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ARTICLE

Restoration of the Genuine Electronic Properties of Functionalized Single-Walled Carbon Nanotubes

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Sidewall functionalization of single-walled carbon nanotubes (SWNTs) has previously been used to effectively attach a variety of functional groups onto SWNTs; however, there has been little investigation into the reversibility of these reactions, which is critical for the restoration of the original optical and electrical properties of SWNTs. In this study, we investigated the complete removal of functional groups attached to the sidewalls of SWNTs by a thermal annealing process at high temperature to restore the genuine optical and electrical properties of SWNTs. Hydroxyphenyl groups were covalently attached to SWNTs for this purpose. Functionalized SWNTs typically show a significantly larger sheet resistance and completely lose their typical characteristic optical properties due to the covalent attachment of the functional groups onto the SWNT surfaces. However, we found that all of the functional groups could be effectively removed by an annealing temperature above 400°C in a nitrogen environment, as confirmed by FT-IR, Raman and UV-vis-nIR absorption analyses. Accordingly, the original optical and electrical properties were also recovered upon annealing at above 400°C, as confirmed by the recovery of the original sheet resistance value. To demonstrate the effectiveness of annealing, we evaluated transparent films, which were prepared predominantly with metallic SWNTs, using the separation technique, which is based on selective covalent functionalization. A functionalized metallic SWNT film recovers its original high conductivity upon annealing at 400°C by the removal of the functional groups, which demonstrates the effectiveness of this annealing process.

Keywords: single-walled carbon nanotubes, sidewall functionalization, high temperature annealing, removal of functional groups, restoration of genuine properties.

Introduction

Single-walled carbon nanotubes (SWNTs) possess unique electrical, optical, and mechanical properties;[1,2] therefore, they have been used as major components either by themselves or as a component in hybridized composite materials together with other elements for various applications.[3-5] In addition to the studies pertaining to properties and applications of SWNTs, SWNT surface functionalization has also been extensively studied as a means to increase their solubility for solution processing;[6] attach functional groups, for example, small molecules or polymers for specific applications;[7-8] manipulate their electronic properties;[9] and enable SWNT composite fabrication with other materials.[10]

Among various surface functionalization schemes, the covalent reaction of SWNTs, based on diazonium chemistry, has been highlighted as one of the more powerful tools for SWNT processing in carbon nanotube chemistry[9,11] because it is reversible and prevents permanent damage of SWNTs, at least to a certain extent,[12] compared to other covalent functionalization schemes, such as strong oxidation processes using strong acids.[13,14] In addition, the diazonium reaction also provides an effective means to anchor new groups onto the sidewalls of SWNTs. Furthermore, this approach is particularly interesting because it provides a method for the selective attachment of functional groups onto metallic SWNTs rather than semiconducting SWNTs,[9,15] thus enabling the tailoring of the metallic SWNT electronic structures.

However, this scheme has inevitable drawbacks, that is, the electronic and optical properties of genuine SWNTs are significantly altered upon covalent functionalization due to local structural defects by sp^3 bond formation among carbon atoms.[12,16] Accordingly, the original SWNT electrical properties, which are critical for application, will deteriorate, and the various functional groups attached to the SWNT surfaces must be removed after their use in processing for the SWNTs to be used in actual applications. To date, thermal annealing has been widely used for this purpose. Thermal annealing is known to remove most of the functional groups and to recover the original SWNT structure; however, it also has been reported that metallic SWNTs compared to semiconducting SWNTs cannot be fully restored to their genuine structure and that a small number of defects still remain on SWNT surfaces, even after annealing. [16]

We previously reported the selective attachment of diazonium moieties to metallic SWNTs when present with semiconducting

SWNTs and the separation of these functionalized metallic SWNTs from the pure semiconducting SWNTs by utilizing differences in densities[8] or electrophoretic mobilities,[17] which are induced by these functional groups. However, if these functional groups cannot be completely removed, the original electrical properties of the metallic SWNTs cannot be restored, restricting the usefulness of their application. Therefore, there has been a significant motivation for the development of a regeneration process that is capable of fully recovering the original electrical properties of SWNTs together with characterization tools to elucidate this reversibility, both of which this works addresses

Previous works implemented Raman studies and electrical measurements of TFT devices to explore the reversibility of the diazonium functionalization of SWNTs;[12,16] however, Raman analysis, by itself, cannot fully characterize the reversibility, and due to the complexity of the TFT devices, reliable interpretation of the results has been challenging. Therefore, simple and direct characterization tools are needed for reversibility characterization.

In this study, we explore the reversibility of SWNT functionalization by a diazonium reagent upon high temperature annealing using Raman, FT-IR, UV-vis-nIR absorption, sheet resistance, and AFM measurements. Based on the these experimental schemes, we demonstrate the complete restoration of the electrical character of functionalized SWNT films, both metallic and semiconducting SWNTs, as characterized by the sheet resistance, after annealing in inert atmosphere.

Experimental

SWNT preparation. As prepared HiPco (Unidym) SWNTs were used for functionalization and annealing without any further purification procedure to minimize side-wall functionalization. SWNTs were suspended in H_2O using 2 w/v% sodium cholate surfactants (SC, Sigma-Aldrich) and were sonicated, after which ultra-centrifugation was used to disperse individually suspended SWNTs in a similar fashion to that previously reported.[8] The final concentration of the SWNT solution was adjusted to be 0.005 w/v%.

Functionalization. The 4-hydroxybenzene diazonium salt, used as a reagent to attach 4-hydroxyphenyl groups to the sidewalls of the SWNTs, was prepared by the reaction of nitrosonium tetrafluoroborate ($NOBF_4$) and 4-aminophenol ($HO\text{-}C_6H_4\text{-}NH_2$), as described in previous studies.[17] Reaction of SWNTs with 4-hydroxybenzene diazonium salt was performed at 45°C and pH 5.5 by the injection of a diazonium salt solution into a reactor vessel containing SWNTs.

Preparation of SWNT films by the vacuum filtration method. The SWNT films were prepared on fused quartz and soda-lime silicate glass substrates. Next, 0.5 ml of each SWNT solution, pristine or functionalized, diluted in aqueous 2 w/v% SC was poured onto a porous alumina membrane filter (200 nm pore size, 25-mm diameter; Whatman) using the vacuum filtration method, and the SC was removed by rinsing the filtered film with deionized water. The alumina membrane was then removed using a NaOH solution. The SWNT film on the substrate was dried in an oven at 60 °C for 12 hrs. SWNT films, either pristine or functionalized, were annealed in an inert environment (N_2, 500cc/min) at various temperatures, i.e., at 200, 400, 600, and 800°C.

Characterization of SWNT films. SWNT films, either pristine or functionalized, were characterized by UV-vis-nIR absorption spectroscopy (Shimadzu UV-310PC absorption spectrometer), Raman spectroscopy (632.8 nm excitation), FT-IR spectroscopy (Bruker), and Atomic Force Microscopy (AFM, Park Systems).

SWNT separation by electronic type. Separation of SWNT by density difference was performed using a density gradient in a similar way as that described in our previous work.[8] A density gradient was made using a non-ionic medium, iodixanol (OptiPrep, 60 w/v% iodixanol, Sigma-Aldrich). The concentration of the initial gradient was adjusted to be 30 w/v% with a volume of 6 ml and was positioned on top of a 60 w/v% stop layer solution that had a volume of 3 ml. The functionalized SWNT solution was placed on top of the gradient and was then centrifuged for 22 hrs at 22°C and 32,000 rpm using a swinging bucket SW 32.1 Ti rotor (Beckman Coulter). The surfactant concentration was maintained at 2 w/v% throughout the tube. SWNT samples were collected and characterized by UV-vis-nIR absorption and Raman spectroscopy.

Results and discussion

Removal of functional groups from the sidewall of SWNTs

We first investigated the effect of annealing at various temperatures on the restoration of the optical properties of SWNTs. Hydroxyphenyl-functionalized SWNTs (f-SWNT) and a control sample without any functionalization (c-SWNT) were compared for this purpose. Both SWNT samples were made into films, and their optical transmittance spectra were obtained. Figure 1 shows the transmittance spectra of f-SWNT films annealed at different temperatures together with that of the c-SWNT film as a reference. The transmittance spectra of the c-SWNT sample (Figure 1(a)) shows typical first- (E_{11}^{SC}, 830 ~ 1700 nm) and second- (E_{22}^{SC}, 600 ~ 800 nm) order optical transitions of semiconducting SWNTs and first-order (E_{11}^{M}, 440 ~ 645 nm) optical transitions of metallic SWNTs for the un-functionalized HiPco SWNTs.[9]

When the sidewalls of c-SWNTs were functionalized with 4-hydroxybenzene diazonium salt, as illustrated in the inset figure of Figure 1, the optical transitions of all of the SWNTs decayed upon the covalent functionalization of the SWNTs with diazonium reagent, as shown in Figure 1(b), due to the localization of electrons by the formation of covalent bonds between the SWNTs and diazonium reagents.[18,19] These results confirm that the sidewalls of SWNTs were fully functionalized with 4-hydroxyphenyl groups under the reaction conditions used in this study.

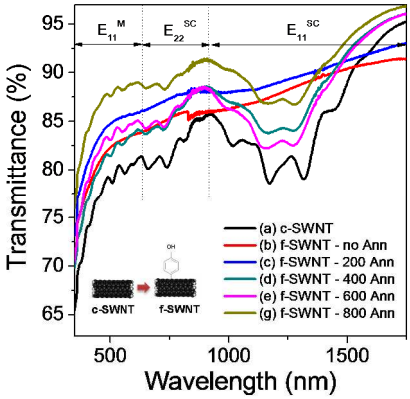

Figure 1. The transmittance spectra of un-functionalized (c-SWNTs) and functionalized SWNTs (f-SWNTs) and those of functionalized SWNTs annealed at various temperatures.

Next, we monitored the removal of functional groups from SWNTs using the transmittance spectra of the SWNT samples after annealing at various temperatures. Upon annealing in a N_2 flow at 200°C, the optical transitions of SWNTs still decayed (Figure 1(c)), indicating that functional groups remained on the SWNT surface and that a temperature of 200°C was insufficient for the removal of the functional groups. However, at annealing temperatures above 400°C (Figure 1(d)-(g)), the optical transitions of both the semiconducting and metallic SNWTs were fully recovered, indicating that the functional groups were fully removed from SWNT surfaces.

Fourier transformed-infrared spectroscopy (FT-IR) analysis also confirmed that the hydroxyphenyl functional groups were completely removed from SWNT sidewalls upon annealing at temperatures higher than 400°C. Figure S1 shows the changes in the peak intensities of the hydroxyphenyl groups attached to the sidewalls of SWNTs upon annealing, i.e., O-H stretching (~3360 cm^{-1}), C-H stretching (~2920 cm^{-1}), and C=C stretching (~1540 cm^{-1}) as well as the C-H bending (~1200 cm^{-1}) mode. The change in the peak intensity of each functional group, upon annealing, were normalized to the intensity of the fully functionalized SWNT sample, and their changes, according to annealing temperature, are plotted in Figure 2. The hydroxyl group (O-H) decomposes at a faster rate than others, possibly because it is in the para position in the hydroxyphenyl group. All of the functional groups are completely decomposed and removed from SWNT surfaces above 400°C, which is in good agreement with the changes observed in the optical properties of functionalized SWNTs upon annealing.

The original optical transitions of all of the semiconducting and metallic SWNTs are fully recovered when all of the hydroxyphenyl groups, including the covalent bonds formed on SWNTs, are completely removed by annealing above 400°C. At 200°C annealing, the optical transitions of SWNTs are not recovered, as shown in Figure 1(c); only the O-H group of the hydroxyphenyl group is removed while all other functional groups still exist on SWNT, as confirmed by FT-IR analysis shown in Figure 2.

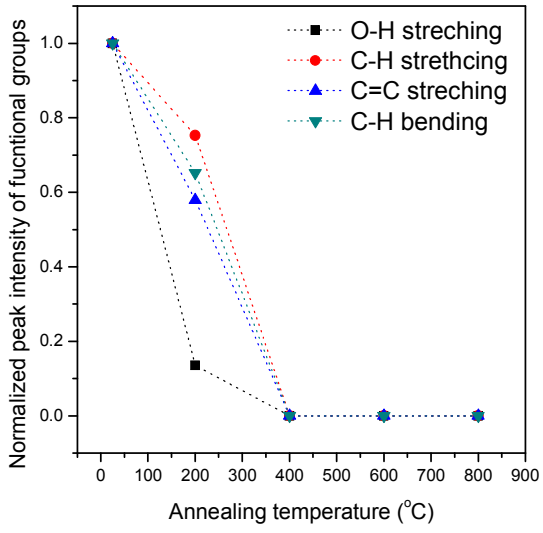

Figure 2. The FT-IR spectra of un-functionalized (c-SWNTs) and functionalized SWNTs (f-SWNTs) and those of functionalized SWNTs annealed at various temperatures.

Figure 3 shows the Raman spectra of each SWNT sample. When SWNTs are functionalized, the disorder mode (~1300 cm^{-1}) is significantly increased and the radial breathing mode (150~1300 cm^{-1}) completely disappears,[20] indicating that the sidewalls of SWNTs are fully functionalized. When annealing at 200°C, Raman features were similar to those of c-SWNTs, indicating that the functional groups were still present on the surface of SWNTs, as confirmed by UV-vis-nIR and FT-IR analyses. Upon annealing above 400°C, the disorder mode completely disappeared, and the radial breathing mode value recovered to one close to those of c-SWNTs. This result is again in good agreement with the transmittance spectra and FT-IR analyses. Based on these results, we conclude that functional groups are effectively removed from the surface of SWNTs after annealing above 400°C. In addition, the difference in the reversibility of optical properties between metallic and semiconducting SWNTs is not significant—for both cases the optical properties were fully recovered.

Changes in the electrical properties of SWNTs upon annealing

In the previous section, we showed that all of the functional groups covalently attached to sidewalls of SWNTs are effectively removed by annealing in N_2 environment above 400°C by optical transmittance, FT-IR, and Raman measurements.

To investigate that the functionalized SWNTs recover their original electrical and optical properties by annealing at high temperatures, we measured the sheet resistance of c-SWNT and two f-SWNT (f-SWNT1 and f-SWNT2 with different transmittance) films annealed at different temperatures and show the results in Figure 4. The black symbols represent sheet resistance versus the transmittance of c-SWNT, and the red and blue symbols represent those of f-SWNT1 and f-SWNT2, respectively. The sheet resistance of c-SWNTs at various transmittances is similar to those reported in the literature for HiPco SWNTs.[21] When SWNTs are fully functionalized (no Ann), they show a significantly large sheet resistance due to the functional groups that serve as defects in the SWNT surfaces.

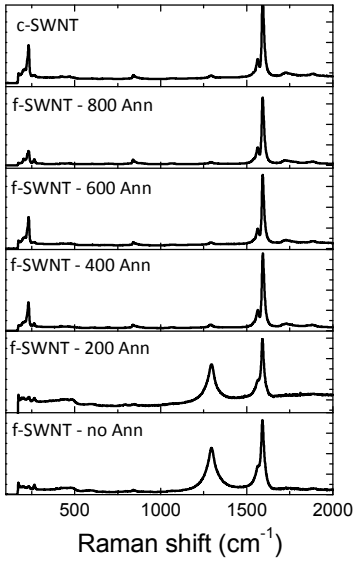

Figure 3. Raman spectra of un-functionalized (c-SWNTs) and functionalized SWNTs (f-SWNTs) and those of functionalized SWNTs annealed at various temperatures.

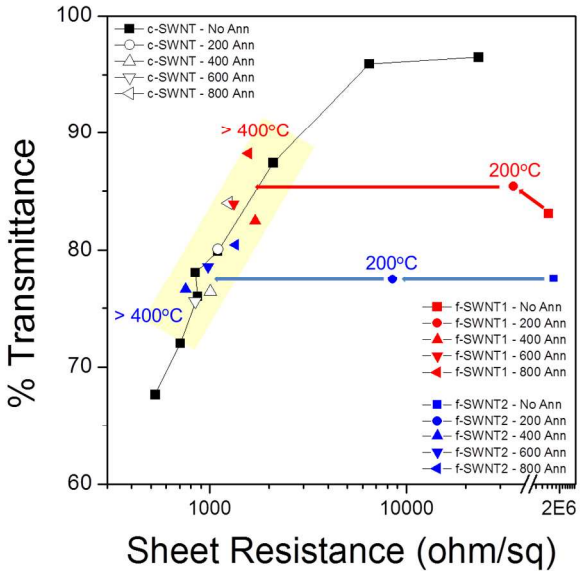

Figure 4. The sheet resistance versus transmittance of un-functionalized (c-SWNTs, black symbol) and two functionalized (f-SWNT1 and f-SWNT2, red and blue symbol, respectivley) SWNT films before and after annealing at various temperatures.

The original sheet resistance value was recovered upon annealing above 400°C for both functionalized SWNTs, indicating that the annealing conditions that recover the original optical properties of the SWNTs, as shown by optical transmittance, FT-IR and Raman measurements, also recover the desired electrical character. The sheet resistances of c-SWNTs, annealed at various temperatures, were also measured to investigate whether annealing itself affects the electrical character of SWNTs, and the results show that annealing, by itself, does not change the electrical character of SWNTs, as confirmed by the finding that the sheet resistances of annealed c-SWNTs are similar to those of the original c-SWNTs.

We also applied this annealing treatment to carboxyphenyl-functionalized SWNTs to investigate that the annealing treatment of this study can be applied to effectively remove other functional groups, other than hydroxyphenyl functional groups used in this study. As shown in Figure S2, we confirmed that carboxyphenyl groups attached to SWNT surfaces were also effectively removed upon annealing at above 400°C in nitrogen environment, as in the case of hydroxyphenyl-functionalized SWNTs.

Previous reports suggested that SWNTs cannot fully recover their original surface structure, even after thermal annealing, due to the residual defects on the sidewalls of SWNTs, especially metallic SWNTs, originating from the breakage of covalent bonds between SWNTs and functional groups,[16] which tends to lead to strong SWNT-SWNT bundle formations.[23] To investigate this possibility, we observed AFM images of functionalized and non-functionalized SWNTs before and after thermal annealing at 800°C (the images are shown in Figure 5). In the case of non-functionalized SWNTs (Figure 5 (a), (b)), there is not a significant change in the surface morphology or the SWNT bundle size. In the case of functionalized SWNTs, the AFM images of SWNTs before annealing are not clear, possibly due to the presence of functional groups on the sidewalls of the SWNTs (Figure 5(c)). When all of the functional groups are removed by annealing, the images become clear, and the bundle size of SWNTs is similar to that of non-functionalized SWNTs. These results show that strong bundle formation by residual defects on SWNTs is not significant upon annealing at high temperatures, thus suggesting that residual defects do not exist or exist in small amounts on the sidewalls of SWNTs contrary to what has been previously reported.

Recovery of electrical property of metallic SWNTs upon annealing

To demonstrate the effectiveness of annealing as a means to recover the original electronic properties of SWNTs that are necessary for nano-electronics and transparent film applications, SWNTs enriched from predominantly functionalized metallic SWNTs were prepared using the separation technique described

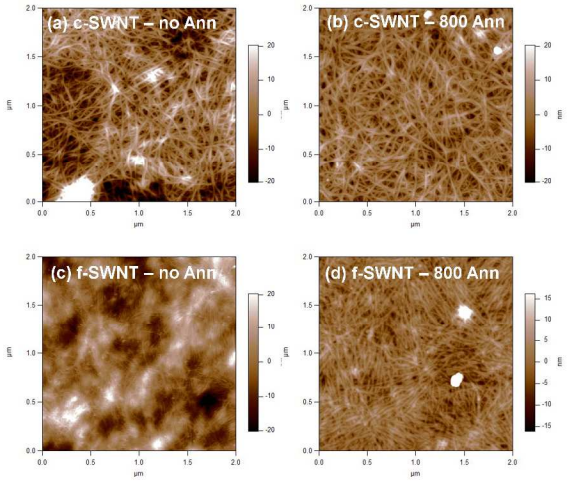

Figure 5. AFM images of c-SWNTs and f-SWNTs before and after annealing at 800°C.

previously,[8] and their property changes upon annealing were investigated. When SWNT mixtures react with 4-hydroxybenzene diazonium salts under controlled conditions; metallic SWNTs, having higher oxidation potentials near the Fermi level than semiconducting SWNTs, preferentially donate electrons and form covalent bonds with 4-hydroxybenzene diazonium over semiconducting SWNTs.[22] The covalently bonded hydroxyphenyl functional groups on the metallic SWNTs increase their density, allowing the separation of functionalized metallic SWNTs from un-functionalized semiconducting SWNTs with high purity. Separated functionalized metallic SWNT films, using this method, were annealed at 800°C to remove the functional groups, and optical measurements were performed to check that all of the functional groups were in fact removed from the SWNTs and to estimate the purity of the de-functionalized metallic SWNT. As shown in Figure S2, annealing at 800°C removes all of the functional groups from SWNTs, and high purity metallic SWNTs were obtained.

The sheet resistances of a metallic SWNT film, together with that of a c-SWNT film in which metallic and semiconducting SWNTs co-exist, were compared, as shown in Figure 6. As evident from Figure 6, the metallic SWNT film, where all of the functional groups used for separation were effectively removed, shows a sheet resistance about ~70% lower than the resistance of the c-SWNT film at all transparency, which is similar to results reported for metallic SWNT films separated by different methods,[21] confirming that the annealing process

removes the functional groups and also recovers the original electronic character.

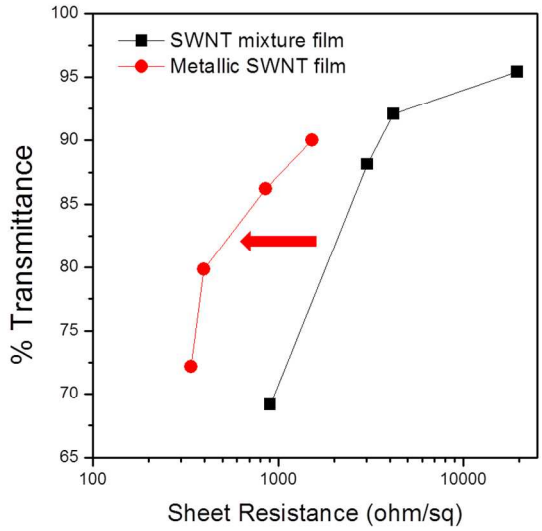

Figure 6. The sheet resistance versus transmittance of metallic SWNTs where the functional groups used for separation were effectively removed after annealing, together with that of un-functionalized SWNTs (c-SWNTs) as a reference.

Conclusions

We showed that annealing functionalized SWNTs at high temperatures, that is, above 400°C, effectively removes functional groups from the sidewalls of SWNTs and recovers their original optical and electrical properties. Furthermore, we showed that there is no observable difference in the extent of de-functionalization between metallic and semiconducting SWNTs based upon the recovery of optical properties of both types of SWNTs and found that the sheet resistance of metallic SWNTs, which had functional groups removed by annealing, was similar to that of metallic SWNTs prepared by other methods that do not use chemical functionalization.

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Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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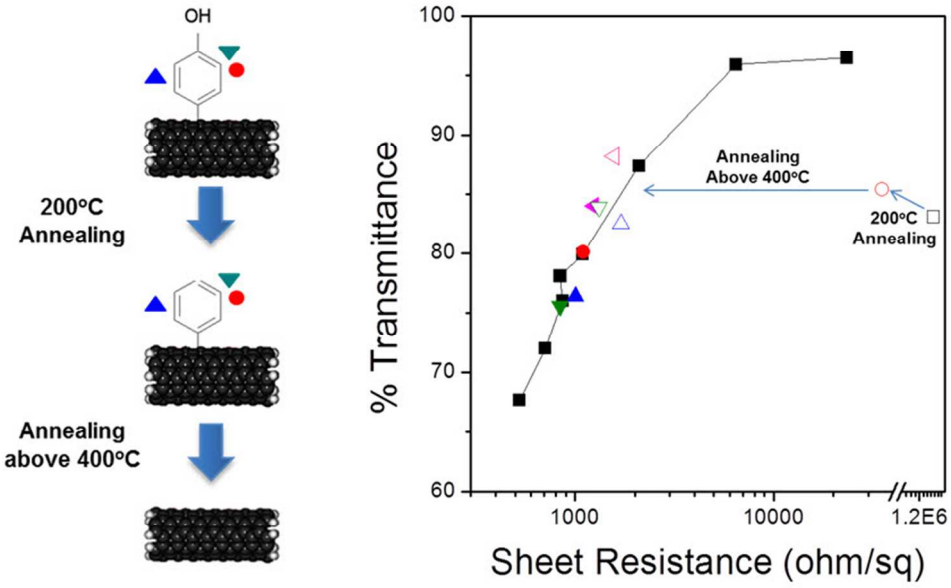

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