Supporting Information

Focused Electron Beam based Direct-Write Fabrication of Graphene and Amorphous Carbon from Oxo-Functionalized Graphene on Silicon Dioxide

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Materials and Methods

Graphite grade 3061 has been provided from Asbury Graphite Mills (USA). Potassium permanganate, concentrated sulfuric acid, hydrogen peroxide and sodium borohydride were purchased from Sigma Aldrich® (Germany). Double distilled water was obtained from Carl Roth® (Germany). All chemicals were used as obtained.

Ultrasonication was performed using a tip sonotrode from Bandelin, Germany, HD 3200, MS 73. Centrifugation was done with Sigma 4K15 centrifuge equipped with both 80 mL (21,000 RCF) and 200 mL beakers (13,000 RCF).

Preparation of oxo-G

Oxo-G dispersion was prepared according to the previously described procedure.\[S1]\,[S2],[S3]

Graphite (1 g; 83.33 mmol) was dispersed in 24 mL of cold (< 10 °C) sulfuric acid (98 %) and reacted overnight with potassium permanganate (2 g, 12.66 mmol). The potassium permanganate was slowly added to the graphite dispersion over a total time of 4 h and the reaction temperature was kept below 10 °C. In the next step 20 mL of diluted sulfuric acid (20 %) were slowly and continuous added over one hour. After that, doubly distilled water (100 mL, 16 hours) followed by hydrogen peroxide solution (40 mL, 5%, 0.5 h) were added. The obtained dispersion was washed by centrifugation and redispersion 6 times with water (10 min at 1,500 RCF). The pH of the final supernatant was neutral. Delamination was performed by 4 min of pulsed tip sonication (20 W; 2 s on 2 s off). The obtained dispersion was centrifuged 3 times (5 min at 1,500 RCF) to remove aggregated particles and then centrifuged at 13,000 RCF for 45 min to remove major amounts of nano-sized particles (supernatant removed). The temperature during purification process was around 25-30 °C which led to introduction of few defects (around 1% density of defects, derived from statistical Raman spectroscopy: \(I_D/I_G=1.5±0.7; \Gamma_{2D}=66±19\)).

FTIR spectra are as previously published, see literature.\[S4]\ TGA-MS data of the sample is presented in recent literature and in agreement with previous results justifying the chemical sketch of Figure 2A.\[S3]\ Elemental combustion analysis of the sample is given in ref. S3: C, 45%; N, 0.0%; H, 2.4%; S, 4.3%.

Preparation of films of flakes of oxo-G

Films of flakes of oxo-G on Si wafers with 300 nm grown SiO\(_2\) surface were prepared by Langmuir-Blodgett technique, as described before.\[S5]\ Statistical Raman spectroscopy (SRS) and Statistical Raman microscopy (SRM)

Raman spectra were recorded in the wavenumber range from 800 cm\(^{-1}\) to 3300 cm\(^{-1}\) using the confocal Raman spectrometer “LabRAM HR Evolution” (Horiba, Japan) (excitation wavelength = 532 nm). Spectra were recorded using a 100x objective (with a numerical aperture of 0.9). For statistical Raman spectroscopy (SRS) a motorized table (Märzhäuser, Germany) was used to generate two-dimensional maps. The scanning increment was 75 nm in x- and y-direction (below the optical resolution) for imaging (SRM). The full-width at half-maximum (FWHM, \(\Gamma\)) of the D-, G- and 2D-Raman bands were determined by the fit with single Lorentz-functions. For the determination of the density of lattice defects > 2000 spectra with an increment of scanning of 3 μm was used (SRS).\[S6]\
Table S1: BSE Simulation Data

<table>
<thead>
<tr>
<th>Primary Energy [keV]</th>
<th>BSE yield</th>
<th>R\textsubscript{99%} [nm]</th>
<th>A\textsubscript{99%} [\mu m\textsuperscript{2}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>15.0 %</td>
<td>60</td>
<td>0.01</td>
</tr>
<tr>
<td>5</td>
<td>12.7 %</td>
<td>260</td>
<td>0.22</td>
</tr>
<tr>
<td>10</td>
<td>13.2 %</td>
<td>870</td>
<td>2.35</td>
</tr>
<tr>
<td>15</td>
<td>15.8 %</td>
<td>1850</td>
<td>10.8</td>
</tr>
<tr>
<td>20</td>
<td>16.1 %</td>
<td>3450</td>
<td>28.8</td>
</tr>
<tr>
<td>30</td>
<td>16.4 %</td>
<td>7160</td>
<td>122</td>
</tr>
</tbody>
</table>

Table S1: Simulation of backscattered electrons using CASINO v2.42. Sample setup: 300 nm SiO\textsubscript{2} on Si, 10\textsuperscript{6} electrons. R\textsubscript{99\%} and A\textsubscript{99\%} are the radius/area within which 99\% of BSE’s are emitted. BSEs exit closer to the point of impact of the primary beam for lower primary energies which leads to a higher density of secondary electrons type 2 (SE\textsubscript{II}). High densities of SEs correlate with the formation of lattice defects in oxo-G, while at low densities reduction of oxo-G to a graphene-like material is observed in Raman spectroscopy.

Figure S1: Thermal testing results

Figure S1: Scanning Raman maps of oxo-G patterned at elevated temperatures: 30 °C (top left), 40 °C (top center), 50 °C (top right), 60 °C (bottom center) show no pronounced differences, indicating that the reduction process is not a thermally activated process in the investigated temperature range.
References: