

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 H_2SO_4 , citric acids, and 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 (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 NO_x 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 is often required to "activate" CNT's surface and acts as starting points for attachment of foreign nanoparticles (6,7). The mechanism of foreign particles/CNT hybridization is through electrostatic interactions between carboxyl groups on a-CNT bodies and cationic nanoclusters (8). That makes the first explanation on the importance of carboxyl groups in foreign particles/CNT hybridization. Apart from electrostatic interactions, improvement of foreign particles/CNT hybridization via

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 compounds under particular thermal or chemical conditions and produce nano-hybrid particles (9). In the year 1992, Broughton and Pederson predicted that CNT absorbs some liquids by capillary action (10), which is caused by extra pressure given by the Laplace equation of capillarity:

$$\Delta P = \frac{2\gamma \cos\theta}{R} \quad (1)$$

where $\Delta P = P_a - P_m$ represents pressure difference between atmospheric pressure, P_a , and pressure under the meniscus, P_m . γ and R represent the surface tension at the liquid/air interface and inner radius of the nanotube, respectively, and θ 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 meniscus 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° . If the contact angle is greater than 90° , extra pressure must be applied to the liquid in order to impregnate the nanotube (11). The angle θ represents degree of wetting of suspension with desired nanocomposites on CNT body itself. Addition of oxygen-containing functional group,

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—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 side-walls 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 (AuCl_3) 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 $10^\circ\text{C}/\text{min}$. 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

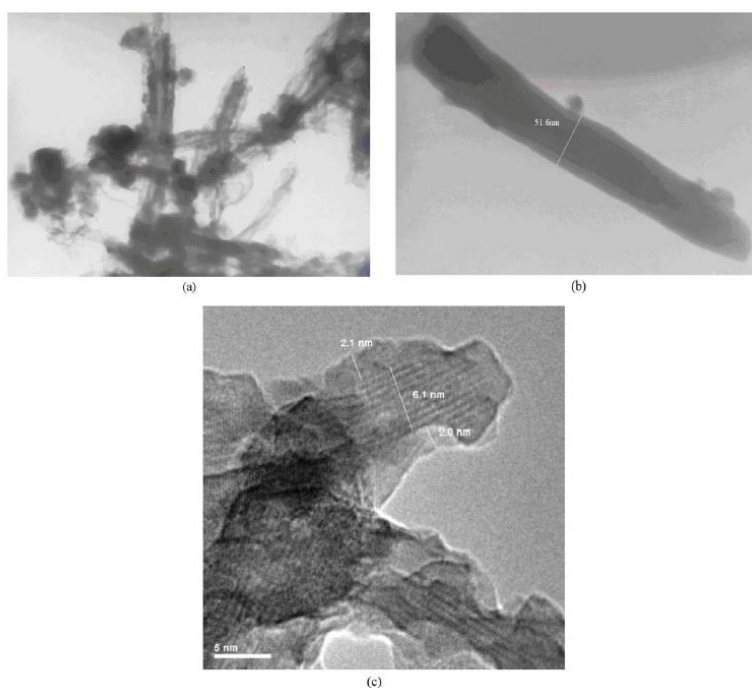


Fig. 1. (a) TEM image of as-synthesized a-CNT bundles ($\times 28,000$ magnification). (b) TEM image of as-synthesized a-CNT ($\times 75,000$ magnification). (c) TEM image of AuCl_3 solution treated a-CNT.

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), Zetascizer, transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), and EDX. TEM viewing was carried out using Libra 120 Carlzeiss. The sample (0.1wt%) 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 Zetascizer, wherein each sample was suspended in distilled water with 0.03wt% 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 (AuCl_3) solution at 1200 rpm for 1 hour at 70°C. The concentration of AuCl_3 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 AuCl_3 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

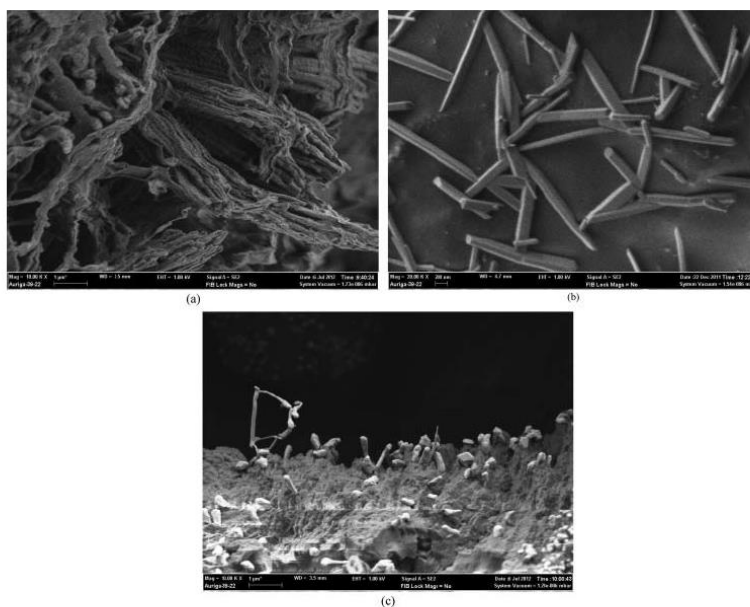


Fig. 2. (a) FESEM image of as-synthesized a-CNT. (b) FESEM image of nitric acid functionalized a-CNT. (c) FESEM image of AuCl_3 solution treated a-CNT.

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 reaggregate 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 presences of amorphous carbon layers on tubes' bodies, which can be removed by sonicating 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 2b shows smoother tube's surface than as-synthesized a-CNT in Figure 2a due to the removal of amorphous carbon layer on the tube's surface. At the same time, 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

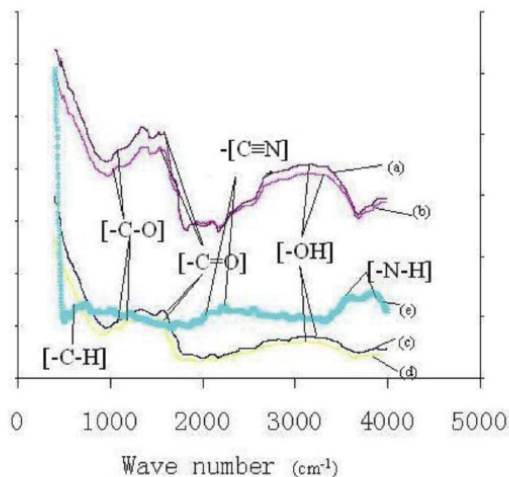


Fig. 3. FTIR spectra for a-CNT functionalized with (a) HNO₃, (b) H₂SO₄, (c) citric acid, (d) HCl, and (e) as-synthesized a-CNT.

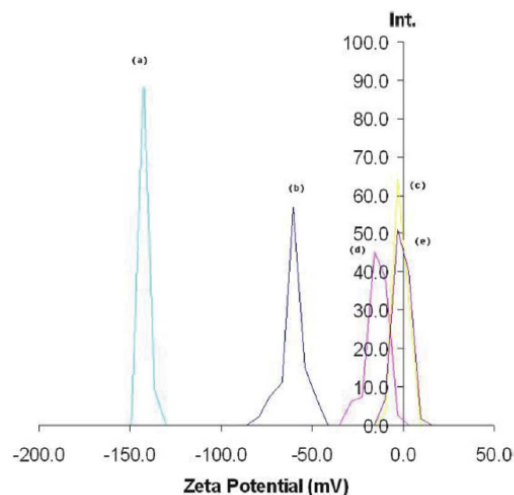


Fig. 4. Zeta potential for a-CNT functionalized with (a) HNO₃, (b) H₂SO₄, (c) HCl, (d) citric acids, and (e) as-synthesized a-CNT.

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—O 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 0.03wt% 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

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

a-CNT	Elements present			
	C (wt%)	N (wt%)	O (wt%)	Cl (wt%)
As-synthesized	61.36	13.55	9.1	16
Functionalized	50.29	13.19	33.76	2.77

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