Graphene nanowalls as ingenious material for catalysts and superconductors

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Abstract: Nitrogen doping of graphene nanowalls (GNWs) has been performed to study the effect of nitrogen on the carbon network of graphene. It’s concluded that N-GNWs provide much higher capacitance for double layer capacitor, which can be attributed to pyridinic nitrogen on the edge of the GNWs of micro-meter grain size. Meanwhile, the intercalation of GNWs with Fe and K has been carried out at an elevated temperature of 350 C to search for potential superconducting behavior.

Introduction: In the past years, our laboratory has developed a CVD growth technique for large-scale production of GNWs, which is drastically different from exfoliated and CVD graphene. Instead of laying flat on a Cu or Ni substrate, the GNWs are layered structure standing out from a Si substrate, which offers much higher surface area for electrochemical applications. Preliminary studies showed controllable number of graphene layers and adjustable residual strain as characterized by TEM and Raman spectroscopy.

In this report, we describe nitrogen doping of the GNWs via in-situ doping during the CVD growth. Based on our experience with nitrogen doping in carbon nanotubes (CNTs), N-doping of CNTs can be achieved to enhance deposition of Pt nanoparticles, which is effective in catalytic performance in fuel cells. We adopted similar idea in CNTs and apply it in the growth of GNWs. The N-GNWs thus produced also show potential for double-layered capacitor with much enhanced Meanwhile, the micro-meter sized GNWs are idea for diffusion and intercalation of other atoms to produce novel transport properties such as superconductivity. Preliminary study shows a change of electrical conductivity at low temperature as described below, which sheds light to a controllable intercalation of few-layered graphene system.

Experiment: The GNWs hetero-architecture is formed by growing edge-oriented SiC nanowalls in a microwave CVD reactor, followed by surface graphitization consequently, resulting in a well-defined heterojunction composed of 2H-SiC nanowall sheathed by few-layer graphene. As shown in Figure 1, by proper control of the precursors, microwave power, and temperature, large-area and uniform GNWs can be produced. In addition, we have developed a technique to grow GNWs on a carbon cloth (CC) substrate, which is widely used in electrodes of a fuel cell and capacitor.

The intercalation of GNWs was performed in a high temperature oven up to a 350 C temperature. FeCl₃ and K were placed together with GNWs at elevated temperature for 80 hours. XRD, Raman and XPS have been used to study the change after the process.
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This report describes nitrogen doping of graphene nanowalls (GNWs) via in-situ doping during CVD growth. Based on the PI's experience with nitrogen doping in carbon nanotubes (CNTs), N-doping of CNTs can be achieved to enhance deposition of Pt nanoparticles, which is effective for catalytic performance in fuel cells. He adopted a similar idea for CNTs and applied it for the growth of GNWs. The N-GNWs thus produced also showed potential for double-layered capacitors with much enhancement. Meanwhile, the micro-meter sized GNWs are idea for diffusion and intercalation of other atoms to produce novel transport properties such as superconductivity.
Results and Discussion: As shown in Figure 2, not only on Si substrate for the GNW growth, but also on other substrate such as a carbon cloth as shown in the SEM images of Figure 2 with GNWs/Si on the left and GNWs/CC on the right, indicating the high density and uniform GNWs on Si and CC substrates.

We applied cyclic voltammetry (CV) on the GNWs/CC for both pristine and N-doped GNWs/CC. As shown in Figure 3, the GNW electrodes exhibit excellent electrode performance with about 61 meV between the oxidation and reduction peaks. They also show very small change in the peak positions when we increased the scan rate. The plot in Figure 3(c) shows straight lines between peak separation and scan rate, indicating that diffusion control of the electrolyte to the electrode is the rate limiting process.

We applied XPS spectroscopy to characterize the surface of GNWs for both pristine and N-doped GNWs. As shown in Figure 4, nitrogen doping effectively change the composition of the surface. It’s interesting that only pyridinic peak appears in the N1s
spectrum and no other components such pyrrolic and graphitic N on carbon network. This can be attributed to the small grain size of the GNWs, which leads to edge dominant behavior for the pyridinic structure.

The effect of the nitrogen doping can also be seen from the change in water contact angle. As shown in Figure 5, the contact angle changes from 146 degrees of super hydrophobic surface to 4.7 degrees of hydrophilic surface after the nitrogen inclusion. The phenomenal change in hydrophilicity after the nitrogen inclusion indicates the effective surface modification by the in-situ N-doping.

The capacitor performance of the N-GNWs/CC is shown in Figure 6 with CV measurement in 1M H₂SO₄ solution. Up to 900 F/g capacitance has been concluded after careful measurement of the weight of GNWs. The 900 F/g energy density is equivalent to 300 Wh/Kg, which is among the top of reports in the literature. Likewise, the power density can be as high as 80 kW/Kg, which also champions in the literature.
The Reagon plot with energy density vs. power density of the N-GNW/CC and GNW/CC is depicted in Figure 7, with the other data points from the best literature reports. It clearly shows that N-GNWs/CC outperforms all the other systems reported to date.

**Figure 7.** Energy density vs. power density plot of the N-GNW/CC and GNW/CC.

To understand better the advantage of the N-GNWs/CC as a capacitor, the scheme sketches are illustrated in Figure 8, wherein a comparison of conventional carbon materials and our CNWs/CC has been sketched. For conventional materials, irregular packing of the nanomaterials has been performed via spin-coating or pasting, whereas the GNWs/CC provides direct growth of well aligned graphene sheets to ensure large surface and good electrical contact. Further N-doping on the graphene edge can create active site for redox reaction while maintaining fast electron transport.

**Figure 8.** Schematics for comparison of conventional carbon materials and our CNWs/CC for capacitor applications.

Last but not least, we've successfully intercalate Fe and K into GNWs, which have been evidenced by XPS measurement. As shown in Figure 9, K-doped GNWs show an abnormal temperature dependence below 100 K. Temperature dependence of the resistance under 4000 B(Oe) also shows that K intercalation is different from the others. Further work is needed to perform detailed investigation about the mechanism of the abnormal temperature dependence. Hopefully, better understanding of the intercalation system and even some lights into superconductivity can be achieved.
Figure 9. Temperature dependence resistance for GNWs, Fe-doped GNWs, and K-doped GNWs under 0 field and 4000 B(Oe).

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