Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information for

A transient component of Solid Electrolyte Interphase in the Li-ion battery

Sergey Yu. Luchkin, Egor M. Pazhetnov*

Center for Energy Science and Technology, Skolkovo Institute of Science and Technology, Moscow, Russia

*Email: s.luchkin@skoltech.ru

EXPERIMENTAL PROCEDURES

SAMPLE PREPARATION

ZYA grade HOPG was purchased from TipsNano (Estonia). The HOPG was mounted onto a steel AFM substrate with conductive silver paint and sealed along perimeter with chemically stable Bisphenol A/F epoxy resin HT2 with hardener HT2 (R&G Faserverbundwerkstoffe GmbH, Germany). Freshly cleaved mounted HOPG samples was placed into the perfusion cell of a Cypher ES AFM (Oxford Instruments Asylum Research) installed inside an Ar filled glove box (MBraun) with $O_2 < 0.1$ ppm and $H_2O < 0.1$ ppm. [1] An external potentiostat/galavanostat (BioLogic SP 150) was connected to the microscope. The sample was connected as the working electrode and a Li foil (Gelon, China) was connected as a reference and a counter electrode in a two electrode configuration. An electrolyte solution was injected into the cell and after that cycling voltammetry was performed at 0.2 mV/s cycling rate. After cycling the samples were washed in DMC/DEC for 10 minutes and then gently rinsed with DMC/DEC using a pipette. Surface of the cycled and washed

HOPG samples was cleaved by the adhesive scotch tape in order to expose the subsurface graphite layers.

1M $LiPF_6$ in EC/DMC=50/50 (v/v)) commercial battery grade electrolyte solution (Sigma Aldrich) was used as received without additional dehydration. 1M $LiPF_6$ in PC electrolyte solution was prepared by dissolving $LiPF_6$ salt (Sigma-Aldrich, >99.99%) in anhydrous propylene carbonate (Sigma Aldrich).

A thermally lithiated HOPG was prepared as follows: a piece of pristine HOPG was wrapped into Li foil (Gelon, China), placed into a steel crucible, and heated at 200 °C for 2 hours on a hotplate inside an Ar-filled glovebox.

SAMPLE CHARACTERIZATION

IN-SITU OPTICAL MICROSCOPY

The optical microscope integrated into the AFM was used to monitor the samples surface evolution upon CV cycling.

ATOMIC FORCE MICROSCOPY (AFM)

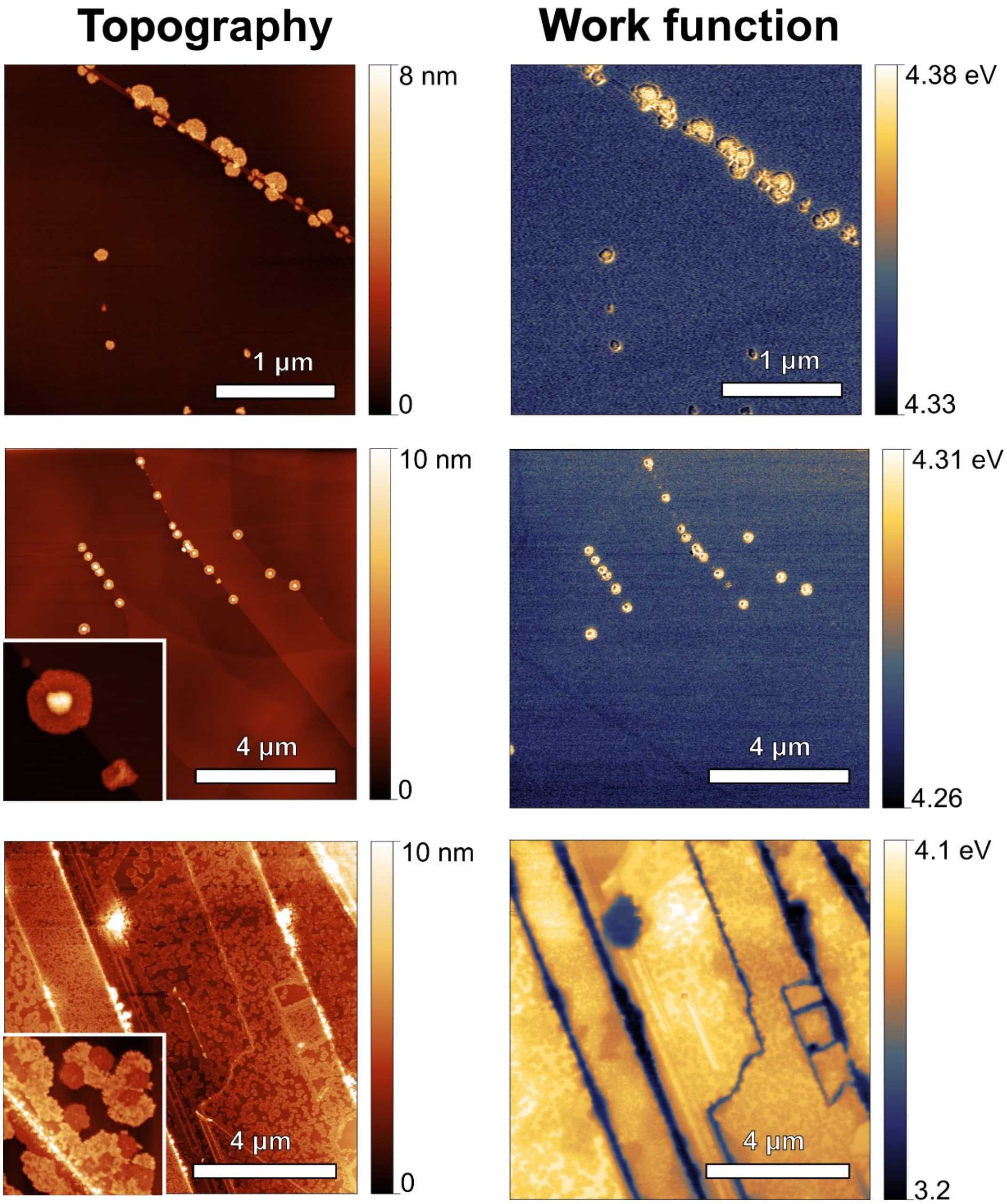
AFM measurements were performed using the Cypher ES microscope (Asylum Research, Oxford Instruments) installed inside the Ar filled glove box (MBraun) with $O_2 < 0.1$ ppm and $H_2O < 0.1$ ppm. A W_2C coated Si cantilever with 3.4 N/m spring constant and 110 kHz resonance frequency was used for Kelvin Probe Force Microscopy implemented in a 2-pass amplitude modulation mode with the second pass height of 20 nm and 0.5 V_{AC} potential applied to the tip. The sample was grounded. The cantilever was calibrated on a freshly cleaved HOPG (4.6 eV work function [2]).

RAMAN SPECTROSCOPY

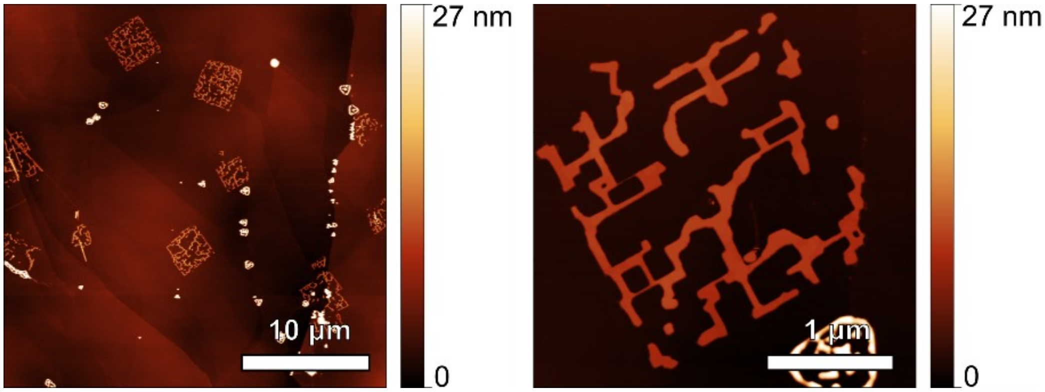
Raman spectroscopy were performed using DXRxi Raman Imaging Microscope (Thermo Fisher Scientific). The lithiated HOPG sample was sealed between two pieces of glass in the Ar-filled glovebox and quickly moved to the Raman microscope (<2 min) in order to minimize impact from ambient water and oxygen.

X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

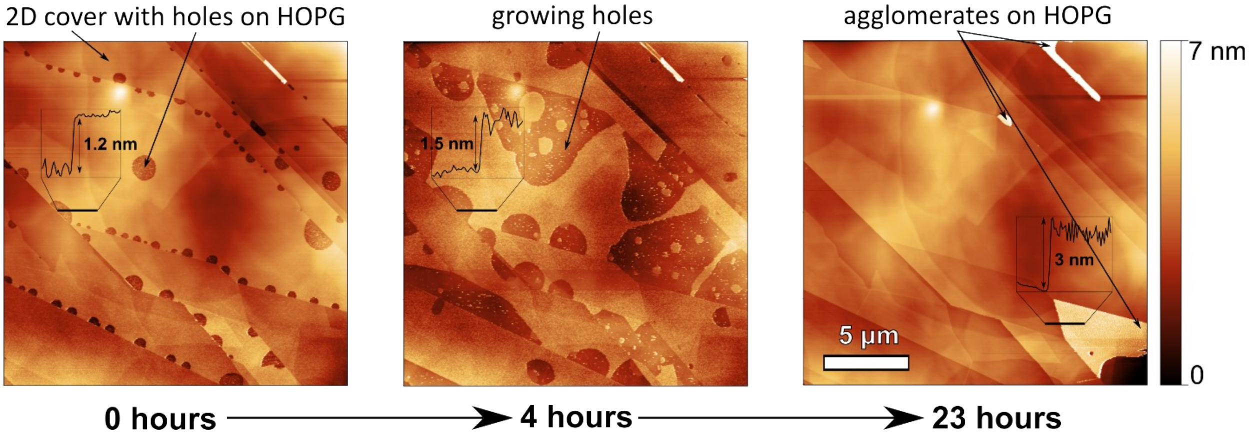
The cleaved parts of the cycled and washed HOPG samples attached to the scotch tape were mounted onto an XPS holder and placed into a sealed XPS transfer chamber in order to avoid contact with ambient atmosphere. The process was carried out in the Ar filled glove box. The transfer chamber was transferred into the XPS chamber. XPS measurements were performed using PHI 500 VersaProbe II spectrometer (ULVAC-PHI) with spherical mirror analyzer. Al Kα monochromatic x-ray source with 1486.6 eV X-ray energy was utilized. A base pressure in analysis chamber was of $5x10^{-10}$ Torr and a working pressure was $< 5x10^{-9}$ Torr. Charge compensation with flood electron gun was used to compensate positive charge occurred with photoelectron process. Survey and high-resolution spectra were recorded with 1.0 eV and 0.1 eV steps respectively. High-resolution XPS spectra were processed to obtain atomic concentrations, following a usual procedure for XPS spectra quantifications. Photoelectron backgrounds were subtracted from the high resolution spectra using Shirley function approximation. Element concentrations were calculated using integrated peak intensities and atomic sensitivity factors from the PHI instrumentation software The binding energy scales for the high resolution spectra were calibrated with the HOPG main C1s peak set to 284.4 eV.



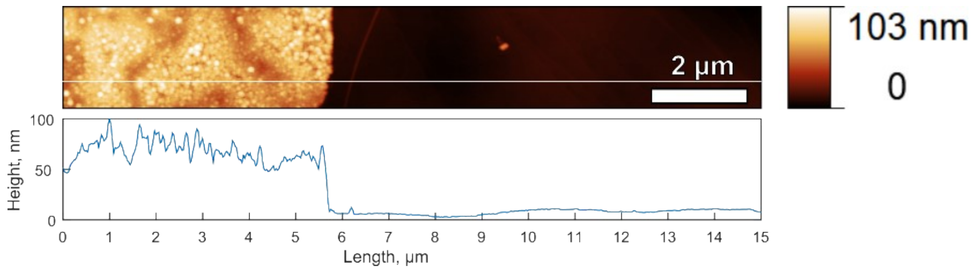
Supporting Figure 1. Typical AFM topography and work function images of cleaved HOPG after Li(solv) cointercalation upon the first CV cycle vs Li^+/Li in a two electrode configuration.



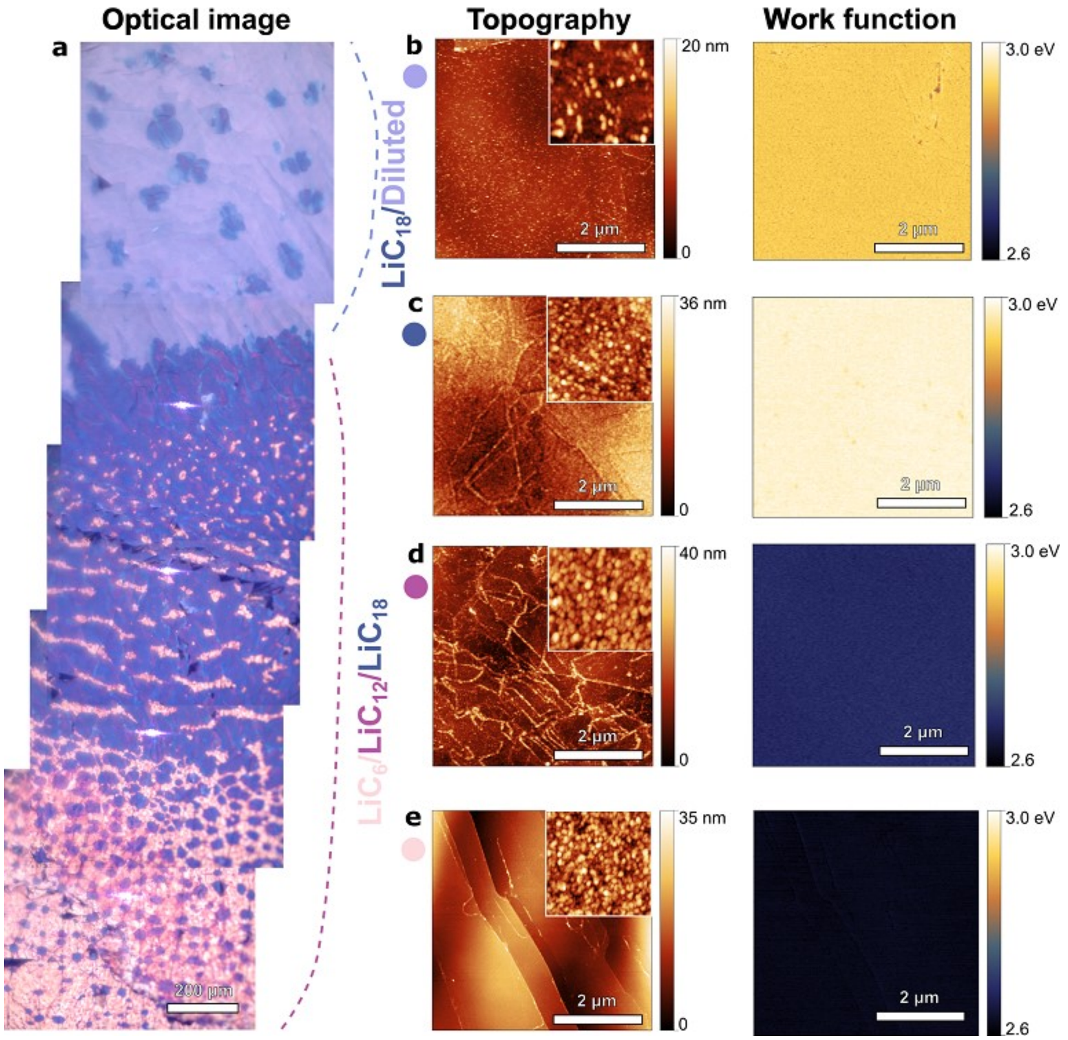
Supporting Figure 2. AFM topography images of the reduced Li(solv) products on the cleaved cycled HOPG after prolonged storage (about two months) inside the Ar-filled glove box.



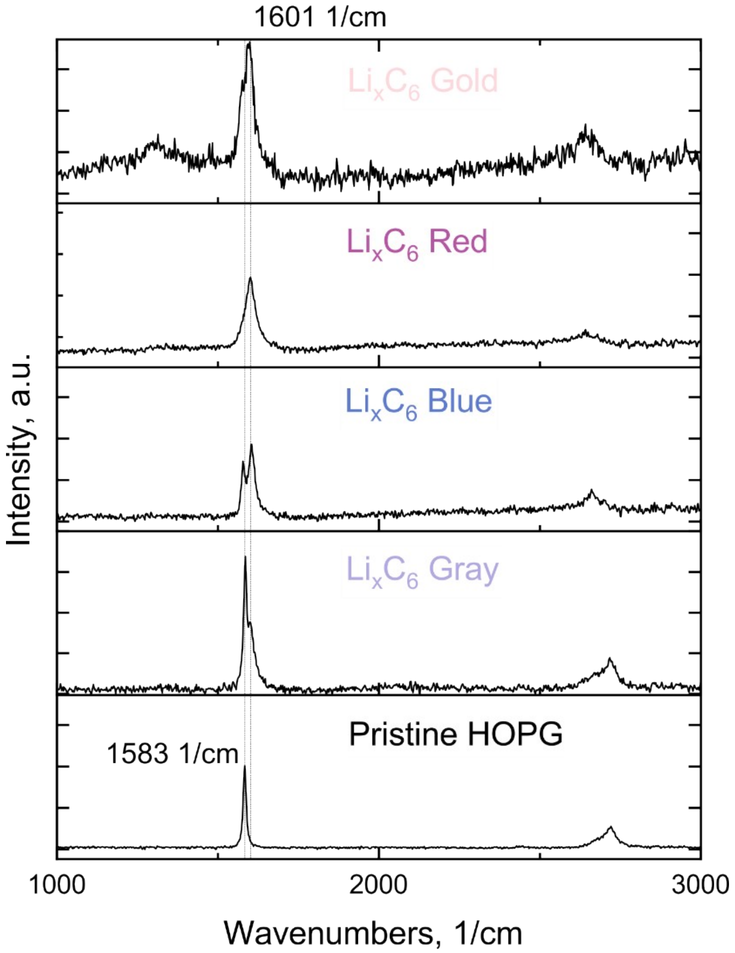
Supporting Figure 3. AFM topography images illustrating dynamics of agglomeration of a layer of intercalated unreduced Li(solv) on cleaved HOPG cycled to 1 V vs Li^+/Li. Left to right: (0 hours) covered HOPG surface with small dewetting spots, (4 hours) dewetting cleans up the HOPG surface, (23 hours) agglomerated droplets. Thickness of agglomerations after 23 hours after cleavage is about 3 times larger than the initial one, while the covered area is about 20 times smaller, which implies volatilization of the larger part of the intercalated material.



Supporting Figure 4. AFM topography of a HOPG illustrating thickness of the cleaved layer. Left part was not cleaved, right part was cleaved.



Supporting Figure 5. Thermally lithiated HOPG consisting of Li_xC_6 at different stages of lithiation as represented by color. Optical microscopy image of different stages and corresponding AFM topography and work function images.



Supporting Figure 6. Raman spectra of the thermally intercalated HOPG collected at different spots corresponding to different stages of Li intercalation.

References:

(1) Luchkin, S. Y.; Lipovskikh, S. A.; Katorova, N. S.; Savina, A. A.; Abakumov, A. M.; Stevenson, K. J. Solid-Electrolyte Interphase Nucleation and Growth on Carbonaceous Negative Electrodes for Li-Ion Batteries Visualized with in Situ Atomic Force Microscopy. *Sci. Rep.* **2020**, *10*, 1–10.

(2) Kawano, H. Effective Work Functions of the Elements: Database, Most Probable Value, Previously Recommended Value, Polycrystalline Thermionic Contrast, Change at Critical Temperature, Anisotropic Dependence Sequence, Particle Size Dependence. *Prog. Surf. Sci.* **2022**, *97*, 100583.