Fullerenes, Nanotubes and Carbon Nanostructures

Functionalization of Amorphous Carbon Nanotubes for Au Nanoparticles Hybridization

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Functionalization of Amorphous Carbon Nanotubes for Au Nanoparticles Hybridization

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Our study focuses on selection of nitric acid, sulfuric acid, citric acid, and hydrochloric acid as the most suitable oxidation agent for a-CNT. Nitric acid functionalized a-CNT has the highest value of zeta potential \(-142.9\) mV, followed by \(\text{H}_2\text{SO}_4\), citric acids, and \(\text{HCl}\) functionalized samples of \(-60.3\) mV, \(-15.9\) mV, and \(-3.2\) mV, respectively. High values of zeta potential represents surface charges, which refers to carboxyl groups present on tubes’ bodies. At the same time, auric chloride (\(\text{AuCl}_3\)) solution treatment was applied on citric acid, nitric acid, hydrochloric acid, and sulfuric acid treated a-CNT at the same condition. Nitric acid treated a-CNT was found to have the highest weight percentage of gold (Au) content. Therefore, indirectly, we have proven that nitric acid adds the most carboxyl groups upon functionalization.

Keywords: carbon nanotubes, characterization, functionalization, gold

Introduction

Due to unique properties of carbon nanotube (CNT), researches involving its potential applications as various devices have been established. However, the usage of CNT does not only limit to pure CNT alone but also exhibits superior performance upon hybridization with various foreign particles. For instance, applications in NOx gas sensors for gold-plated CNT (1), electrical conductivity enhancement by attachment of silver nanocomposite on CNT (2), or even attachment of gold nanocomposite for DNA hybridization biosensor (3) has raised great interests. However, due to hydrophobic and inert nature of as-prepared CNT (4, 5), functionalization of CNT with carboxyl groups can be explained via a few approaches. One of the main mechanisms of attaching nanoparticles on CNT bodies is based on wet chemistry, wherein nanotubes are filled with some liquids by capillary action (10), which is caused by extra pressure given by the Laplace equation of capillarity:

\[
\Delta P = \frac{2\gamma \cos \theta}{R}
\]

where \(\Delta P = P_a - P_m\) represents pressure difference between atmospheric pressure, \(P_a\), and pressure under the meniscus, \(P_m\). \(\gamma\) and \(R\) represent the surface tension at the liquid/air interface and inner radius of the nanotube, respectively, and \(\theta\) is the liquid-solid contact angle. From the Laplace equation, we see that the difference \(\Delta P = P_a - P_m\) will be positive when \(\theta < 90^\circ\), and negative when \(\theta > 90^\circ\). As the menisci forms spontaneously, this extra pressure will pull the liquid into the nanotube if \(\Delta P > 0\), provided that the pressure in the reservoir is atmospheric. In other words, to fill the nanotubes with some liquid, the contact angle that the meniscus forms with the nanotube wall must be less than \(90^\circ\). If the contact angle is greater than \(90^\circ\), extra pressure must be applied to the liquid in order to impregnate the nanotube (11). The angle \(\theta\) represents degree of wetting of suspension with desired nanocomposites on CNT body itself. Addition of oxygen-containing functional group,
—COOH group for instance, will increase the degree of wetting. Therefore, it can be said that functionalization of CNT would ease the hybridization of foreign particles on it.

At the same time, carboxyl groups’ formation on CNT improves hydrophilic properties of CNT via formation of hydrogen bonds with water molecules. As most hybridization of foreign particles/CNT is carried out in distilled water medium, addition of carboxyl groups would expect a favorable impact on the degree of dispersion of CNT in water (12–14). Defects on tubes’ bodies are potential sites for chemical modification, as discussed in end and defect-side chemistry functionalization (15). By treatment of nanotubes with acidic-oxidizing environment, the oxygen-containing groups will be introduced to the ends and sidewalls of the tubes (16). Combining the above, as compared with fully crystalline nanotubes, amorphous CNTs (a-CNTs) are known to be highly porous and highly defective (17), which expects more significant properties alternation after hybridization process.

To study the agglomeration or dispersion of functionalized amorphous CNT, zeta potential measurement can be applied. In general, zeta potential can represent surface charges of particles provided that the charges on the particles remain unchanged, where a higher value of measured zeta potential would represent increased number of carboxyl group functionalized on tubes’ bodies (18). As to study the hybridizing ability of a-CNT functionalized by each individual type of acid, energy-dispersive X-ray (EDX) can be applied to a-CNT functionalized with different acids and solution treated with auric chloride (AuCl₃) solution in the same condition to investigate its Au content.

Experimental Method

**Chemical Synthesis of Amorphous Carbon Nanotubes**

a-CNT samples are prepared using the existing method (19, 20). In a typical experiment process, all reagents used were analytically pure. Two gram of ferrocene powder and 4 g of aluminum chloride powder were mixed evenly and placed in a ceramic crucible with 50 ml capacity. A lid was used to cover the boat to prevent ferrocene from escaping rapidly as sublimation. Then, the quartz boat was put into an air furnace and heated to 200°C at a rate of 10°C/min. After holding for 0.5 hours, the furnace was allowed to cool down at room temperature and black powder was found in the boat. Black powder obtained was suspended into diluted HCl solution. The suspension is then heated to 80°C for 45 min and particles in black powder form will sediment completely. Excessive HCl was removed after complete sedimentation and more diluted

**Fig. 1.** (a) TEM image of as-synthesized a-CNT bundles (×28,000 magnification). (b) TEM image of as-synthesized a-CNT (×75,000 magnification). (c) TEM image of AuCl₃ solution treated a-CNT.
HCl was added to form a suspension with black powder particles. The washing and sedimentation at elevated temperature steps are repeated until a clean HCl solution is obtained after settling. The obtained black powders were then washed with distilled water and dried at 150°C to remove residual volatile materials before the obtained final product can be functionalized and characterized.

**Functionalization of Amorphous Carbon Nanotubes**

Around 0.5 g of synthesized amorphous CNTs was mixed with 30 ml of 20 wt% nitric acids and sonicated for 30 min. The obtained mixture is then diluted and excessive acids were dried at a temperature of 150°C. It is realized that this process creates plenty of –COOH moieties on the CNT surface and enhances the CNT dispersion in water. The functionalization process is then repeated by replacing nitric acids with citric acids, sulfuric acids, and hydrochloric acids. The obtained functionalized products will be characterized with Fourier transform infrared spectroscopy (FTIR), Zetaseizer, transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), and EDX. TEM viewing was carried out using Libra 120 Carlzeiss. The sample (0.1 wt%) is mixed in distilled water and sonicated for 30 min. After that, the a-CNT distilled water suspension is dropped on a copper grid and allowed to dry for 3 days before TEM viewing is carried out. FESEM was carried out using Auriga Zeiss FESEM. Zeta potential measurement was performed using Zetaseizer, wherein each sample was suspended in distilled water with 0.03 wt% and sonicated for 30 min.

**Solution Treatment of Functionalized Amorphous Carbon Nanotubes**

Nitric acid, citric acid, hydrochloric acid, and sulfuric acid functionalized samples were stirred with 100 ml of auric chloride (AuCl₃) solution at 1200 rpm for 1 hour at 70°C. The concentration of AuCl₃ was 1.0 g/dm³. After this, 50 ml of citric acid was added dropwise to the solution as a reducing agent for Au cations. Again, stirring was continued for another 4 hours followed by washing with distilled water to remove residual nano-gold particles. After that, the samples are filtered and air dried. Obtained samples were characterized with EDX, TEM, high-resolution transmission electron microscopy (HRTEM), and FESEM.

**Results and Discussion**

Figure 1 shows TEM images of as-synthesis and modified a-CNTs. The presence of TEM bundles (Figure 1a) shows the re-agglomeration properties of a-CNT. The diameter of individual tube is measured as 51.6 nm, which has almost the same diameter value as discovered in previous research (19). The diameter of a-CNT is greatly reduced when it is treated with auric chloride solution (Figure 1c). The diameter of AuCl₃ solution treated a-CNT that reduced to 10.2 nm indicates further removal of amorphous carbon layers on the tube. Ordered and even fringes found on the tube’s body are preliminary determined to be caused by successful attachment of gold (Au) nanoparticles on tubes’ bodies. The

![Fig. 2.](image)
morphology of as-synthesized, functionalized, and Au-decorated a-CNT can be further observed in Figure 2. Figure 2a shows the FESEM image of as-synthesized a-CNT. As-synthesized a-CNTs are generally open-ended and tubes tend to reagglomerate and form bundles as observed in Figure 2a. Moreover, the uneven and disordered surface of the tubes explains the highly porous and defective structure of a-CNT compared with fully crystalline CNT. Highly disordered and defective tube’s surface indicates presence of amorphous carbon layers on tubes’ bodies, which can be removed by sonication with nitric acid. Figure 2b shows FESEM image of acid-treated a-CNT. The tubular shape can be clearly observed where tubes are generally separated from each other, as compared with Figure 2a, in which tubes are agglomerated. Moreover, Figure 2c shows FESEM image of Au-decorated a-CNT. Surface morphology of tubes in Figure 2c is observed to be smoother than the ones in Figure 2a. However, powdery texture seen on the tube’s surface compared with the smooth surface of functionalized a-CNT in Figure 2b is preliminary predicted to be Au nanoparticles formed on the tube’s body. Although layers of amorphous carbon have been removed via acid sonication and AuCl3 solution treatment, the overall properties of the tubes are still amorphous, as crystallization can only occur at an elevated temperature of 1700°C (20).

FTIR scanning was performed on a-CNT samples functionalized with HNO3, HCl, citric acids, and H2SO4 as shown in Figure 3. Nitrogen content observed from as-synthesized a-CNT is due to residuals of ammonium chloride used in synthesis process. As compared with as-synthesized a-CNT, a broad peak occurs in the range from 3472 to 2746 cm⁻¹ for functionalized a-CNT, which indicates the presence of H-bonded and O—H stretch. The peak at approximately 1678 cm⁻¹ shows the presence of C=O stretch, which proves the presence of carboxyl groups. A tiny peak observed at approximately 1168 cm⁻¹ shows the presence of C—H stretch. However, the O—H stretch broad peaks of citric acid and HCl functionalized a-CNT are relatively insignificant, which indicates that lower abundance of —OH group is present. Presence of C—O, O—H, and C=O stretches proves the successful formation of carboxyl groups, —COOH, on tubes’ bodies. The overall optical absorption of citric acids and HCl-treated a-CNT is significantly lower than HNO3 and H2SO4-functionalized a-CNT. Zeta potential measurement was performed using Zetasizer. Each sample was suspended in distilled water with 0.03 wt% and sonicated for 30 min. The obtained results are shown in Figure 4, in which HNO3-functionalized samples have the highest zeta potential of −142.9 mV, followed by H2SO4, citric acids, and HCl-treated samples of −60.3 mV, −15.9 mV, and −3.2 mV, wherein HCl-functionalized samples have a close zeta potential value with as-synthesized a-CNT. Negative values of zeta potential indicate negative ends of carboxyl groups. AS zeta potential represents charge amount or number of carboxyl group present (18), it is preliminary proven that HNO3 has

![Fig. 3. FTIR spectra for a-CNT functionalized with (a) HNO3, (b) H2SO4, (c) citric acid, (d) HCl, and (e) as-synthesized a-CNT.](image)

![Fig. 4. Zeta potential for a-CNT functionalized with (a) HNO3, (b) H2SO4, (c) HCl, (d) citric acids, and (e) as-synthesized a-CNT.](image)

Table 1. Elements present in as-synthesized and nitric acid functionalized a-CNT

<table>
<thead>
<tr>
<th>Elements present</th>
<th>C (wt%)</th>
<th>N (wt%)</th>
<th>O (wt%)</th>
<th>Cl (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-synthesized</td>
<td>61.36</td>
<td>13.55</td>
<td>9.1</td>
<td>16</td>
</tr>
<tr>
<td>Functionalized</td>
<td>50.29</td>
<td>13.19</td>
<td>33.76</td>
<td>2.77</td>
</tr>
</tbody>
</table>
Table 2. Elements present in Au-decorated a-CNT functionalized with various acids

<table>
<thead>
<tr>
<th>Acid types</th>
<th>C (wt%)</th>
<th>N (wt%)</th>
<th>O (wt%)</th>
<th>Fe (wt%)</th>
<th>Au (wt%)</th>
<th>Cl (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>54.16</td>
<td>9.54</td>
<td>23.86</td>
<td>3.95</td>
<td>4.76</td>
<td>3.73</td>
</tr>
<tr>
<td>Citric</td>
<td>50.79</td>
<td>10.57</td>
<td>23.46</td>
<td>2.99</td>
<td>10.27</td>
<td>1.91</td>
</tr>
<tr>
<td>H2SO4</td>
<td>47.75</td>
<td>9.96</td>
<td>20.13</td>
<td>3.38</td>
<td>13.76</td>
<td>5.02</td>
</tr>
<tr>
<td>HNO3</td>
<td>44.70</td>
<td>7.29</td>
<td>30.4</td>
<td>0</td>
<td>15.94</td>
<td>1.68</td>
</tr>
</tbody>
</table>

the highest functionalization ability for modification of a-CNT bodies in purpose of nanocluster hybridization. The functionalizing ability of HNO3 can be further proven by EDX scanning results. EDX scanning is performed on as-synthesized, nitric acid treated, and Au-decorated a-CNT, which is treated by nitric acid, citric acid, hydrochloric acid, and sulfuric acid. The EDX results of each sample are summarized in Tables 1 and 2 and the zeta potential of functionalized samples is summarized in Table 3.

Table 1 shows the elements present in as-synthesized and nitric acid treated a-CNT. High abundance of C indicates the formation of CNTs. Nitrogen and chloride content, summarized in both Tables 1 and 2, is due to the residual of ammonium chloride during chemical synthesis process, which agrees well with findings from FTIR earlier, whereas presence of Fe content in certain samples is due to residual of ferrocene present on the solution-treated samples. Note that from Table 1, functionalized a-CNT has a relatively high oxide content compared with as-synthesized a-CNT. This indicates the high oxidizing ability of nitric acid and formation of oxide-containing carboxyl groups on a-CNT body. From Table 2, Au content was found to be highest (15.94%) at nitric acid treated a-CNT, followed by sulfuric acid, citric acid, and hydrochloric acid, which are 13.76wt%, 10.27wt%, and 4.76wt% respectively. It is obvious that hydrochloric acid treated a-CNT has relatively low efficiency when applying in Au nanoparticles hybridization and nitric acid treated a-CNT exhibits the highest content of Au nanoparticles. Note that for sulfuric acid, nitric acid, and citric acid treated a-CNT, they show a similar amount of Au present when treated with AuCl3 solution under the same conditions. However, zeta potential values of sulfuric acid, nitric acid, and citric acid treated a-CNT vary largely where nitric acid treated a-CNT shows a relatively high zeta potential. Combining zeta potential and EDX results, nitric acid, citric acid, and sulfuric acid treated a-CNT have almost similar ability in Au nanoparticles attachment; however, nitric acid treated a-CNT forms the most stable suspension with water.

Conclusion

Synthesis of a-CNT with ferrocene and ammonium chloride at 200°C with presence of air creates amorphous-structured CNTs with approximately 40 nm of diameter and 298 nm in length. FTIR shows carboxyl groups present on all functionalized samples. Zeta potential measures HNO3-functionalized samples, which have the highest zeta potential of −142.9 mV, followed by zeta potential of −60.3 mV, −15.9 mV, and −3.2 mV for H2SO4, citric acids, and HCl-functionalized samples, respectively. Zeta potential values represent carboxyl groups present on tubes’ body. Moreover, EDX scanning shows that nitric acid treated a-CNTs contain the highest amount of Au nanoparticles compared with citric acid, sulfuric acid, and hydrochloric acid treated a-CNT when they are solution treated at the same condition. Therefore, it is proven that HNO3-functionalized samples create the most significant carboxyl groups functionalization.

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