Supplementary Information

Controlling the Surface Chemistry of Graphite

by Engineered Self-Assembled Peptides

*Dmitriy Khatayevich, Christopher So, Yuhei Hayamizu, Carolyn Gresswell, and Mehmet Sarikaya**

GEMSEC, Genetically Engineered Materials Science and Engineering Center
Materials Science and Engineering, Roberts Hall, Box: 352120,
University of Washington, Seattle, WA, 98195, USA

*Contact Author: sarikaya@u.washington.edu

Table of Contents:

1) Detailed experimental procedure

Materials: Peptides were prepared on an automated solid-phase peptide synthesizer (CS336X, CSBio Inc., Menlo Park, CA) employing standard batch-wise Fmoc chemistry procedures as reported previously. The synthesis was verified by MALDI-TOF mass spectrometry (Figure S1).

Surface Modification: Samples for contact angle measurements were prepared on HOPG pieces no smaller than 5mm by 5mm. The surfaces were prepared by removing a layer of graphite *via* scotch tape. An 80µl drop of the appropriate 1µM peptide solution in water was placed on the surface for times ranging from 10min to 5hrs. The drop was wicked with tissue and the sample dried in a nitrogen stream. The samples were allowed to equilibrate in air for 30min prior to contact angle measurements.

Contact Angle Measurements: Static contact angles were measured using an FTA1000B Goniometer (First Ten Angstroms, Inc., Portsmouth, VA) with an automatic camera system by placing 2µl of the same solution as was used to produce the sample in two different locations on each surface. The measurement was made immediately. The liquid surface tension was determined by pendant drop shape method, and was found not to vary significantly for different solutions (Table S1). In all, two measurements were taken on two different samples for each data point. The samples were then dried with nitrogen and the coverage was measured by AFM.

AFM measurements: Atomic force imaging was carried out on a Digital Instruments (Veeco, Santa Barbara, CA) Multimode Nanoscope IIIa scanning probe microscope equipped with high frequency NanoSensors PPP-NCHR (NanoandMore USA, Ladys Island, SC, USA) non-contact probes, with a 42 N/m spring constant. Coverage was determined by image analysis of at least two 0.5µm x 4µm areas in at least three parts of each sample.

2) Mass spectrometry of peptides

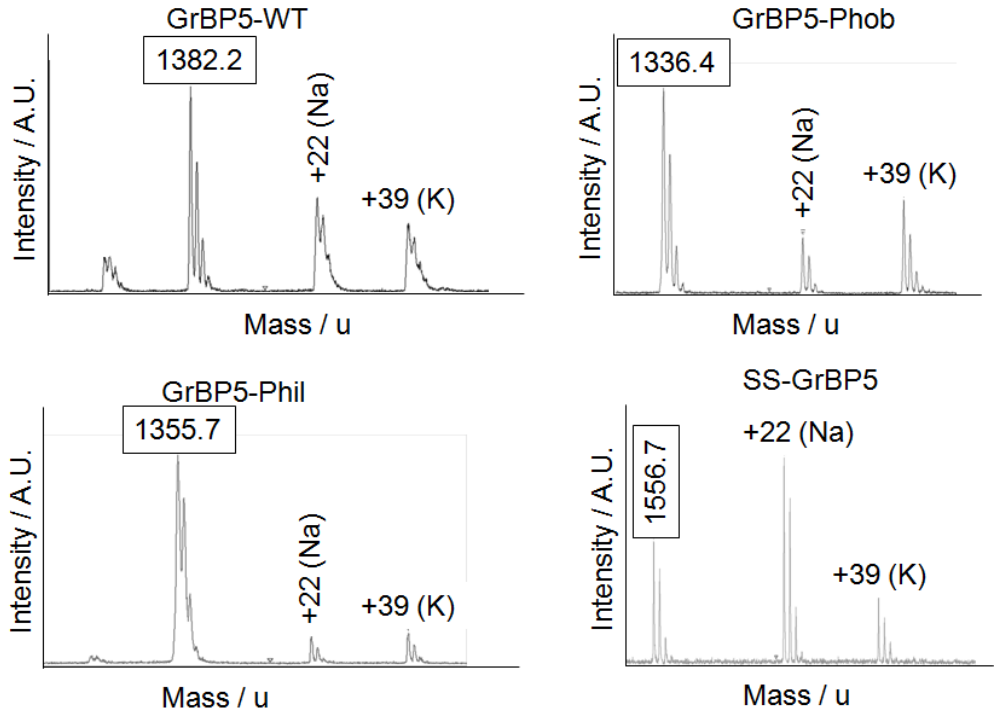

Figure S1: Mass spectra of the purified peptides used in all experiments; all significant peaks shown; expected mass of the peptide is outlined.

3) Normalization of peptide coverage and application Cassie's Law

Young's equation indicates that the surface energy varies linearly with the cosine of the contact angle:

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}$$

It is possible to model the contact angle of a more complex surface by linear addition of the weighted contributions of their constituents, as is shown by Cassie's law.

$$\cos\theta = \varphi_1 \cos\theta_1 + \varphi_2 \cos\theta_2$$

Where, ϕ_n and θ_n are the coverage and surface energy associated with each constituent respectively, it is possible, therefore, to normalize the contact angles with respect to coverage of each peptide, and to extrapolate the hydropathy of a theoretical fully covered surface, as long as the two displayed phases have uniform and distinct properties and no superhydrophobic effect is taking place.

Samples of varying coverage were prepared to contain either the ordered or disordered phases as determined by AFM and subjected to contact angle measurement. Figure 3 shows the relationship between contact angles and coverage for ordered and disordered domain for each mutant. The relationship between the coverage and cosine of the contact angle was linear over the range of coverages produced, indicating that no superhydrophobicity was occurring, justifying the assumptions of Cassie's law. Furthermore, by introducing a third term ($\varphi_3 \cos(\theta_3)$, the analysis could be extended to a three part system (Figure 4).

4) Amorphous versus ordered phase roughness comparison

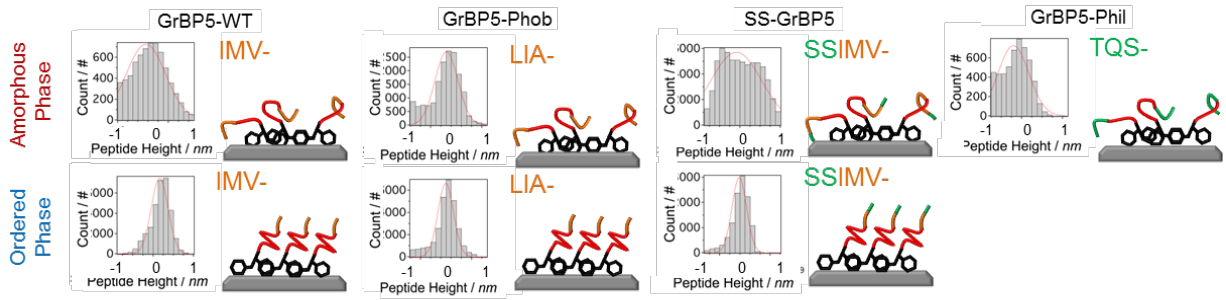

Figure S2: Height distributions of various peptide sequences as measured by AFM. The distribution is wider for the amorphous phases than the ordered phases in the case of each peptide, indicating that the display is more uniform in the ordered phase. The schematics illustrate the postulated peptide conformation.

5) Liquid surface tension data

Table S1: Interfacial tension calculated from at least 3 pendant drop shapes. The results indicate that there is no significant difference in the interfacial energies of various peptide solutions and that the contact angle measurements, therefore, can be compared directly.

Liquid (1μM solutions in water)	**Interfacial Tension / mN m^{-1}**
Water	72.8 ± 0.4
GrBP5-WT	69.5 ± 0.2
GrBP5-Phob	69.6 ± 0.4
GrBP5-Phil	68.2 ± 0.8
SS-GrBP5	69.1 ± 0.3

6) Verification of assembly of SS-GrBP5.

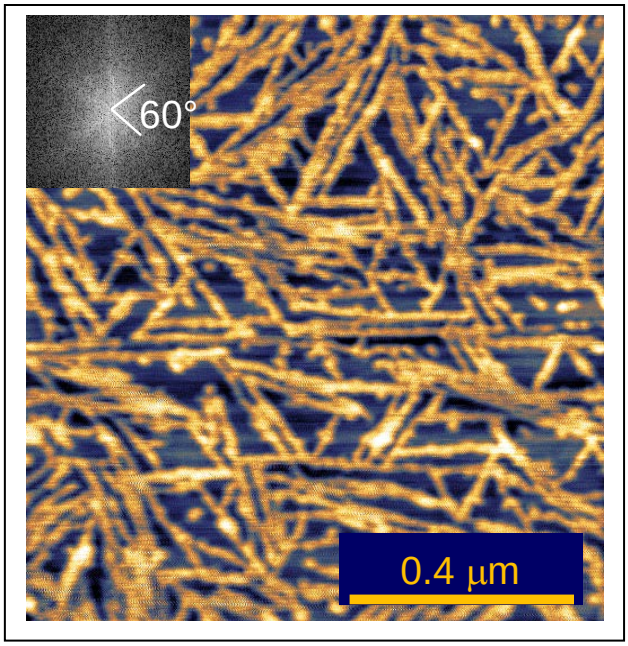

Figure S3: AFM image of ordered SS-GrBP5. The sample was prepared by incubation with 1µM SS-GrBP5 solution for 30min, via procedures described above. The inset is the Fast Fourier Transform of the image, showing six-fold symmetry.