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Assessment of the Reaction Time on the Morphology and Quality of Carbon Nanotubes – Silica Microparticles

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Abstract

Carbon nanotube has been grafted in-situ on the surface of spherical silica gel via floating-catalyst chemical vapour deposition method. The reaction temperature was set to be 760°C and 5 wt. % of ferrocene catalyst (dissolved in toluene) injected into the furnace at a rate of 0.04 ml/min. The reaction time was varied from 1 hour to 8 hours, with one hour interval. It was found that the reaction time of 3 hours yields the best quality hybrid particles. Prolonging the reaction time more than 3 hours resulted in the formation of CNT that consists of thicker tubes, based on the observation via Field Emission Scanning Electron Microscope (FESEM) and Transmission Electron Microscope (TEM). Secondary overgrowth was observed via TEM for tubes synthesized at 7 hours and 8 hours. These results were in agreement with Raman Spectroscopy analysis where the I_G/I_D ratio were very small, indicating high defects and impurities in the samples synthesized at reaction time higher than 3 hours.

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1. Introduction

Carbon Nanotube is known as a multifunctional filler that may impart an extraordinary mechanical properties¹, electrical properties², and thermal properties³ in a composite. One big challenge faced during the composite processing is CNT agglomeration due to strong Van der Waals interaction and physical entanglements originating from their growth process. It has been reported elsewhere that direct growth of CNT onto fibres⁴⁻⁶ and

microparticles⁷⁻⁹ could address issues related to dispersion. The CNT growth on silica⁵, stainless steel¹⁰, and alumina particles ($\mu\text{Al}_2\text{O}_3$)⁹ are also described where an increase in thermal conductivity in an epoxy matrix is achieved¹¹. These substrates not only function as the growth sites, but also as transport medium to carry CNTs within the matrices.

Prolonging the reaction time results in supplying more carbon and catalyst source. For example, the CNTs yield on silica fibre increased to 4.93 mg/cm^2 from 0.09 mg/cm^2 by increasing reaction time from 15 to 240 minutes⁵. The growth of CNT on silica microparticles have been described in previous publication, where the growth time up to 3 hours has already been investigated¹². This paper aims to investigate further on the effects of increasing the reaction time up to 8 hours, on the morphology and quality of the CNT.

Nomenclature

CNT	Carbon Nanotube
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
ID	Inner Diameter
OD	Outer Diameter

2. Experimental

The CNTs were grafted on spherical silica gels with pore size of 6 - 8 nm at 760°C , as described in details in¹². Prior to that, the ferrocene (5 wt. %) was first dissolved in toluene and preheated to 200°C before injected into the furnace at a flow rate 0.04 ml/min. The reaction time is varied from 1 to 8 hours, with 1 hour interval. The other parameters were kept constant such as reaction temperature, ferrocene concentration, and injection rate, while varying the reaction time.

The morphology of the particles was assessed via Philips XL 30 FEG SEM at 10 kV and Philips CM200 TEM. The pin stub with adhesive carbon disc was slightly pressed onto nanoparticles before having it coated with gold using Edward S150B Sputter Coater. The topography was then viewed at 10kV acceleration voltage. For TEM characterisation, the images of the particles were recorded and viewed under bright field mode. Raman analysis were performed to assess the quality of the synthesized CNT. The measurements were performed at least three times per sample to ensure data accuracy.

3. Results and Discussion

3.1 Morphology

Figure 1 shows the typical SEM images of the particles synthesized at 1 hour, 3 hours, 6 hours, and 8 hours. It can be deduced from high magnification images (Figure 1, left column) that prolonging the reaction time resulting in higher coverage of CNT on the silica surface. Full silica coating is observed for the samples synthesized at 3 hours and more (Figure 1d, 1f, and 1h). The CNTs remain entangled although the reaction time has increased further. The tubes appear thinnest when reaction time is at 3 hours. Further increasing reaction time results in the presence of thicker tubes. It is also observed that there are two types of tubes for the sample synthesized at 8 hours. The CNTs at the 'bottom' layer seem thinner compared to the CNTs at the 'top' layer (Figure 1g). It may be inferred that after 6 hours, additional carbon source contributes to the tubes thickening that protrude up to the top layer. The tubes at the bottom layer appear thinner as these thick CNTs at the top layer prevent the diffusion of carbon source to the tubes underneath.

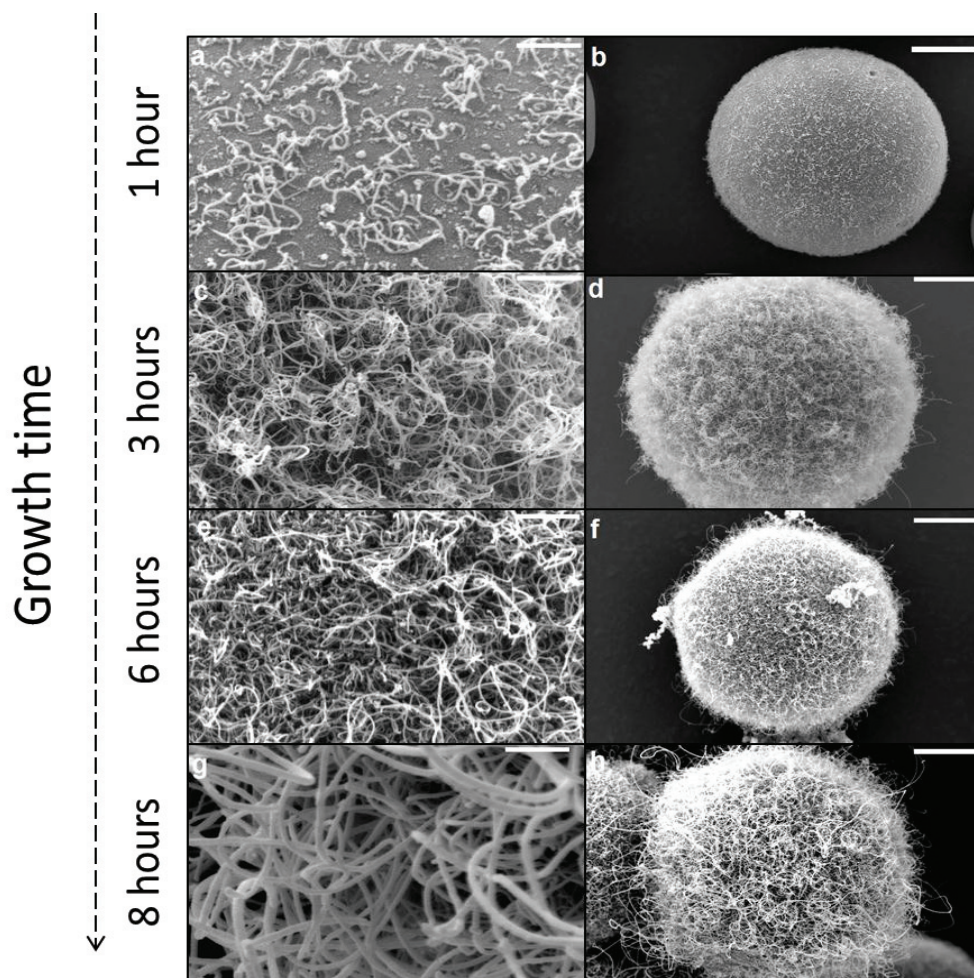


Fig. 1. High (left column) and low (right column) magnification SEM images of the particles synthesized at 1 hour (a) and (b); 3 hours (c) and (d); 6 hours (e) and (f); and 8 hours (g) and (h), highlighting the effects of growth time on morphology and topology of the microparticles. Scale bar is equivalent to 1 μm (high magnification, left column) and 10 μm (low magnification, right column).

TEM investigation further demonstrates the variation of inner diameter (ID) and outer diameter (OD) for samples synthesized under different reaction time, as shown in Figure 2. Overall, the tubes synthesized are not straight and the diameters increases as the reaction time is increased. As shown in Figure 2d (red ringed tubes), overgrowth appears to have taken place, where the thin CNT is observed to protrude from a thicker CNT. It is speculated that the thin CNT was originally grown within the silica pores while excess carbon keep adding on the outer tube wall contributing to the tube thickening process.

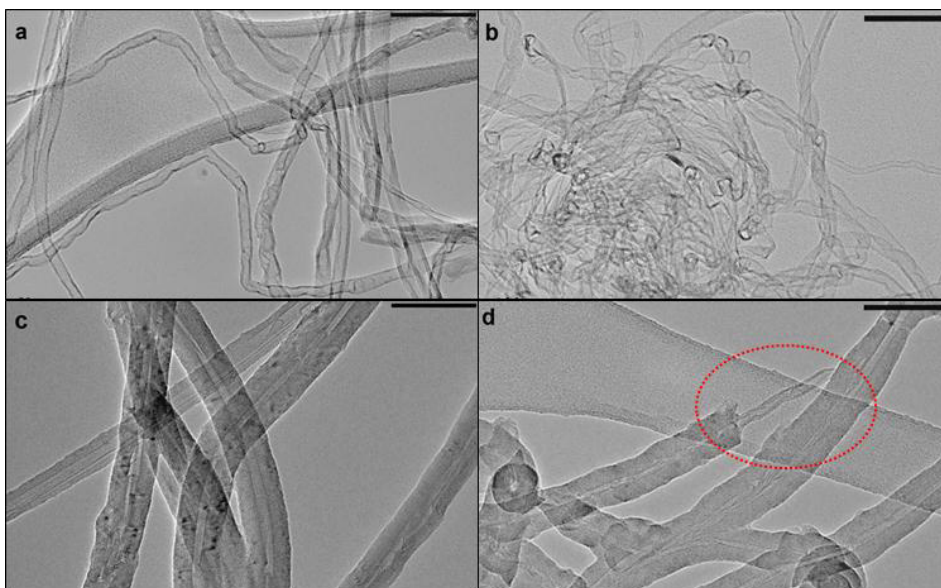


Fig. 2. Typical TEM images for tubes synthesized at 1 hour (a), 3 hours (b), 6 hours (c), and 8 hours (d). Scale bar is equivalent to 100 nm. The circled tubes showed the over-growth (2d).

Image J software¹³ is further used to measure ID and OD of at least 100 tubes synthesized for every sample. The size distribution is as shown in Figure 3. The two parallel dotted lines are purposely drawn at diameter equals to 6 and 8 nm to investigate the pore size of the silica with the tubes synthesized. The ID distribution (Figure 3a) is in unimodal pattern for all tubes except for the ones synthesized at 8 hours. The peak for samples synthesized at 1 hour and 3 hours still fall within 6–8 nm demonstrating a close relation between the pore size and the ID values (Figure 3a). Although the sample synthesized at 6 hours demonstrates a unimodal distribution, the peak is seen to shift slightly to ~11 nm. On the other hand, the sample synthesized at 8 hours exhibit a bimodal distribution, with a peak at ~8 nm and a second, slight broader peak at ~14 nm. No bimodal distribution is observed in the case of OD (Figure 3b). However, the distribution peak is seen to shift towards larger value as the reaction time is increased as a result of tube coarsening due to excess carbon source supplied.

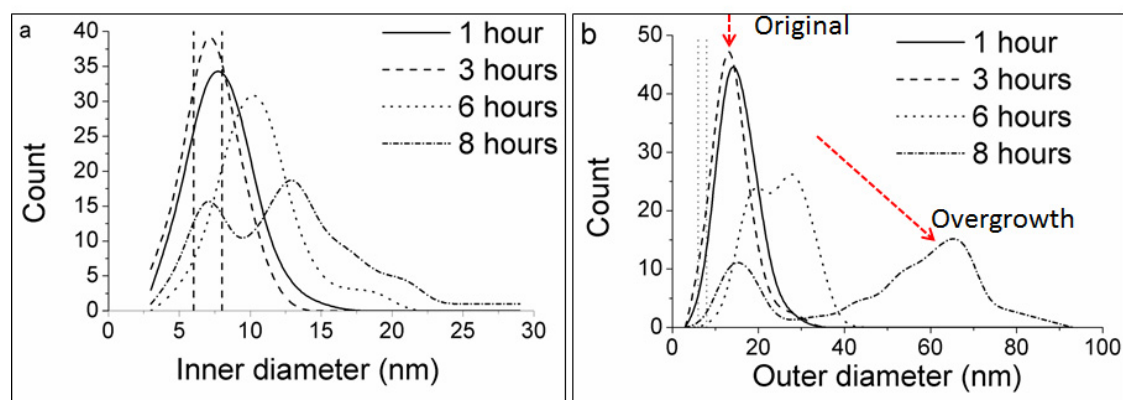


Fig. 3. Graphs showing (a) ID and (b) OD for CNT grown at 1 hour, 3 hours, 6 hours, and 8 hours. Vertical lines are drawn at 6 nm and 8 nm to relate pore size of the substrate and diameter of the tube diameter.

3.2 Raman Study

Raman characterisation is further performed to assess the quality and quantity of the CNTs synthesized, respectively. Raman provides a quick and non-destructive technique to detect the presence of impurities within the sample and crystallinity of the CNTs by analysing three bands which are D mode, G mode, and G' mode. D mode ($\sim 1321\text{ cm}^{-1}$) is often associated with impurities, while G mode ($\sim 1570\text{ cm}^{-1}$) and G' mode ($\sim 2642\text{ cm}^{-1}$) are related to the CNT's crystallinity and the presence of CNT, respectively¹⁴.

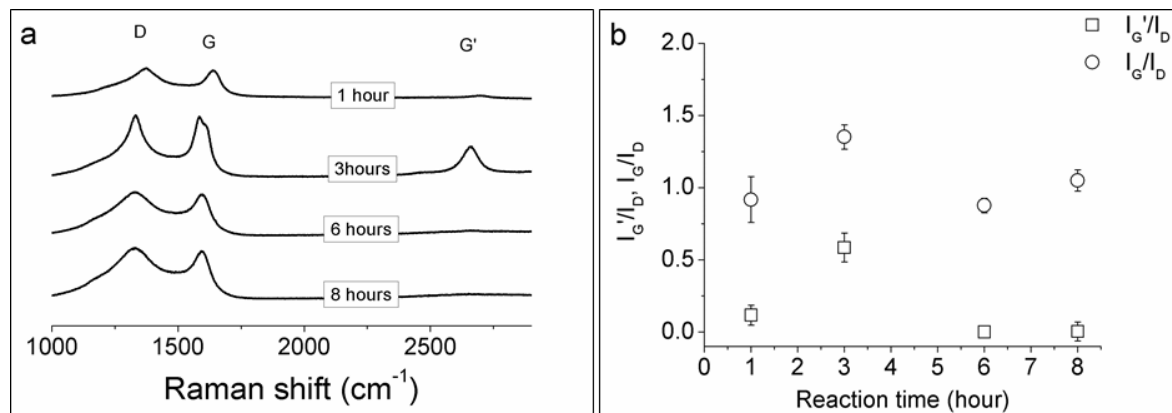


Fig. 4. Raman Spectra (a) and ratios of $I_{G'}/I_D$ and I_G/I_D (b) for all samples synthesized at different reaction time.

Figure 4 shows the Raman Spectra as well as $I_{G'}/I_D$ and I_G/I_D ratios for all samples. The G' seems to appear only at samples synthesized at 3 hours (Figure 4a). The disappearance of G' in sample synthesized after 1 hour is due to the incomplete coverage of the CNT. In the case of sample synthesized after 6 hours and 8 hours, the disappearance of G' could be due to the amorphous coating on the CNTs on top layer. Figure 4b shows the G to D (I_G/I_D) intensity ratio and G' to D intensity ratio ($I_{G'}/I_D$). Higher ratios, which indicate higher CNTs' crystallinity can be seen when reaction time is at 3 hours. This analysis is in agreement with morphology characterization, where thinner and least amorphous carbon formation is minimized.

4. Conclusions

In this work, CNTs were synthesized on the surface of porous silica gel via FC-CVD. It was found that prolonging the reaction time above 3 hours causes the increment in both ID and OD. Excess carbon supply contributed to the tube coarsening, where overgrowth was observed for the tubes synthesized at 8 hours. Raman Spectra confirms the SEM and TEM characterization where the sample produced at 3 hours yield the CNT with the best quality and crystallinity.

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