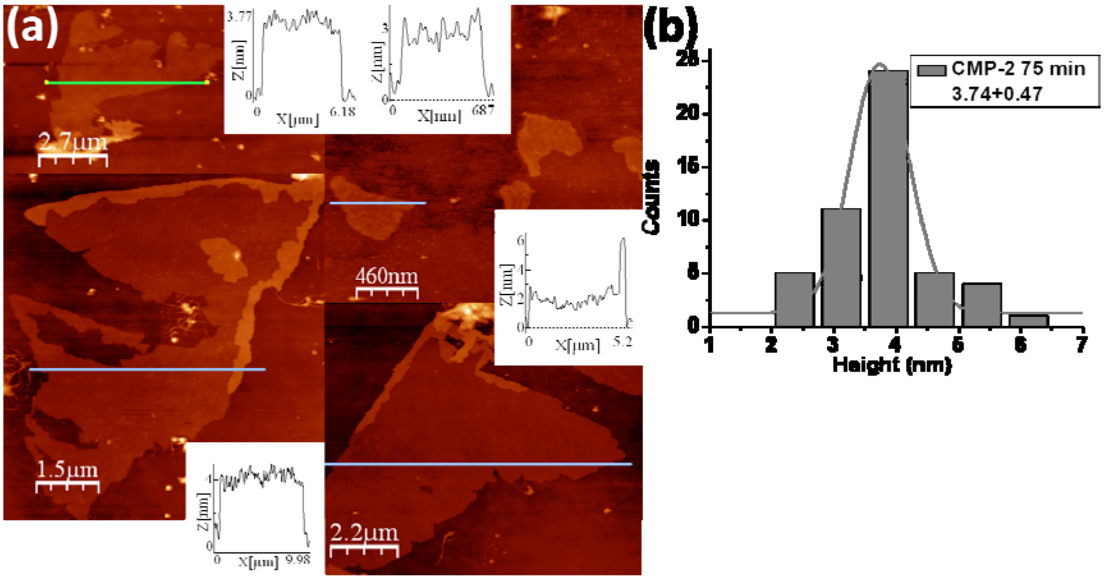

Fig. S.I.9 (a) Representative AFM images found for CMP-2 suspensions generated by 75 min. of sonication (b) Histogram corresponding to statistical analysis of nanolayers found from solutions resulting from sonication of CMP-2 during 75 min.

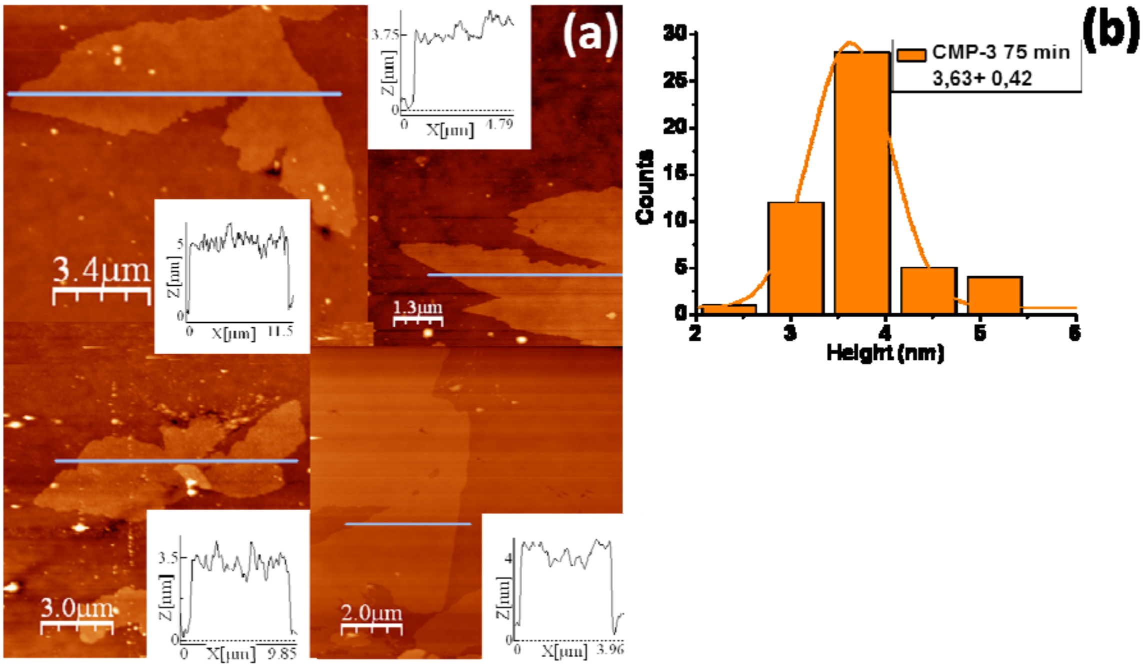

Fig. S.I.10 (a) Representative AFM images found for CMP-3 suspensions generated by 75 min. of sonication. (b) Histogram corresponding to statistical analysis of nanolayers found from solutions resulting from sonication of CMP-3 during 75 min.

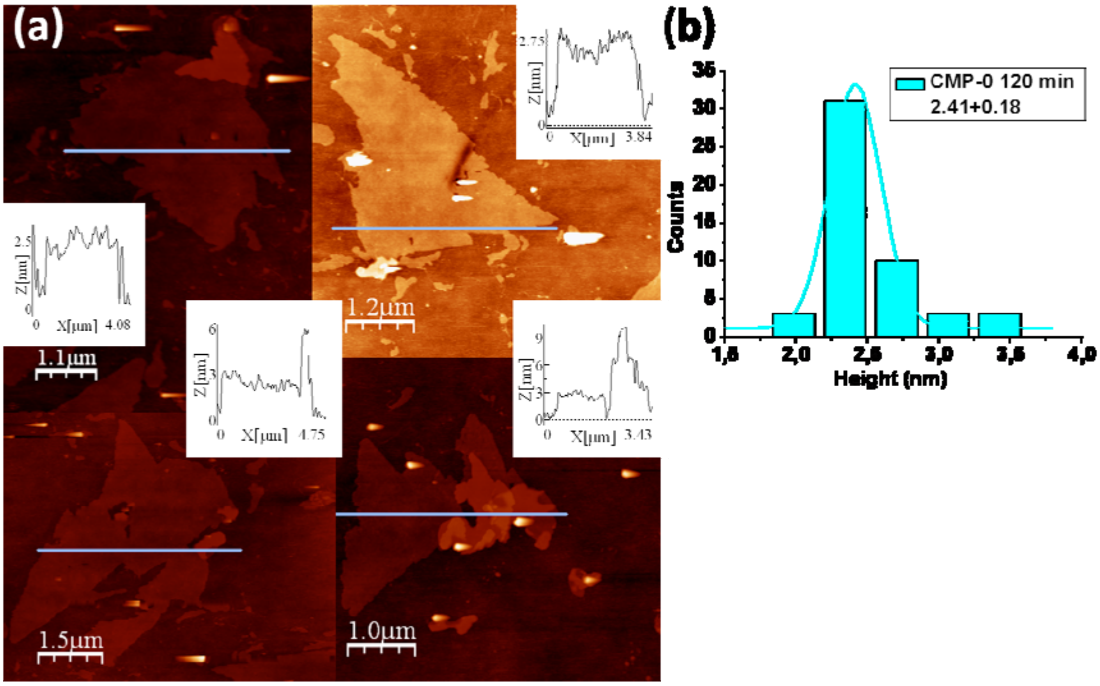

Fig. S.I.11 (a) Representative AFM images found for CMP-0 suspensions generated by 120 min. of sonication. (b) Histogram corresponding to statistical analysis of nanolayers found from solutions resulting from sonication of CMP-0 during 120 min.

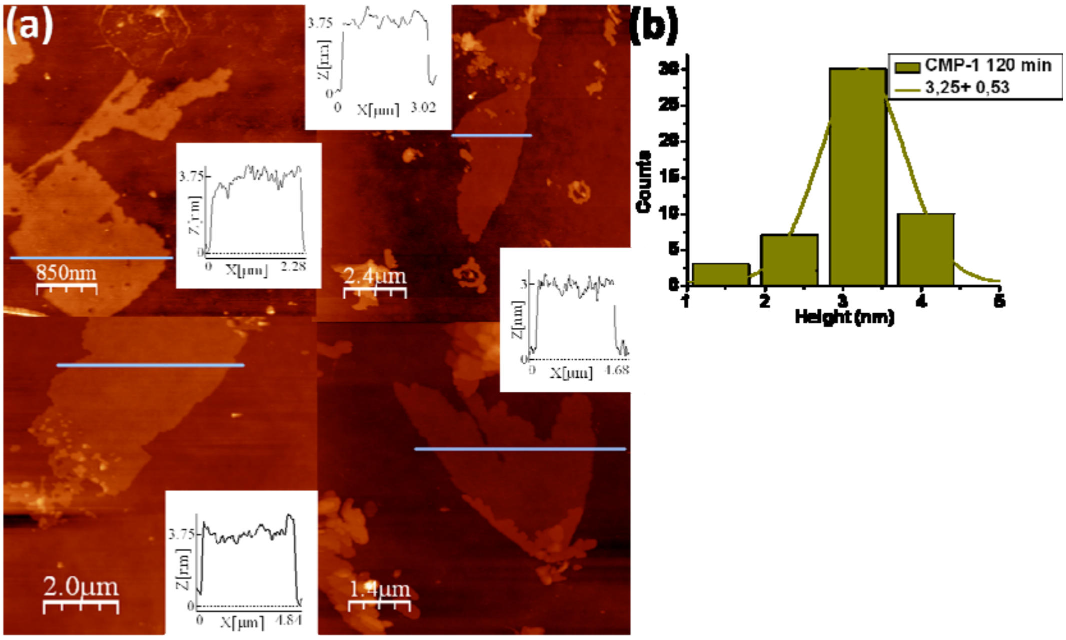

Fig. S.I.12 (a) Representative AFM images found for CMP-1 suspensions generated by 120 min. of sonication. (b) Histogram corresponding to statistical analysis of nanolayers found from solutions resulting from sonication of CMP-1 during 120 min.

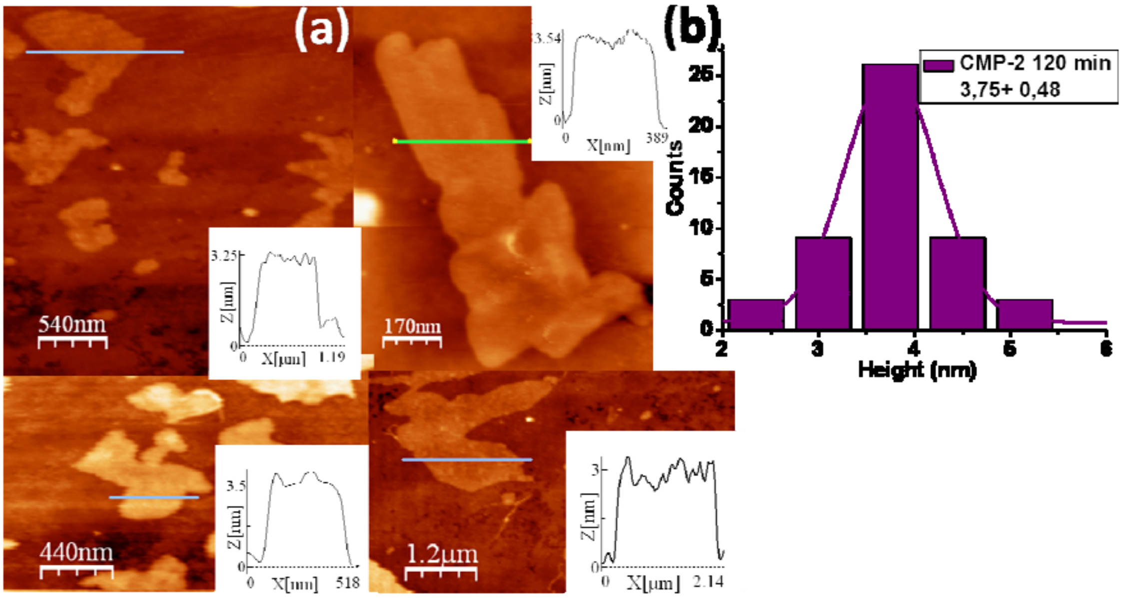

Fig. S.I.13 (a) Representative AFM images found for CMP-2 suspensions generated by 120 min. of sonication. (b) Histogram corresponding to statistical analysis of nanolayers found from solutions resulting from sonication of CMP-2 during 120 min.

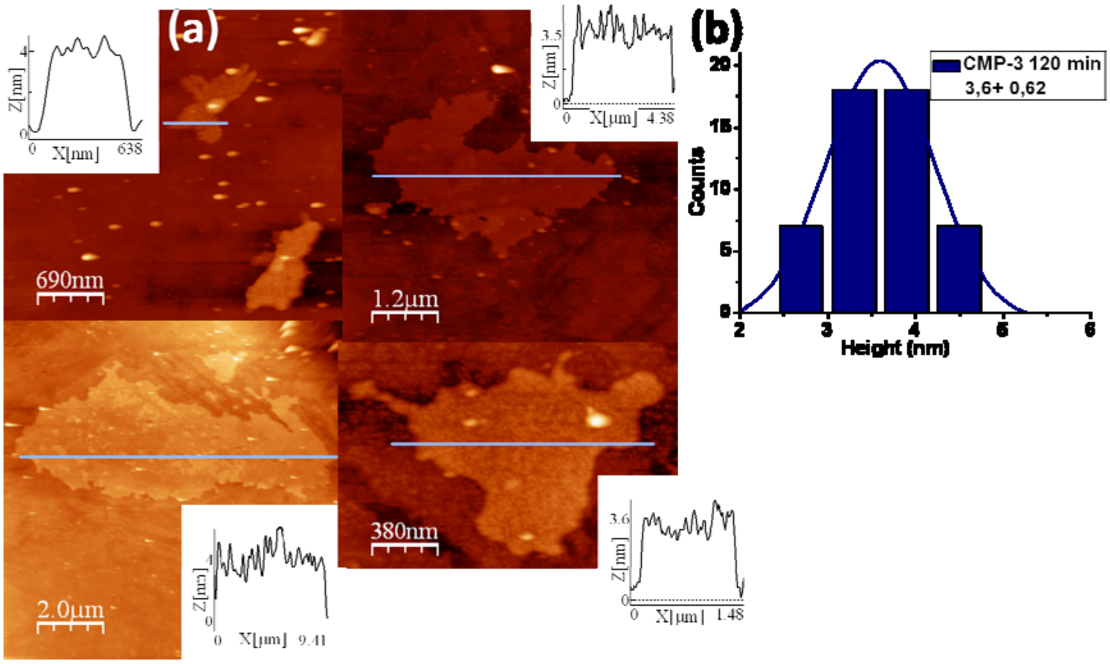

Fig. S.I.14 (a) Representative AFM images found for CMP-3 suspensions generated by 120 min. of sonication. (b) Histogram corresponding to statistical analysis of nanolayers found from solutions resulting from sonication of CMP-3 during 120 min.

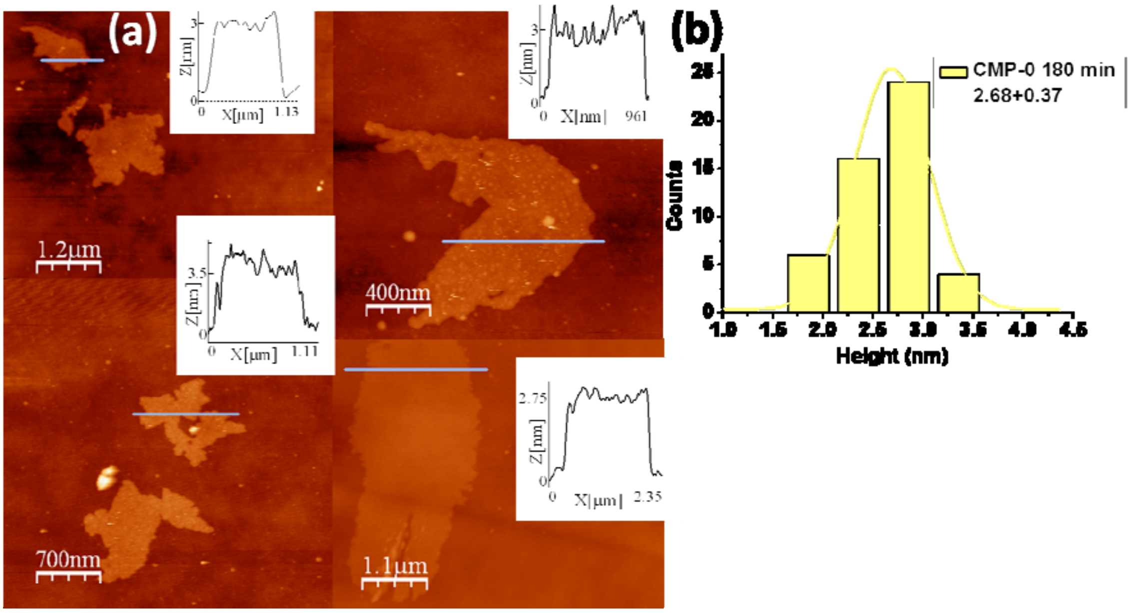

Fig. S.I.15 (a) Representative AFM images found for CMP-0 suspensions generated by 180 min. of sonication (b) Histogram corresponding to statistical analysis of nanloayers found from solutions resulting from sonication of CMP-0 during 180 min.

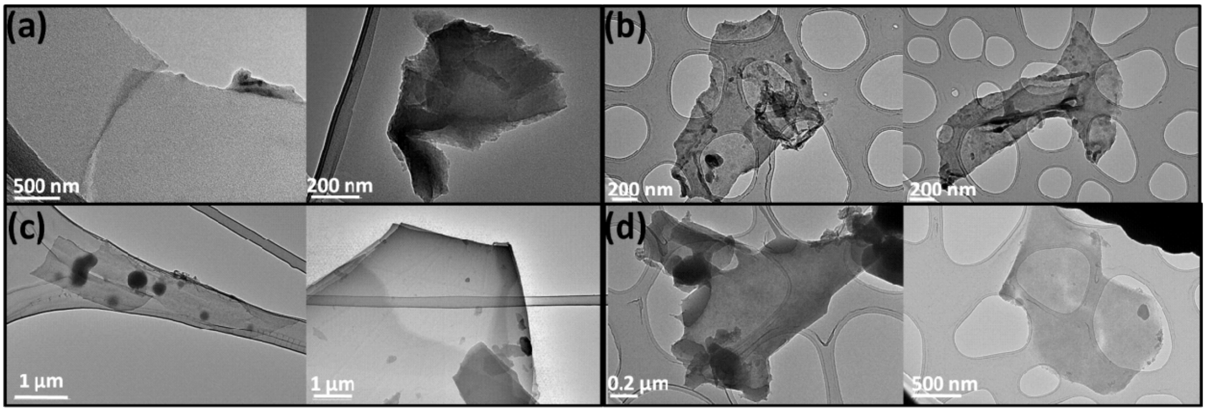

Fig. S.I.16. Representative TEM images found for suspensions generated by 45 min. of sonication of (a) CMP-0, (b) CMP-1, (c) CMP-2 and (d) CMP-3.

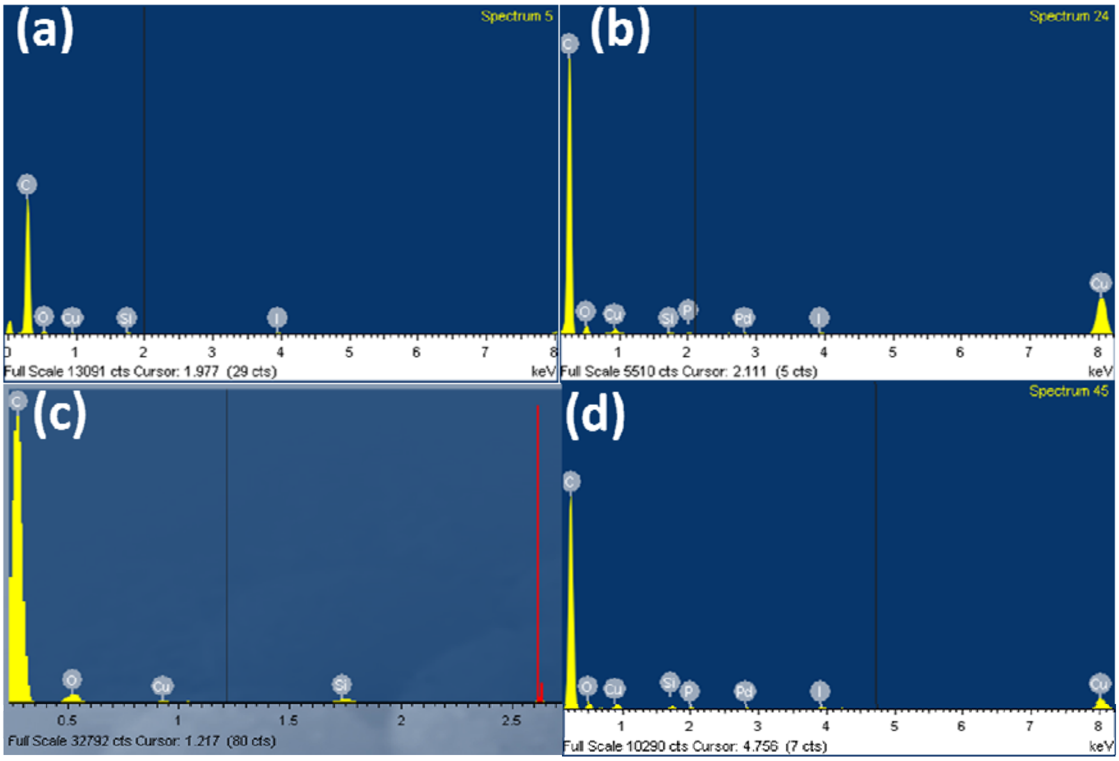

Fig. S.I.17 EDXS microanalysis of structures observed by TEM corresponding to sonication during 45 minutes of (a) CMP-0, (b) CMP-1, (c) CMP-2 and (d) CMP-3.