The synthesis and electrical transport properties of Carbon/Cr$_2$GaC MAX phase composite microwires

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Supplementary Information

Rietveld Refinement
Structural refinements were performed using Topas[1] and structure models from ICSD[2]. The refinement process started with the background polynomial (order: 10) and the sample displacement factor. For each identified phase, the lattice parameters and profile were alternately refined, until a R$_{wp}$ minimum was found. Atomic positions were subsequently refined. Lastly, thermal displacement factors (Beq) and occupancies were calculated, whereby only physically meaningful values were retained ($\geq 0$ and $\leq 1$, respectively).
For the profile, a modified Thompson-Cox-Hastings pseudo-Voigt function (pV-TCHZ) with the parameters $u$, $v$, $w$, and $x$ was used.
In the following, all refined parameters for FW and MW are presented separately. The phase fraction is given behind each phase in parentheses.

Furnace wires

Table S 1: Refined parameters of Cr$_2$GaC, based on XRD data. Errors shown in parentheses.

<table>
<thead>
<tr>
<th>Cr$_2$GaC (86.2(4) wt%)</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
<th>Beq</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr1</td>
<td>0.3333</td>
<td>0.6667</td>
<td>0.086(2)</td>
<td>0.926(6)</td>
<td>3.3(2)</td>
</tr>
<tr>
<td>Ga1</td>
<td>0.3333</td>
<td>0.6667</td>
<td>0.75</td>
<td>0.97(2)</td>
<td>3.9(3)</td>
</tr>
<tr>
<td>C1</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>1.00(8)</td>
<td>16(2)</td>
</tr>
<tr>
<td>a /Å</td>
<td></td>
<td></td>
<td></td>
<td>2.8923(3)</td>
<td></td>
</tr>
<tr>
<td>c /Å</td>
<td></td>
<td></td>
<td></td>
<td>12.606(2)</td>
<td></td>
</tr>
<tr>
<td>a$^{[3]}$ /Å</td>
<td></td>
<td></td>
<td></td>
<td>2.88</td>
<td></td>
</tr>
<tr>
<td>c$^{[3]}$ /Å</td>
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<td>12.61</td>
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<td>Crystallite size /nm</td>
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<td></td>
<td></td>
<td>190(7)</td>
<td></td>
</tr>
<tr>
<td>R$_{Bragg}$</td>
<td></td>
<td></td>
<td></td>
<td>0.978</td>
<td></td>
</tr>
<tr>
<td>R$_{wp}$</td>
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<td></td>
<td></td>
<td>4.37</td>
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</tbody>
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Table S 2: Refined parameters of Cr$_3$C$_2$, based on XRD data. Errors shown in parentheses.

<table>
<thead>
<tr>
<th>Cr$_3$C$_2$ (13.8(4) wt%)</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
<th>Beq</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr1</td>
<td>0.01991</td>
<td>0.2500</td>
<td>0.356(3)</td>
<td>1.00(5)</td>
<td>11(2)</td>
</tr>
<tr>
<td>Cr2</td>
<td>0.169(5)</td>
<td>0.2500</td>
<td>0.815(3)</td>
<td>1.00(6)</td>
<td>3(2)</td>
</tr>
<tr>
<td>Cr3</td>
<td>0.809(6)</td>
<td>0.2500</td>
<td>0.979(4)</td>
<td>1.00</td>
<td>3(2)</td>
</tr>
<tr>
<td>C1</td>
<td>0.24(7)</td>
<td>0.2500</td>
<td>0.17(4)</td>
<td>1.00</td>
<td>0</td>
</tr>
</tbody>
</table>
Microwave-wires

Table S 3: Refined parameters of Cr$_2$GaC, based on XRD data. Errors shown in parentheses.

<table>
<thead>
<tr>
<th>Cr$_2$GaC (82.1(1) wt%)</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
<th>Beq</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr1</td>
<td>0.3333</td>
<td>0.6667</td>
<td>0.086(2)</td>
<td>0.9(2)</td>
<td>2.2(2)</td>
</tr>
<tr>
<td>Ga1</td>
<td>0.3333</td>
<td>0.6667</td>
<td>0.75</td>
<td>1.00(8)</td>
<td>3.0(4)</td>
</tr>
<tr>
<td>C1</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.99(4)</td>
<td>4.2(4)</td>
</tr>
<tr>
<td>a /Å</td>
<td>2.8923(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c /Å</td>
<td>12.606(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a[3] /Å</td>
<td>2.88</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c[3] /Å</td>
<td>12.61</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystallite size /nm</td>
<td>71.6(8)</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$R_{\text{Bragg}}$</td>
<td>1.643</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_{\text{wp}}$</td>
<td>3.72</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Table S 4: Refined parameters of Cr$_3$C$_2$, based on XRD data. Errors shown in parentheses.

<table>
<thead>
<tr>
<th>Cr$_3$C$_2$ (62 wt%)</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
<th>Beq</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr1</td>
<td>0.01991</td>
<td>0.2500</td>
<td>0.356(3)</td>
<td>0.90(6)</td>
<td>5(2)</td>
</tr>
<tr>
<td>Cr2</td>
<td>0.169(5)</td>
<td>0.2500</td>
<td>0.815(3)</td>
<td>1.00(9)</td>
<td>2(2)</td>
</tr>
<tr>
<td>Cr3</td>
<td>0.809(6)</td>
<td>0.2500</td>
<td>0.979(4)</td>
<td>1.00(7)</td>
<td>4(2)</td>
</tr>
<tr>
<td>C1</td>
<td>0.24(7)</td>
<td>0.2500</td>
<td>0.17(4)</td>
<td>1.00</td>
<td>0(6)</td>
</tr>
<tr>
<td>C2</td>
<td>0.2(2)</td>
<td>0.2500</td>
<td>1.16(5)</td>
<td>1.00</td>
<td>0</td>
</tr>
<tr>
<td>a /Å</td>
<td>5.532(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b /Å</td>
<td>2.834(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c /Å</td>
<td>11.430(5)</td>
<td></td>
<td></td>
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<tr>
<td>a[4] /Å</td>
<td>5.5329(5)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>b[4] /Å</td>
<td>2.8290(2)</td>
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<tr>
<td>$R_{\text{Bragg}}$</td>
<td>2.151</td>
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<tr>
<td>$R_{\text{wp}}$</td>
<td>3.72</td>
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Table S 5: Refined parameters of Cr$_2$O$_3$, based on XRD data. Errors shown in parentheses.

<table>
<thead>
<tr>
<th>Cr$_2$O$_3$ (5.5(4) wt%)</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
<th>Beq</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr1</td>
<td>0</td>
<td>0</td>
<td>0.358(3)</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>O1</td>
<td>0.25(2)</td>
<td>0</td>
<td>0.25</td>
<td>0.9(2)</td>
<td>1</td>
</tr>
<tr>
<td>a /Å</td>
<td>4.962(4)</td>
<td></td>
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</tr>
<tr>
<td>c /Å</td>
<td>13.56(2)</td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>a /Å</td>
<td>4.960(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c /Å</td>
<td>13.599(5)</td>
<td></td>
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<tr>
<td>RBragg</td>
<td>0.313</td>
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</tr>
<tr>
<td>$R_{wp}$</td>
<td>2.31</td>
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</tbody>
</table>

Table S 6: Refined parameters of Cr$_7$C$_3$, based on XRD data. Errors shown in parentheses.

<table>
<thead>
<tr>
<th>Cr$_7$C$_3$ (5.8(3) wt%)</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
<th>Beq</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr1</td>
<td>0.02(6)</td>
<td>0.2500</td>
<td>0.69(2)</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Cr2</td>
<td>0.21(4)</td>
<td>0.2500</td>
<td>0.19(2)</td>
<td>1.00</td>
<td>7(5)</td>
</tr>
<tr>
<td>Cr3</td>
<td>0.25(5)</td>
<td>0.2500</td>
<td>0.43(2)</td>
<td>1.00</td>
<td>0(3)</td>
</tr>
<tr>
<td>Cr4</td>
<td>0.00(4)</td>
<td>0.0642</td>
<td>0.79(2)</td>
<td>1.00</td>
<td>1</td>
</tr>
<tr>
<td>Cr5</td>
<td>0.22(3)</td>
<td>0.0657</td>
<td>0.02(2)</td>
<td>1.00</td>
<td>3(3)</td>
</tr>
<tr>
<td>C1</td>
<td>0.8(3)</td>
<td>0.2500</td>
<td>0.55(8)</td>
<td>1.00</td>
<td>1</td>
</tr>
<tr>
<td>C2</td>
<td>0.0(2)</td>
<td>0.0291</td>
<td>0.38(4)</td>
<td>1.00</td>
<td>1</td>
</tr>
<tr>
<td>a /Å</td>
<td>4.4175(8)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b /Å</td>
<td>6.831(5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c /Å</td>
<td>11.983(9)</td>
<td></td>
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<td>a /Å</td>
<td>4.511</td>
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<td></td>
<td></td>
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<tr>
<td>b /Å</td>
<td>6.903</td>
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<tr>
<td>c /Å</td>
<td>12.08</td>
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<tr>
<td>RBragg</td>
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</tr>
<tr>
<td>$R_{wp}$</td>
<td>2.31</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
SEM

Apart from the in the main text describing SEM preparation, both FW and MW were analyzed in a cross-sectional view. For this purpose, a few wires were glued between two silicon wafers. Next, using sandpaper initially, the to be analyzed side was ground and polished with increasing grit. Lastly, a silica suspension (~ 0.02 µm diameter) was used to finely polish the surface. Prior to mounting the sample, a 7 nm layer of Pd/Au was sputter coated to prevent charging of the glue surface. The analysis was carried out in the same instrument using the same conditions as described in the main text.

Figure S 1: (Left) Cross section view of a furnace wire, showing the inhomogeneity of phase distribution, with a Cr richer center. (Right) furnace wire showing FW depositions being homogeneously distributed contrasting the wire insides. Elemental maps taken from indicated area (red square).

Similar to the FW’s surface, the core region also shows significant carbon excess (>90 at-%). Since the wires were glued in place, an exact determination is not possible, however, the measurements strongly indicate excess carbon.

MW cross-sections (Figure S2), while not showing Cr-rich areas, also have carbon excess throughout the wires’ cross section.
**Figure S 2:** *(Left)* Cross section view of a microwave wire showing homogeneity of phase distribution within the wire. *(Right)* Microwave wire with hexagonal plates on its surface. Elemental maps taken from marked plate (red square).

**Figure S 3:** *(Left)* SEM micrograph showing a typical fused wire. *(Right)* EDS line scan across the Ga-segregation shown in Figure 3c.
Synthesis of bulk Cr$_2$GaC reference samples

In order to compare the 1D Cr$_2$GaC microwires to the bulk material, respective bulk furnace and microwave samples were prepared. For the both syntheses, the elemental precursors Cr, Ga, and C were mixed in a 2:1.2:1 ratio (Cr: Alfa Aesar, -325 mesh, 99%; Ga: Alfa Aesar, ingot, 99.99%; C: Alfa Aesar, -325 mesh, 99.9995%) in an Ar filled glovebox. Hereby, Cr and C were pre-mixed, and then layered with Ga flakes (cut from the ingot) into the pellet die (Specac, 10 mm die). The mixture was pressed into a pellet using ~3 tons of pressure for 30 seconds, to prevent the gallium from melting completely. The obtained pellet was placed in a quartz ampoule, which was sealed under vacuum. For the furnace synthesis, the ampoule was placed in a chamber furnace (Carbolite, model CWF), in which the sample was heated to 1100 °C (10K/min). The max temperature was held for 10 h, before cooling to room temperature. After the heating cycle, the sample was ground and repalletized, and underwent the same cycle again to increase the sample’s homogeneity as well as run the reaction to completeness.

As for the microwave synthesis, the sample was heated in a household microwave oven (Panasonic, model NN-SN936B with inverter technology). To this extend, an insulation housing (custom) built from alumina fiber boards (Skyline Components, LLC, Tucson Arizona) was placed off-center in the microwave, fitted around a ~50 mL alumina beaker. The top of the housing had a hole, in order to accommodate ampoules sticking out. 7 g of activated charcoal (Honeywell, DARKO, 12-20 mesh) were placed in the crucible, into which the ampoule was embedded. The microwave oven was run at max power level (1250 W) for 30 minutes. After cooling to room temperature, the sample was ground and repalletized. To achieve a single phase sample, the procedure was repeated 3 times total. Below in Figure S 4 Rietveld refinements of both the furnace and the microwave bulk sample are presented (for refinement details, see above). The refined parameters can be found in Tables S 7 and S 8 for furnace and microwave samples, respectively.

Figure S 4: (Left) Rietveld refinement of bulk furnace Cr$_2$GaC XRD data; (Right) Rietveld refinement of bulk microwave Cr$_2$GaC XRD data. In both panels the black dots represent the data, the difference curve is shown in grey, the refined profile is orange, and the $hkl$ markers of Cr$_2$GaC$^3$ are shown in blue.
Table S 7: Refined parameters of Cr$_2$GaC (bulk furnace sample), errors in parentheses.

<table>
<thead>
<tr>
<th>Cr$_2$GaC (100 wt%)</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
<th>Beq</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr1</td>
<td>0.3333</td>
<td>0.6667</td>
<td>0.0850(4)</td>
<td>0.959(8)</td>
<td>3.7(2)</td>
</tr>
<tr>
<td>Ga1</td>
<td>0.3333</td>
<td>0.6667</td>
<td>0.75</td>
<td>0.97(2)</td>
<td>4.2(3)</td>
</tr>
<tr>
<td>C1</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.98(3)</td>
<td>0</td>
</tr>
<tr>
<td>a /Å</td>
<td></td>
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<td>2.89276(9)</td>
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<tr>
<td>c /Å</td>
<td></td>
<td></td>
<td>12.6143(4)</td>
<td></td>
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</tr>
<tr>
<td>a$^{[3]}$/Å</td>
<td></td>
<td></td>
<td>2.88</td>
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</tr>
<tr>
<td>c$^{[3]}$/Å</td>
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<td></td>
<td>12.61</td>
<td></td>
<td></td>
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<td>Crystallite size /nm</td>
<td></td>
<td></td>
<td>151(2)</td>
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</tr>
<tr>
<td>R$_{Bragg}$</td>
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</tr>
<tr>
<td>R$_{wp}$</td>
<td></td>
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<td>1.2</td>
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</tbody>
</table>

Table S 8: Refined parameters of Cr$_2$GaC (bulk microwave sample), errors in parentheses.

<table>
<thead>
<tr>
<th>Cr$_2$GaC (100 wt%)</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
<th>Beq</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr1</td>
<td>0.3333</td>
<td>0.6667</td>
<td>0.0834(7)</td>
<td>0.9(2)</td>
<td>2.2(3)</td>
</tr>
<tr>
<td>Ga1</td>
<td>0.3333</td>
<td>0.6667</td>
<td>0.75</td>
<td>0.8(2)</td>
<td>2.2(5)</td>
</tr>
<tr>
<td>C1</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<td>1(2)</td>
</tr>
<tr>
<td>a /Å</td>
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<td>2.8928(3)</td>
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</tr>
<tr>
<td>c /Å</td>
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<td></td>
<td>12.615(2)</td>
<td></td>
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</tr>
<tr>
<td>a$^{[3]}$/Å</td>
<td></td>
<td></td>
<td>2.88</td>
<td></td>
<td></td>
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<tr>
<td>c$^{[3]}$/Å</td>
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<td>12.61</td>
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<tr>
<td>Crystallite size /nm</td>
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<td>143(2)</td>
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<td>R$_{Bragg}$</td>
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<tr>
<td>R$_{wp}$</td>
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<td>1.71</td>
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</tr>
</tbody>
</table>

Figure S 5: Normalized resistivity vs. temperature data of furnace derived (pink) and microwave derived (blue) pelletized (solid state, bulk) samples.
Iodine treatment in carbonaceous Cr$_2$GaC wires

Iodine treatment on Cr$_2$GaC wires was performed on furnace samples due to their consistent electrical response with temperature. For iodine treatment, individual wires were extracted and introduced in a glass container with 500 mg of iodine and was sealed to prevent the escape of iodine vapor. The container was heated to 200 °C for 1.5 and 2 hours for two different wires. Raman and EDX measurements were carried out within 2 hours after treatment.

**Figure S 6:** a. Fitting of Mott Variable Range Hopping (VRH) model to five furnace-derived Cr$_2$GaC based carbon wires b. Fitting of Mott Variable Range Hopping (VRH) model to five microwave-derived Cr$_2$GaC based carbon wires. c. Resistivity vs. Temperature curve of microwave samples showing metallic trend and d. mixed response with resistivity minima at low temperature.

**Iodine treatment in carbonaceous Cr$_2$GaC wires**

Iodine treatment on Cr$_2$GaC wires was performed on furnace samples due to their consistent electrical response with temperature. For iodine treatment, individual wires were extracted and introduced in a glass container with 500 mg of iodine and was sealed to prevent the escape of iodine vapor. The container was heated to 200 °C for 1.5 and 2 hours for two different wires. Raman and EDX measurements were carried out within 2 hours after treatment.

**Figure S 7:** EDX spectra of carbonaceous Cr$_2$GaC wires shown in the main text after iodine treatment showing prominent Iodine peaks
Bromine treatment in carbonaceous Cr$_2$GaC wires

Bromine treatment on Cr$_2$GaC wires was performed on furnace samples by a similar procedure as iodine treatment. An individual furnace wire was extracted and introduced into a glass container with 2ml of bromine and heated to 130 °C for 1.5 hour after sealing. Raman measurement was performed immediately and EDX measurements were performed 2 hours after treatment.

![Figure S 8](image)

**Figure S 8**: a. EDX mapping of elements Cr, Ga, C and Br after Bromine treatment in carbonaceous Cr$_2$GaC wires; b. Corresponding EDX spectra from the mapped region showing prominent Bromine peak; c. Raman spectra from bromine doped wires showing molecular Bromine and Bromine anion peaks around 250 cm$^{-1}$; the signal to noise ratio is poor, most probably due to defects created by highly reactive bromine; d. Time dependent conductivity of a Brominated wire. The red dashed line is the fit to the equation $\sigma = \sigma_0 + A e^{-t/\tau}$ with derived parameter $\tau = 9.1$ hrs

**Table S 9**: Parameters $\sigma_0$, A and $\tau$ derived from $\sigma = \sigma_0 + A e^{-t/\tau}$ fitting to the $\rho$ vs. $t$ data of brominated Cr$_2$GaC based carbon wires.

<table>
<thead>
<tr>
<th>Wire radius (µm)</th>
<th>Treatment time (hr)</th>
<th>$s_0$ (S/m)</th>
<th>A (S/m)</th>
<th>% increase in conductivity ($S/ s_0$)</th>
<th>t (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>56.90 ± 2.37</td>
<td>1.5</td>
<td>1573.45 ± 2.69</td>
<td>127.78 ± 4.13</td>
<td>8.1</td>
<td>9.10</td>
</tr>
</tbody>
</table>

**References**