†Electronic Supporting Information

Superhydrophobic states of 2D nanomaterials controlled by atomic defects modulate cell adhesion

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Experimental Methods

Materials & Synthesis: Defect-rich MoS_2 nanoassemblies were synthesized by dissolving Hexaammonium heptamolybdate tetrahydrate, $(NH_4)_6{\cdot}Mo_7O_{24}{\cdot}4H_2O$ and Thiourea, NH_2CSNH_2 (procured from Alfa Aesar) in 35 mL of deionized water. This solution was then autoclaved at 220°C for 18h. After the solution cooled down to room temperature, the MoS_2 was washed with water and ethanol several times and dialyzed against ultrapure water to remove unreacted reagents and other impurities. To synthesize all the compositions of MoS_2 nanoassemblies (1:1, 1:2, 1:4, and 1:6) the molar ratios of the reagents were accordingly varied, (e.g. 1:1 MoS_2 was synthesized using 1 mmol of $(NH_4)_6{\cdot}Mo_7O_{24}{\cdot}4H_2O$ and 7 mmol of thiourea).[1, 2]

Morphological Characterizations: For morphological of MoS_2 nanoassemblies and transverse section of coated film were obtained using FEI Quanta 600 field emission-scanning electron microscopy (FE-SEM). Typically, the operational voltage was maintained between 15 to 20 keV with secondary electron mode selected. Prior imaging samples were exposed to Pt/Pd plasma coating of the thickness of approx. 8 nm to enhance surface conductivity. For transmission electron microscopy (TEM) images and selected area electron diffraction (SAED), JEOL 2010 operated at 200 keV was used. For sample preparation, aqueous dispersion of MoS2 samples were drop-casted and air-dried on copper grid (procured from Ted Pella Inc.). Raman spectra is strong tool to confirm the crystallographic phase composition of the 2D MoS_2 nanoassemblies. Solid powder samples (1:1 to 1:6) were placed

on glass slides and were excited by 532 nm green laser to obtain Raman spectra (LabRam HR confocal Raman microscope, Horiba Inc. Japan).

XPS analysis: The X-ray photoelectron spectroscopy (XPS) data for the samples were recoded using Omicron DAR 400 model equipped with Argus detector at 0.8 eV resolution. The magnesium source (Kα, 1253.6 eV) was used for X-ray radiation and binding energies (BE) for molybdenum characteristic peaks at $3d_{5/2}$ and $3d_{3/2}$ while for Sulfur $2p_{3/2}$ and $2p_{½}$ were analyzed for all the four MoS_2 samples. Fityk software with Voigt distribution was used for deconvolution of the energy bands. The acquired spectra were calibrated for adventitious carbon (C 1s, 484.8 eV) as reference.

Calculation of active sites by cyclic voltammetry: Cyclic voltagram was performed for the calculation of active sites in the samples following the standard protocol with minor modifications.[3] For this study, a three-electrode configuration was used. During the measurements, a glassy carbon electrode (GCE, diameter ϕ = 2 mm), a platinum wire, and an Ag/AgCl (KCl saturated) electrode were used as the working, the auxiliary and the reference electrode, respectively. Prior, experiments, the electrodes were properly cleaned by polishing with different Alpha-alumina powder (1.0 and 0.3 micron and 0.05 micron provided by *CH Instruments*) suspended in ultrapure water on a Nylon polishing pad (*CH Instruments*). After polishing with different alumina powder, the electrodes were thoroughly rinsed with water. The electrodes were further sonicated with water and ethanol for 5 min to make them clean properly. Electrochemical measurements were carried out using an electrochemical workstation (Model No. CHI-660D instrument). All MoS_2 samples (labeled 1:1, 1:2, 1:4, 1:6) were then deposited on the glassy carbon electrode as working electrode. Typically, 10 mg mL^{-1} of each sample was dispersed in ultrapure water and 50 µg of the sample was deposited on the GCE and dried it at room temperature. The active sites were calculated by taking the absolute components of voltammetric charges (cathodic and anodic) from the Cyclic Voltammetry scan between -0.2 and 0.6 V (vs. RHE) with 50 $mV.s^{-1}$ scan rate in phosphate buffer solution (pH~7.0) and shown in Fig. S1. By considering one electron redox process was occurred during the reaction; therefore, the total charges were divided by two. The number of active sites was obtained for the sample deposited on the electrode by using the following equation.
Number of active sites (mol/g), n = Q/2F, where F: Faraday constant (C mol^{-1}); Q: Voltammetric charges.

Contact Angle Measurement: A sessile droplet goniometer (KSV CAM200) equipped with optical imaging system was used to determine contact angle on surface. First MoS_2 were deposited on required surface (glass, silica, rubber, or paper) using solvent deposition/evaporation approach. Each measurement was performed thrice at the interval of 5 seconds of which the average was considered. Using automated dispenser, droplet (~volume was 5uL) which was allowed to rest on the substrate coated with MoS_2 before recording the data.

Surface roughness with AFM: The microscopic roughness analysis of all the four MoS_2 compositions (1:1 to 1:6) was carried out using atomic force microscopy (AFM) to ascertain the contribution to hydrophobicity from the topographical features. 20 by 20 µm area was imaged for each composition and the value for root-mean square roughness (R_q) was

calculated for 400 μm^2 and 25 μm^2 projected area using the software NanoScope Analysis version 1.9 (Bruker Inc.).

Cellular adhesion: Human mesenchymal stem cell (hMSC) cells (Lonza, passage 3) were incubated on the substrate coated with MoS_2 (1:1) and (1:6) samples. In brief, predefined quantity of working reagent was added to the wells in triplicates coated with the sample in a 96-well plate. The experiments were carried out with and without the addition of serum. 24h later, the imaging was carried out using Scanning electron microscope (SEM, Quanta 600) after cells fixation.

Platelet activation: The MoS_2 samples (1:1, 1:2, 1:4, 1:6) were coated on a glass coverslip in triplicate and placed in a 12-well plate. The samples were then incubated with coagulation activated bovine blood (supplemented with $CaCl_2$ and sodium citrate) at 37 ˚C for predefined time interval. The SEM imaging of the platelets on the sample surface was done by critical point drying of the samples incubated with blood in HMDS followed by serial dehydration in alcohol subsequently fixing the cells in 2.5% glutaraldehyde.

Live Subject Statement: All the blood related experiments were carried out in compliance with ethics and guidelines set by Texas A&M University Institutional Animal Care and Use Committee. The Citrate Phosphate Dextrose Adenine Solution, USP (CPDA-1) anticoagulant treated bovine blood was obtained from the Veterinary Medical Park on campus. The blood was drawn following the protocol titled 'Copy of Veterinary Medical Park of Blood Donors and Feeding Animals' (AUP no. 2017-0059) as approved by the Texas A&M University.

Size-distribution histograms (obtained from SEM):

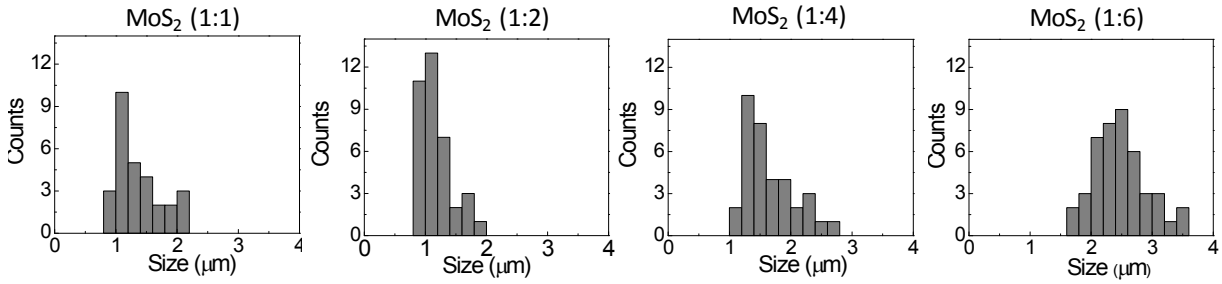

Figure S1: The size-distribution presented by histograms shows the cumulative counts of three pictures for each sample from 1:1 to 1:6. The representative images are presented in figure 1c. The results indicate the avg. size to be about 1.5-3 μm for each nanoflower with slight rise due to increase in sulfur precursor from MoS_2 (1:1) through MoS_2 (1:6).

References:

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