Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Nanostructures on Graphene using Supramolecule and Supramolecular Nanocomposites

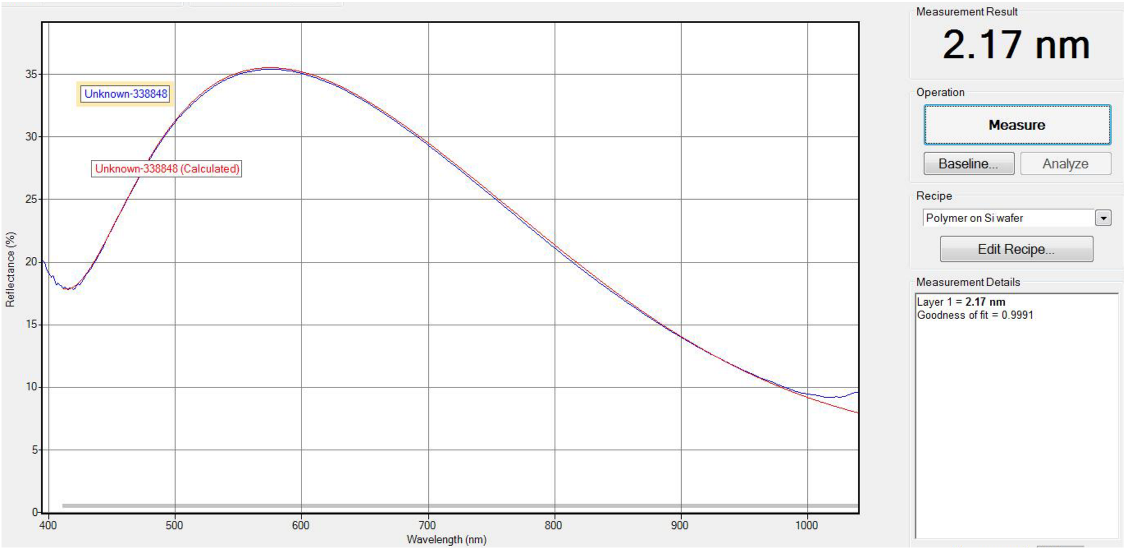
Peter Bai[a], Joseph Kao[a], Jian-Hao Chen[b‡], William Mickelson[b], Alex Zettl[b,c], Ting Xu*[a,c,d]

[a] Department of Materials Science and Engineering, University of California, Berkeley, Berkeley, CA, USA.
[b] Department of Physics, Univeristy of California, Berkeley, Berkeley, CA, USA.
[c] Materials Sciences Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA, USA.
[d] Department of Chemistry, Univeristy of California, Berkeley, Berkeley, CA, USA.
[*] Corresponding Author, Email: tingxu@berkeley.edu
‡ Current Address: International Center for Quantum Materials, Peking University, 6th Floor, Science Building 5, No. 5 Yiheyuan Road, Haidian District, Beijing, 100871, China

ESI 1. Film thickness measurements

The thickness of a graphene substrate before and after spin casting a PS-b-P4VP(PDP) supramolecule thin film is measured using a Filmetrics F20 interferometer. The film thickness reading for the substrate is a) ~2 nm before spin casting and b) ~60 nm higher after spin casting, indicating the formation of a 58 nm supramolecule thin film on graphene.

a)



Measurement Result

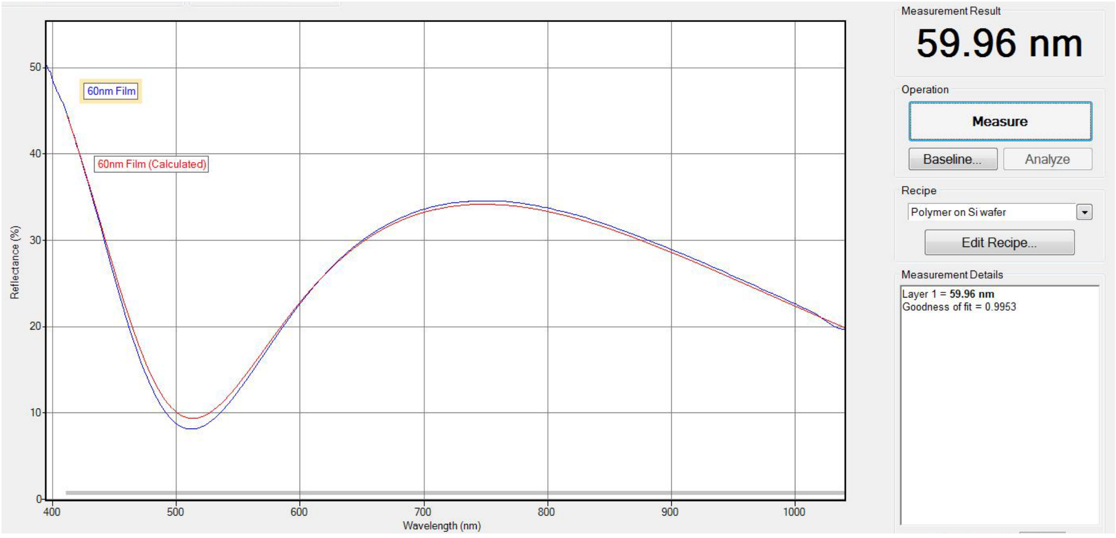
2.17 nm

Recipe: Polymer on Si wafer

Measurement Details

Layer 1 = **2.17 nm**
Goodness of fit = 0.9991

b)



Measurement Result

59.96 nm

Recipe: Polymer on Si wafer

Measurement Details

Layer 1 = **59.96 nm**
Goodness of fit = 0.9953

ESI 2. Experimental Details

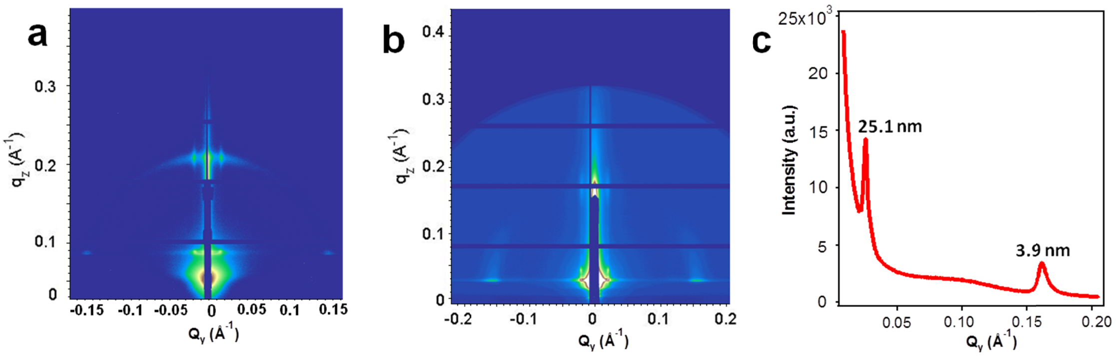
Materials: PS(19,000)-b-P4VP(5200) (PDI = 1.09) and PS(24,000)-b-P4VP(9,500) (PDI = 1.10) are purchased from Polymer Source, Inc. 3-n-Pentadecylphenol (95%) was purchased from Acros. 4-(4'-butylphenyl diazenyl)phenol was purchased from Sigma Aldrich. Chloroform was purchased from Fisher. All chemicals were used as received. Au NPs were synthesized using a method described by Sun et al [1]. Graphene is obtained by chemical vapor deposition (CVD) on polycrystalline copper (99.8 % Alfa Aesar, Ward Hill, MA) with a growth temperature 1035 °C [2]. After synthesis, the one side of the graphene-on-copper sample is coated with polymethyl methacrylate (PMMA). The copper foil is then etched away by soaking the sample in an aqueous solution of 100 mg/mL sodium persulfate ($Na_2S_2O_8$) for approximately three hours. The resulting graphene, supported by PMMA, is then transferred to a silicon substrate with a 300 nm SiO2 dielectric layer. The PMMA is subsequently removed by soaking in hot acetone. The experiments were also reproduced on CVD-grown graphene deposited on Si wafers (with 285 nm SiO_2 layer) purchased from Graphene Laboratories Inc.

Nanocomposite Thin Film Preparation: The BCP supramolecule is prepared by separately dissolving PS-*b*-P4VP and PDP in $CHCl_3$ at 15 mg/mL concentration. The PDP solution is then added dropwise to the PS-*b*-P4VP solution while stirring to achieve the desired P4VP:PDP molar ratio. The mixture is stirred for a further 12 hours to allow for the formation of P4VP-PDP hydrogen bonds. The supramolecule solution is mixed with a 20 mg/mL NP solution in $CHCl_3$ to form the nanocomposite solution. The nanocomposite solution is spuncast onto the graphene-coated substrate at a spinning rate of ~3,000 rpm for 10 s to form a BCP/NP nanocomposite thin film on graphene. The thickness of the film is measured using a Filmetrics F20 interferometer. For solvent annealing, nanocomposite thin film samples are suspended in a 250mL top-capped jar at room temperature. 200-300uL of $CHCl_3$ is injected into the jar, which is immediately sealed for 12-15 minutes to allow $CHCl_3$ to vaporize and swell the thin film. The cap is then opened to allow the $CHCl_3$ to freely evaporate. The PDP small molecules are removed by depositing 50 μL of isopropyl alcohol onto the film, followed by spinning at 3,000 rpm for 10 s.

Characterization: Sample thicknesses were measured using a Filmetrics F20 interferometer. Tapping mode Atomic Force Microscopy (AFM) images are taken on a Digital Instruments BioScope with a Nanoscope IIIa controller using silicon cantilevers (RTESP from Veeco Inc.) with a resonant frequency of 300-350 kHz. Transmission Electron Microscopy (TEM) images are taken on a FEI Tecnai 12 TEM at an accelerating voltage of 120 kV. The thin film TEM samples are prepared by cutting the spuncast wafers into ~2mm by 2mm pieces and floating the pieces on top of a 5v% aqueous solution of hydrofluoric acid (HF) solution. The HF etches away the SiO_2 within minutes, thereby detaching the nanocomposite and graphene layers from the underlying Si substrate. The detached films are collected onto carbon-coated 200 mesh copper grids from Ted Pella Inc. for top view TEM and onto epoxy resin (Araldite 502, Electron Microscopy Sciences) for cross-sectional TEM. For cross-sectional TEM samples, the epoxy with the thin film sample are cured at 60°C for 12 hours to ensure good contact between the epoxy and the nanocomposite thin film. The sample is then cut into ~60 nm thin sections using an RMC MT-X Ultramicrotome (Boeckler Instruments) and collected on copper grids. TEM samples containing supramolecule alone are stained using iodine vapor for 30 min to highlight the P4VP(PDP) microdomain as darker regions. Grazing Incidence Small Angle X-ray Scattering (GISAXS) is taken at Beamline 7.3.3 of the Advanced Light Source at Lawrence Berkeley National Laboratory and at Beamline 8-ID-E of the Advanced Photon Source at Argonne National Laboratory. X-ray energies of 10 keV and 7.35 keV were used. The scattered beam was collected using a Pilatus 1M X-ray Si pixel detector. Line averaged intensities are reported as I vs. q, where $q = (4\pi/\lambda)\sin(\theta/2)$, where λ is the incident X-ray wavelength and θ is the scattering angle.

SI 3. GISAXS of PS-*b*-P4VP(PDP) with perpendicular cylindrical thin film on graphene

The GISAXS pattern of a PS(24,000)-*b*-P4VP(9,500)(PDP)$_2$ thin film with perpendicular cylindrical morphology (a) and a PS(19,000)-*b*-P4VP(5,200)(PDP)$_{1.7}$ thin film with parallel cylindrical morphology (b) are shown below. Distinct scattering peaks at $q_y \sim 0.15$ Å^{-1} are visible in both GISAXS patterns. A horizontal linecut along the q_y axis shows the peaks at $q_y \sim 0.155$ Å^{-1}, which corresponds to the PDP lamellae lateral periodicity of 4.1 nm, suggesting a layer of perpendicularly oriented PDP small molecules and the graphene/film interface.



References

1. S. Peng, Y. Lee, C. Wang, H. Yin, S. Dai and S. Sun, *Nano Res.*, 2008, 1, 229-234.
2. X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. K. Banerjee, L. Colombo and R. S. Ruoff, *Science*, 2009, 324, 1312-1314.