

Diameter controlled synthesis of carbon nanotubes by CVD using steric-stabilized nanoparticle catalysts

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ABSTRACT

Surface modified iron nanoparticle catalysts are used for the diameter controlled carbon nanotube forest growth at 650°C using chemical vapor deposition. Temperature induced aggregation of nanoparticles commonly observed when preformed nanoparticle catalysts are employed was successfully prevented by surface modification of nanoparticles with APS. APS formed a siliceous deposit around the nanoparticles that prevented the agglomeration of nanoparticles at the early stages of nanotube growth.

Keywords: Carbon nanotubes, CVD, surface modification, Iron nanoparticle catalysts.

1 INTRODUCTION

The extraordinary chemical, mechanical and electrical properties of the carbon nanotubes make them ideal candidates for various applications like interconnects [1], field effect transistors [2a-d], single electron transistors [2e-g], biological sensors [3] etc., and have been investigated in great detail since its discovery in 1991[4]. A number of different methods are reported for their synthesis that include, HiPCo process [5], chemical vapor deposition [6], and more recently solution based room temperature synthesis [7], etc. Among these, chemical vapor deposition has been widely used since it allows growth of isolated individual nanotubes on catalyst covered surfaces at lower process temperatures [8], while also being compatible with semiconductor processes for potential interconnect applications [1b]. Chemical vapor deposition commonly involves growth of carbon nanotubes using carbon sources like acetylene, alcohol, carbon monoxide on surfaces covered with catalysts typically composed of transition metals or their precursors. The properties of the carbon nanotubes are strongly dependent on their diameter, chirality and length which are in turn dependent on the process parameters, like temperature, concentration and nature of the carrier gas, catalysts etc [9]. A number of reports in the literature suggest that the diameter of the nanotubes is strongly dependent on the size of the nanoparticle catalyst used to grow them [10]. Among the various forms of catalysts used, nanoparticles catalysts synthesized by chemical methods are best suited since a wide variety of metal nanoparticles with well defined size

and size distribution can be synthesized in large quantities using this method [11]. Also, they can be further subjected to post synthesis solution based processing to realize functional nanoparticles with tailored properties [12].

Growth of carbon nanotube typically involves temperatures in the range 600-1000°C. At these temperatures, nanoparticles aggregate to form larger diameter particles due to various reasons like (a) the loss of the protecting agent (b) reduced melting temperature of metal nanoparticles due to the higher ratio of surface atoms compared to inner atoms and (c) sintering due to high surface mobility resulting from poor catalyst-substrate interaction; hence leading to the formation of larger diameter nanotubes [13]. To circumvent this problem, T.Hyeon and coworkers recently employed zirconia based nanoparticle spacers in the Langmuir monolayer of iron oxide nanoparticle catalysts to grow nanotubes with diameter equal to the size of the catalysts [10e]. Zirconia nanoparticles prevented aggregation of iron oxide nanoparticles at the process temperatures of 900°C employed for the growth. However, the presence of zirconia nanoparticles does not allow deposition of high density of nanotubes required for most applications. Here we report on a simple approach for the synthesis of diameter controlled synthesis of carbon nanotubes using aminopropyltriethoxysilane (APS) modified iron nanoparticles (APS-Fe nanoparticles) as catalysts by chemical vapor deposition at 650°C. APS modification of the nanoparticle serves the dual purpose of (a) binding the nanoparticles strongly to the substrate and; (b) provide steric stabilization against aggregation by precipitation of siliceous deposit around the nanoparticles at elevated temperature. Carbon nanotubes with diameter equal to the size of APS-Fe nanoparticles were successfully grown on silicon oxide surfaces. This strategy allows the successful deposition of high density of carbon nanotubes with controlled diameter at a scale enabled by chemical vapor deposition.

2 EXPERIMENTAL

2.1 Fe nanoparticle synthesis.

Iron oxide nanoparticles ~3.5 nm was synthesized using the method reported by T.Hyeon et al that involved thermal

decomposition of iron pentacarbonyl-oleic acid complex [10e]. Briefly, 1.28g of oleic acid in 10 mL phenyl ether was heated to 100°C. 0.2mL of Fe(CO)₅ was added to this mixture and heated to reflux. The refluxing was continued for 1 hour following which the solution was cooled to room temperature. The nanoparticles were separated by addition of 20 mL of ethanol to obtain a black precipitate that was washed two more times with ethanol. The black precipitate was dispersed in 10 mL chloroform and used as stock solution.

2.2 Self assembly of APS modified nanoparticles onto planar supports.

Silicon wafer with 100 nm thermal oxides was pre-cleaned by sonication in isopropyl alcohol, and water followed by heating in a solution containing hydrogen peroxide, ammonia solution and water in the ratio 1:1:5 at 70°C for 10 min. 3 mL stock solution of iron nanoparticles in chloroform was diluted to 10 mL by addition of chloroform. 0.2 mL of APS was added to this solution and used as the depositing solution. The nanoparticles were deposited by immersing the substrates overnight in the APS-Fe nanoparticle dispersion following which the substrates were removed from the depositing solution and washed with copious amounts of chloroform and dried.

2.3 CNT growth

Carbon nanotubes were grown on the catalyst covered surface by thermal CVD at 650°C using acetylene as the carbon feedstock. The growth of carbon nanotubes was performed by placing the samples in the quartz tube furnace followed by evacuating to below $\sim 10^{-3}$ Torr and introducing Ar as a purge gas to $\sim 10^{-1}$ Torr. Subsequently, the furnace was heated to growth temperature of 650°C and then acetylene was introduced to 1.6 Torr for 10 min maintaining the growth temperature. The nanotube growth on all the samples described in this report were grown under identical conditions.

3 RESULTS AND DISCUSSION

Figure 1 shows the transmission electron microscopy image of the synthesized iron nanoparticles. Relatively monodisperse ~ 3.5 nm Fe nanoparticles self-assemble to form ordered structures because of the size uniformity. The size of the largest sized nanoparticles did not exceed 5 nm (image not shown). The APS derivatization of Fe nanoparticle was rendered by the addition of APS (1mM) to the chloroform solution of iron nanoparticles. APS binds to the Fe nanoparticles via the $-\text{NH}_2$ group while exposing the silane group for their self-assembly onto a 100-nm-thick silicon oxide covered silicon substrates. Figure 2 is a scanning electron microscopy (SEM) image of the APS-Fe nanoparticles deposited on the silicon oxide surface by dip

coating. APS-Fe nanoparticle based film with relatively high surface coverage of nanoparticles is deposited.

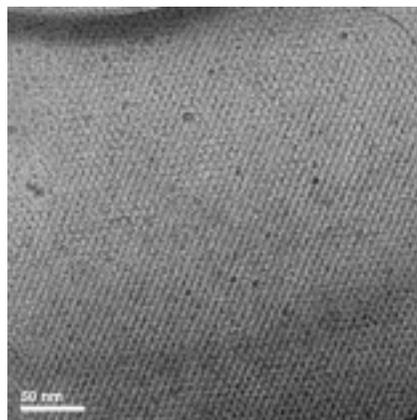


Figure 1: TEM image of the synthesized Fe nanoparticles.

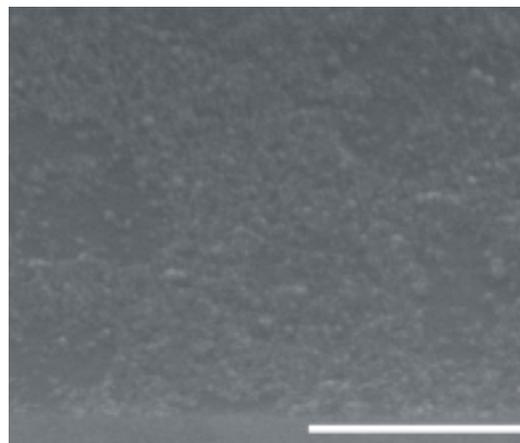


Figure 2: SEM image of APS modified Fe nanoparticles adsorbed onto SiO₂.

A control experiment involving adsorption from chloroform solution of unmodified Fe nanoparticles under similar adsorption time and washing conditions showed very few nanoparticles adsorbed onto the surface (figure not shown) clearly showing that the nanoparticle deposition in the case of APS-Fe nanoparticles is facilitated by APS. The nanoparticle deposition is likely to involve a combined process of APS self-assembly on the oxide support followed by particle attachment via the $-\text{NH}_2$ group; and/or direct attachment of APS modified nanoparticles to the substrate by binding of the terminal silane group to the oxide surface. Please note that the nanoparticle dispersion also contains unreacted APS since, APS-Fe nanoparticles were not subjected to additional washing after capping with APS.

Recently M. Mizuno *et al* reported that, FePt nanoparticles immobilized on an oxide support by a self-assembled monolayer of APS prevented aggregation upon annealing at 800°C [14]. They found traces of silicon oxide around the nanoparticle on annealing that provided

the stabilization against coalescence. In our case however, APS is likely to be present both on the surface of the nanoparticles as well as on the substrate. Also, the effect of annealing would be pronounced in our case, due to higher surface coverage of nanoparticles. As observed by Mizuno *et al*, APS may undergo thermal decomposition to form submonolayer siliceous coating around the nanoparticles when exposed to elevated temperatures required for chemical vapor deposition. The siliceous coating around the particles may thus prevent growth of the nanoparticles as observed previously [14], while facilitating the growth of nanotubes with diameter equal to the size of Fe nanoparticles.

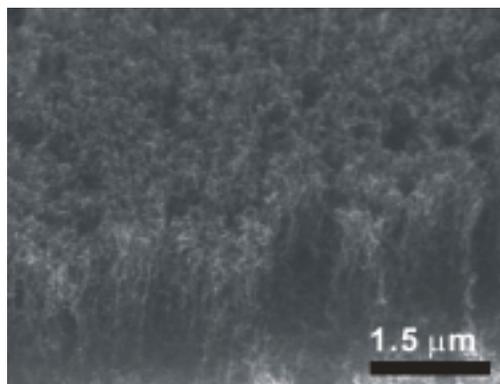


Figure 3: SEM image of CNT forest grown using APS modified Fe nanoparticles as catalysts.

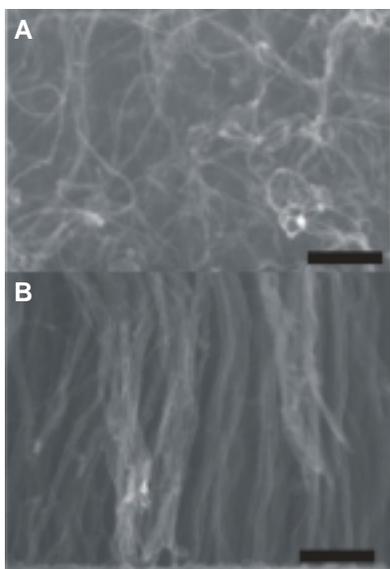


Figure 4: SEM image of CNTs grown with (A) and without (B) APS modification. Scale bar = 200 nm

As seen in Figure 3, densely populated carbon nanotubes that are well separated from each other were grown on the APS modified Fe nanoparticles. The synthesized nanotubes had diameters of 3 to 5 nm, which is close to the size of the nanoparticle catalysts (Figure 4A). The absence of catalyst nanoparticles at the tip of the nanotubes indicates that the

nanotubes grew by the base growth mechanism. For comparison Fe nanoparticles without APS modification was spin coated onto to the oxide surface at 6000 rpm for 30 seconds. Nanotubes were subsequently grown under identical conditions described for APS-Fe nanoparticles. As seen in Figure 4B the nanotubes with diameter ~ 10 nm and above were obtained for Fe nanoparticles without APS modification indicating that Fe nanoparticles aggregate at 650°C in accordance with previous observation.¹² Figure 4 clearly shows that aggregation of nanoparticles at elevated temperatures can be prevented by surface modification of the catalysts with APS, thus leading to carbon nanotubes with diameters equal to the size of the nanoparticles. Previous reports on the growth of nanotubes from nanoparticle films involved a two step process of heat treatment followed by growth at temperatures ~800°C in the presence of carbon feedstock. At these temperatures mostly single walled carbon nanotubes were obtained. Here however, diameter controlled multiwalled nanotubes are grown at 650°C, (a much lower temperature compared to the previous reports [10]) using APS modified Fe nanoparticles as catalysts without the pretreatment step. In order to study the effectiveness of APS stabilization against aggregation of nanoparticles at elevated temperatures, APS modified nanoparticles were subjected to same thermal treatment (*without* the carbon source gas) that are used for CNT growth. The carbon nanotubes were subsequently grown on the thermally treated samples. Carbon nanotubes of ~ 20 nm diameter and 12 μ m length were obtained (SEM will be presented during the oral presentation). The diameter and the length of the nanotube are higher than that obtained for APS-Fe nanoparticles without the annealing step (Figure 3). This clearly indicates that while APS modification prevents aggregation of the nanoparticle catalysts at the early stages of nanotube growth, it cannot prevent nanoparticle aggregation on prolonged heat treatment at 650°C. The increased growth rate in the case of thermally treated catalysts is directly related to the area on the substrate surface (silicon oxide) freed by agglomeration of nanoparticles, which in turn clearly indicates that the growth process is dominated by the diffusion of carbon species on the oxide surface towards the catalyst than by impingement of carbon species at the nanoparticle catalysts directly from the gas phase. Various growth models proposed in the literature suggest that the catalytic activity of the catalyst particle while is important for the nucleation of nanotubes, but is not for the subsequent growth of the nanotube [8]. The above control experiment shows that for nanotube growth without pretreatment step, even though APS stabilization cannot prevent particle growth by aggregation at high temperatures, they are sufficient to stabilize them at the early stages of the nanotube growth, thus providing enough stability for the diameter control synthesis of carbon nanotubes. Control experiments involving the pretreatment step were also performed by employing higher concentration of APS (5mM) in the nanoparticle depositing solution. Increase in APS

concentration in the APS-Fe depositing solution led to the deposition of catalyst based film with higher surface coverage and multilayer formation. While higher APS concentration had a marginal effect on the diameter and length of the nanotube without the annealing (pre-treatment) step, nanotube density obtained was much higher (as observed from SEM) owing to the higher nanoparticle density and multilayer formation. On the other hand, diameter of the nanotubes grown from the annealed sample (with pre-treatment step) was smaller (~10 nm), when 5mM APS was used to cap the nanoparticles compared to the 1mM APS concentration sample; proving conclusively that APS plays a significant role in the diameter controlled synthesis of carbon nanotubes. TEM investigation of the grown nanotubes showed that the diameter of nanotubes to be about 5 nm (Image will be included during the oral presentation). Energy Dispersive Adsorption of X-rays analysis of catalyst seeds in the nanotubes showed the presence of both Fe and Si indicating the presence of APS in the thermally decomposed form on the nanoparticles..

4. CONCLUSIONS

We have demonstrated that APS modification of colloidal Fe nanoparticles can be used to control the diameter of the carbon nanotubes. At elevated temperatures involved in the growth of carbon nanotubes, APS prevents aggregation of nanoparticles leading to the growth of carbon nanotubes with diameter equal to the size of catalyst nanoparticles. While APS stabilization cannot prevent the aggregation of nanoparticles completely, they are effective in controlling the diameter of the nanotubes during the initial stage of the growth. Our results on diameter control by surface modification of catalyst nanoparticles is significant considering the recent reports on synthesis of single walled nanotubes at temperatures as low as 600°C using Ni catalysts.⁸ Our strategy therefore provides an additional parameter to control the diameter of nanotubes grown using CVD. Future work would involve growth of carbon nanotubes using nanoparticle catalysts stabilized with molecules containing higher silicon content (e.g. polysiloxanes) per molecule and also core-shell nanoparticles.

5. REFERENCES

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