

# Electrical Conductivity and Transport Properties of Gold Decorated Amorphous Carbon Nanotubes/Epoxy Composites

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In this work, chemically synthesized, carboxyl groups functionalized, gold particles hybrid amorphous carbon nanotubes (a-CNT) were characterized. Transmission electron microscopy (TEM) shows that Au/a-CNT hybrid possesses smaller diameter of 10.2 nm than as-synthesized a-CNTs (40 nm). Moreover, even, well-ordered fringes formed on Au/a-CNT hybrid justified successful attachment of Au particles on a-CNT. Impedance plots shows lower resistivity on high Au content's Au/a-CNT hybrid. At the same time, Au/a-CNT hybrids possesses low electrical transference numbers as compared with as-synthesized a-CNTs. Au nanoparticles contribute conducting electrons to Au/a-CNT hybrids and tend to overcome the dominating ionic conduction of a-CNT as Au content exceeds 30 wt%.

**Keywords:** amorphous materials, carbon nanotubes, electrical properties

## Introduction

Due to unique structure and outstanding properties, numerous studies involving properties and applications of amorphous carbon nanotubes (a-CNTs) have been carried out. Low synthesis costs, high production yield, and simple synthesis steps of a-CNT create a highly potential alternative to the tight production limitations of fully crystalline CNT (1). However, porous (2) and defective structure (3) of a-CNT tends to limit its usage in many applications. As an effort to be competent against fully crystalline CNT, surface modification of a-CNT has played a major role in enhancing various properties of a-CNT. For instance, oxidation of CNTs by HNO<sub>3</sub> and hybridization of Au nanoparticles on a-CNTs remarkably improve its overall electrical properties by “activating” the inert surface of a-CNT (4). In surface oxidation of CNT, previous research suggested “end and defect-side chemistry” as a mechanism to explain the tendency of functional groups’ formation (5). According to this mechanism, carboxyl functional groups have high tendencies to form at the edges and defect sites of CNT upon oxidizing with a concentrated acid (6). As hybridization of foreign cations/CNT

occurred via electrostatic interactions between positively charged cations and negative ends of carboxyl groups, these functional groups acted as important starting points for such actions (7, 8). Therefore, the defective properties of a-CNT have positioned itself to be advantageous in foreign cation hybridization. As a-CNT also possesses high surface-to-volume ratio as compared with fully crystalline CNT (9), it is expected to present more significant effects upon hybridization.

As stated in a previous study, the electrical conduction of pure a-CNTs is dominated by hopping and tunneling mechanisms (10). However, studies involved exposure in electrical conduction contributed by gold nanoparticles in Au/a-CNT hybrids, which is yet to be discovered. To investigate the percentages of electron/ionic conductions, transference number acted as a useful parameter that explains the fractional contribution of cations in electrical conduction. Wagner’s dc polarization method (11–13) offers a simple approach to determine the transference number. When a steady potential difference is applied between two terminals of a composite, at  $t = 0$  s, both ions and electrons move and contribute to the current flow. The level of current flow drops gradually until a steady current is reached, at which only ions can be depolarized and move. The equation can be described as follows:

$$t = \frac{I_0 - I_{ss}}{I_0} \quad (1)$$

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$t$ ,  $I_{ss}$ , and  $I_0$  are transference number, current at steady state, and current at initial state, respectively. From the equation,

changes in transference number represent changes in fractional contributions of ions in electrical conduction.

## Experimental

Amorphous carbon nanotubes were prepared from a bottom-up method by heating ferrocene and ammonium chloride powders in a quartz boat at 200°C (13). Attachment of gold (Au) nanoparticles on the body of a-CNTs was carried out by using a modified wet method (14). At first, 0.5 g of synthesized a-CNTs was functionalized with 30 ml of nitric acids followed by sonication for 30 min. The obtained mixture was then diluted with distilled water and dried at 150°C for 3 h. This sample was labeled as “functionalized sample.” Au/a-CNT hybrid was synthesized via solution treatment. Around 0.5 g of the functionalized a-CNTs was dispersed in auric chloride ( $\text{AuCl}_3$ ) solution having a concentration of 2.5 g/dm<sup>3</sup> and 70°C for 1 h. In another set of experiment, the concentration of  $\text{AuCl}_3$  used was 5, 7.5, and 10 g/dm<sup>3</sup>. Fifty milliliters of citric acid was added drop-wise to the solution as a reducing agent for Au cations followed by stirring for 4 h (15). The result products were then filtered, washed thoroughly, and allowed to dry at room temperature. Transmission electron microscopy (TEM) of the as-synthesized a-CNT and Au/a-CNT hybrids was carried out by using Libra 120 Carlzeiss machine. Field emission scanning electron microscopy (FESEM: Auriga Zeiss) equipped with energy dispersive X-ray (EDX) was carried out by using SE2 detector.

The preparation method of Au/a-CNT hybrid/epoxy resins composites was described by Zhu et al. (16). Epoxy resin

suspensions were prepared by incorporating 5 wt% of the as-synthesized, functionalized, and  $\text{AuCl}_3$  treated a-CNTs in epoxy. High-speed (1200 rpm) mechanical stirring was performed at room temperature for 4 h. Two milliliters of amine-based hardener was added in the mixture and each mixture is allowed to cure at room temperature. The cured samples in the form of solid coins were collected for electrical properties test.

The electrical impedance analyses of all samples were obtained using impedance spectroscopy (IS, Hioki Hitester 3532). The frequency range was set from 50 to 5,00,000 Hz, taking 500 measurements per sample, where each measurement was taken every 1 s. The obtained data were plot as Nyquist plots and resistances of all samples were taken when the frequency of alternating current is zero ( $\omega = 0$ ). The resistivity values of all samples were then calculated by using the thickness and diameter of all samples. The electrical transference number study was carried out using Gamry Potentiostat 600, wherein 5 mV was applied on all samples to investigate the variation of current with time.

## Results and Discussion

Transmission electron microscopy images for as-synthesized a-CNTs and gold (Au) Au/a-CNT hybrid are shown in Figure 1. The average diameter for a-CNTs was measured as 40 nm with a length of 298 nm (Figure 1a). The obtained result agrees well with the previous study with a-CNT diameter of 50 nm, which is 10 nm larger than our measured value (16).

Au/a-CNT hybrids possess somehow a smaller diameter, which is about 10.1 nm (Figure 1b). Well-ordered fringes

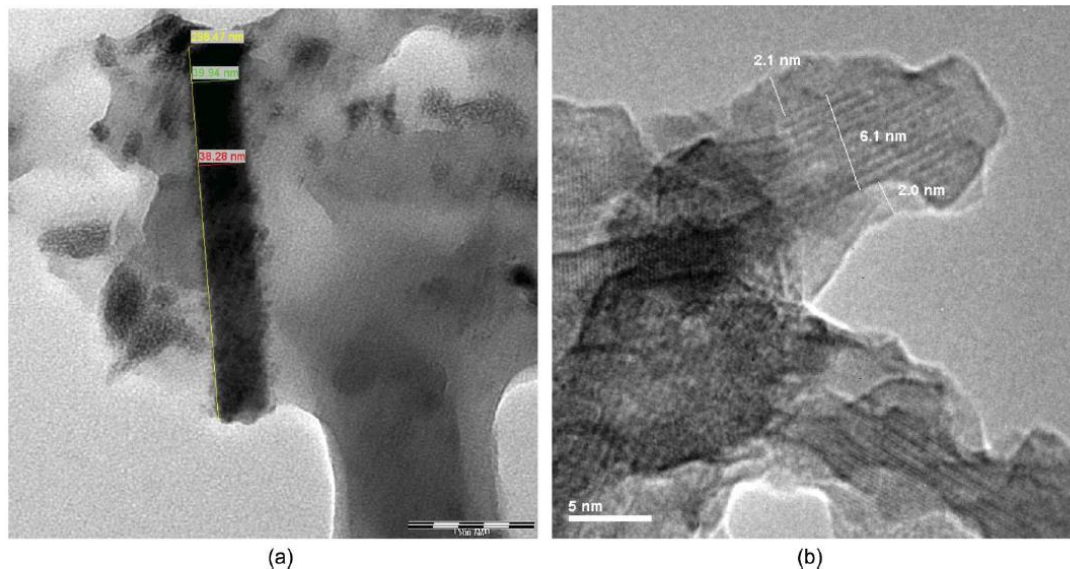
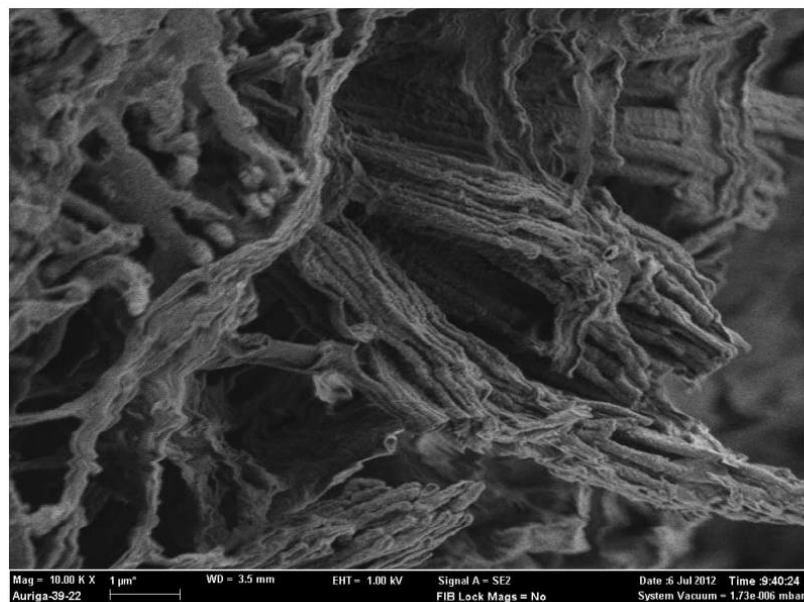


Fig. 1. (a) TEM image of as-synthesized a-CNT. (b) TEM image of hybridized Au/a-CNT treated with 10 g/dm<sup>3</sup>  $\text{AuCl}_3$  solution.



(b)

Fig. 2. (a) FESEM image of as-synthesized a-CNTs. (b) FESEM images of Au nanoparticles decorated a-CNTs treated with 10 g/dm<sup>3</sup> AuCl solution.

found on Au/a-CNT hybrid prove successful attachment of Au nanoparticles on a-CNT.

Figure 2 shows the FESEM images for as-synthesized a-CNTs and Au/a-CNTs hybrid. As both samples exhibit tubular structure, as-synthesized a-CNTs show elongated, agglomerated tubular shape (Figure 2a). Presence of rougher, uneven, and defected surface of a-CNTs suggested the amorphous structure of tubes. At the same time, the surface texture of the Au/a-CNT hybrid is relatively smoother, even, and homogenous (Figure 2b). It is thought that the changes in surface structure are due to the successful attachment of Au nanoparticles on the body of a-CNTs.

Energy dispersive X-ray is performed on Au/a-CNT hybrid via solution treatment with various concentrations of auric chloride ( $\text{AuCl}_3$ ) solution, as it is represented in Figure 3. It is seen that the Au content in the sample increases with increasing the concentration of  $\text{AuCl}_3$  in the solution. The loading values of Au nanoparticles on a-CNTs are 17.1, 19.38, 28.95, and 33.47 wt% for the addition of a-CNTs treated with 2.5, 5.0, 7.5, and 10  $\text{g/dm}^3$   $\text{AuCl}_3$  solution, respectively. Au in Au/a-CNTs hybrid increases when treated by increasing concentration of  $\text{AuCl}_3$  solution. As attachment of Au nanoparticles on a-CNT enhances electrical conduction, this variation of Au content in a-CNT would expect a large impact on its electrical properties.

The Nyquist plots of all samples are shown in Figure 4 and respective electrical resistivity of all samples are summarized in Table 1. It is seen that as-synthesized a-CNT/epoxy and functionalized a-CNT/epoxy composites possess resistivity of  $7.5 \times 10^8$  and  $5.69 \times 10^8 \Omega \cdot \text{cm}$ , respectively. However, there is a slight drop in resistivity when functionalized a-CNTs are used to form a composite with epoxy. As compared with as-synthesized and functionalized a-CNT, loading of Au particles on a-CNT results in a steep decrease in electrical resistivity. This further proves the enhancement of electrical conductivity by Au particles.

As electrical resistivity of a-CNT decreases upon increment of loaded Au content, it is justified that loading of Au particles on a-CNT improves electrical conductivity. However, the fractional contribution of ions and electrons determines the overall electrical conduction properties of Au/a-CNT hybrids. The variations of electrical current at

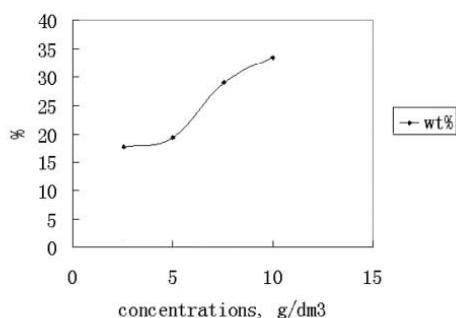


Fig. 3. Effects of the concentration of auric chloride ( $\text{AuCl}_3$ ) on the Au nanoparticles content on a-CNTs.

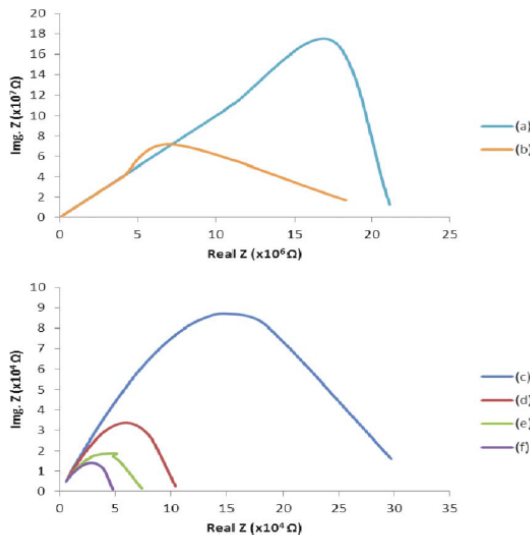


Fig. 4. Nyquist plots of (a) as-synthesized; (b) functionalized; hybridized (c) 2.5  $\text{g/dm}^3$ ; (d) 5  $\text{g/dm}^3$ ; (e) 7.5  $\text{g/dm}^3$ ; (f) 10  $\text{g/dm}^3$   $\text{AuCl}_3$  solution; a-CNT/epoxy composites.

different time of all samples are shown in Figure 5. It is seen that the initial current is dropped until a steady state current is formed. By using a modified method of Wagner's dc polarization (11–13), the transference numbers of as-synthesized, functionalized, and solution-treated a-CNTs epoxy composite were measured. The electrical resistivity and transference numbers of all samples are summarized in Table 1.

Transference number of as-synthesized and functionalized a-CNTs is relatively low, which indicates that the overall conduction of a-CNTs is dominated by ions as suggested by previous studies (17, 18). However, transference number decreases with the increase of Au nanoparticles content on a-CNTs. Electron conduction starts as a-CNTs are treated with 2.5  $\text{g/dm}^3$   $\text{AuCl}_3$  solution and dominate more than half of the total conductivity when the concentration reaches to 7.5  $\text{g/dm}^3$ . Combining results and analysis described above, it is proven that Au nanoparticles on a-CNT bodies contribute electron conduction to a-CNT overall electrical conductivity. This represents a mechanism of conducting changing behavior either in metallic or semiconducting states. This area would be the focus in the future study.

Table 1. Resistivity and  $t$  values for all samples.

Samples	Resistivity ( $\Omega \cdot \text{cm}$ )	$t$
(a)	7.50E+08	0.95
(b)	5.69E+08	0.94
(c)	9.92E+06	0.77
(d)	3.39E+06	0.54
(e)	1.67E+06	0.49
(f)	1.50E+06	0.34

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