Spontaneous Selective Deposition of Iron Oxide Nanoparticles on Graphite

Supporting information

Chathura de Alwis¹, Timothy R. Leftwich²,
Pinaki Mukherjee², Alex Denofre¹, Kathryn A. Perrine¹,*

¹Department of Chemistry, ²Department of Material Science & Engineering, Michigan Technological University, Houghton, MI 49931

FESEM images of the graphene coated lacy carbon 300 mesh copper grid, before and after iron oxide deposition, and after annealing in air at 400 °C. Before deposition (A), the lacey carbon is observed in the regions between the copper grid. After exposure to the FeCl₂(aq) solution (B), the graphene coated lacy carbon becomes coated with iron oxide after rinsing with water. After annealing (C), the iron oxide nanoparticles become visible among large mesoparticles of iron oxide. The nanoparticles were imaged using STEM, as a reasonable representation of the nanoparticles observed on the defects on the HOPG surface.

Figure S1: FESEM images of the A) graphene coated lacey carbon (Cu) TEM grids, B) after iron oxide deposition at room temperature, and C) after subsequent annealing at 400°C for 2 hours. The iron oxide nanoparticles on the grid were imaged using STEM after annealing (red arrow).
AFM was used to image the HOPG and sputtered HOPG samples. The room mean squared (RMS) of select areas was analyzed as a measure of surface roughness.

Figure S2: AFM images of A) unsputtered HOPG, B) Ar$^+$ sputtered HOPG and C) Ga$^+$ FIB sputtered HOPG (in 1 μm area). The RMS measurements were A) 104 +/- 23 pm, B) 195 +/- 38 pm, and C) 1.44 +/- 0.45 nm, respectively.

FESEM images comparing the iron oxide nanoparticles grown on HOPG defects and annealed separately to 400 °C and then 500 °C. Large channels are etched into the HOPG surface, beginning at the defects at 500 °C.

Figure S3: FESEM images of annealed iron oxide nanoparticles on HOPG. Channels are formed in the terrace after annealing to 500 °C in air.
XPS of the O1s region before and after sputtering is analyzed for the freshly cleaved HOPG surface. The sample was Ar⁺ sputtered and exposed to air for 1 hour. This data suggests the O1s peak at 532.4 eV and 533 eV (from Ga⁺ FIB sputtering) is from air oxidation and reacts with the carbon defects (dangling bonds) on the sputtered HOPG surface.

Figure S4: O1s region shows no/little O1s signal on HOPG after air exposure. After sputtering with either Ar⁺ or Ga⁺, the surface oxidizes, presumably from exposed dangling carbon bonds. The O1s signals of the samples after FeCl₂(aq) exposure indicates that the Fe-OH peak is from either air oxidation (sputtered HOPG) or iron nanoparticle formation (sputtered and unsputtered HOPG).
Freshly cleaved HOPG has three main peaks in the XPS C1s region. They are due to sp\(^2\) graphitic peak, sp\(^3\) defect peak and \(\pi-\pi^*\) shake up peak. The only significant differences observed between the HOPG and Ar\(^+\) sputtered HOPG are that the FWHM have increased. Peak broadening is expected on the Ar\(^+\) sputtering HOPG due to more defects on the surface.

Figure S5: The C1s region shows an increase in a minor component of a C-O species after iron oxide nanoparticles growth and annealing to 400 °C. There is broadening of the peaks in the C1s region of the sputtered HOPG sample, with a higher concentration of sp\(^3\) carbon, from the Ar\(^+\) sputtering. This peak decreases after annealing to 400 °C. No apparent features appear from the iron oxide nanoparticles in the C1s region.
Figure S6: Cl2p region shows no chloride was observed after iron oxide nanoparticles deposition on A) HOPG and B) Ar$^+$ sputtered HOPG, after rinsing with ultra-pure water.

Figure S7: EDS spectrum of a STEM image. The Fe:O ratio was computed as 2:3 indicating the particles are primarily hematite (Fe$_2$O$_3$ stoichiometry).