Growth and characterization of CNT Forests using Bimetallic Nanoparticles as Catalyst

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ABSTRACT

The synthesis of Fe, Fe-Pt and Fe-Co nanoparticles were carried out using the bottom-up polyol process using standard ari free techniques. Using these nanoparticles, multiwalled carbon nanotubes were synthesized in an atmospheric pressure plasma enhanced chemical vapor deposition(APPECVD) process with a mixture of helium and acetylene gases. The APPECVD process produced dense carbon nanotube forests that were 30μm for Fe, 5μm for Fe-Pt and 80~100μm for Fe-Co nanoparticles.

Keywords: bometallic nanoparticles, iron-platinium, iron-cobalt, carbon nanotubes

1 INTRODUCTION

Multiwalled carbon nanotubes (MWCNTs) promise to be useful many applications of great technological importance as they have excellent behaviors as nano-electronics [1], field electron emitters [2], contact electrode [3], sensors [4], etc. Current efforts have been concentrated on using zerovalent metal ions such as Fe, Ni, Co as catalysts, we have expanded our horizons to using bimetallic nanoparticles as catalyst materials. Bimetallic nanoparticles have great improved catalytic properties of the original single metal catalyst and create new properties which may not be achieved by monometallic catalysts [5]. One of the main advantages of using bimetallic nanoparticles is that both the external (size and shape) and internal composition (atomic ordering) can be well controlled.

Fe-Pt and Fe-Co nanoparticles have been demonstrated to be suitable catalysts for growth of carbon nanotubes [6], with some growth recipes reported to yield single-walled nanotubes (SWNTs) [7]. Nanoparticles make for attractive catalysts because, in addition to the possibility of making high-quality CNTs, they are suitable for a variety of growth conditions [8] and applications [6, 9-11]. It is widely believe that the diameter of the catalyst form affects the diameter of carbon nanotubes, the nanoparticle, which can be controlled for size is a good candidate for selective growth of CNTs [10].

Here, we report a simple and efficient way of producing iron-platinum and iron-cobalt (Fe-Pt, Fe-Co) bimetallic nanoparticles which are subsequently used to catalyze continuous growth of multi-walled carbon nanotube (MWCNTs) forests. We compared growth behaviors of MWCNTs grown on monometallic nanoparticles and bimetallic nanoparticles.

2 EXPERIMENT

2.1 Synthesis & Preparation of Nanoparticles

The synthesis of Fe, Fe-Pt, and Fe-Co nanoparticles were carried out using the bottom up polyol process using standard air free techniques [11]. Fe, Fe-Pt, and Fe-Co nanocrystals were prepared by thermal decomposition at 280 ^{o}C for 30 minutes of iron acetylacetonate, platinium acetylacetone, and cobalt acetylacetonate with octyl ether in the presence of 1,2-hexadecanediol, oleic acid, and lleyamine. The ratio of platinum acetylacetonate to iron acetylacetonate and cobalt acetylacetone to iron acetylacetonate was 3:1 and 2:1 respectively. After 30minutes, the solution was cooled to room temperature, and the nanoparticles were precipitated using ethanol. The nanoparticles was isolated by centrifuge, were re-dispersed in hexane and then spin-coated onto a silicon substate. Previous studies have demonstrated that the synthesized nanoparticles are typically surrounded by the organic stabilizer shell [12], which in our case is oleic acid. Additionally, some nanoparticles spin coated on the Si wafer were first heated to 680 ^{o}C and then treated with oxygen plasma, in order to expose the nanoparticles.

2.2 Growth of Carbon Nanotubes

Subsequent growth of MWCNTs forests was accomplished with an atmospheric pressure plasma jet(APPJ) procedure previously published by our group [13].

The plasma jet was maintained bt 13.56 MHz and the RF power was limited to 30W. Nanoparticles were spin-coated on the SiO_2 covered Si wafer. Acetylene as the carbon-precursor gas was delivered through a capacitively coupled plasma source onto the growth surface. The substrate with spin-coated nanoparticles was heated to the growth temperature on the Cu heating block, after which acetylene carried in the helium plasma was supplied to the surface. Growths were preformed at 680 ^{o}C for 3 min with RF power at 30W. After 3 min, the substrate was cooled under helium environment to the room temperature.

2.3 Characterization

Samples for transmission electron microscopy (TEM) were prepared by sonicating the nanoparticles in hexane, dropping a dilute suspension on a copper grid, and then drying. TEM images and energy-dispersive X-ray analysis (EDS) were acquired using a JEOL JEM-2100F TEM. Scanning electron microscopy (SEM) images were obtained at 10kV using the LEO 1350V. For carbon nanotube growths, SEM and TEM images were obtained using the same equipment.

In observing growth products, the CNT forests were checked for long range order at low magnification to check for nanotubes, The forest contains disordered content such as estimate of the quality of these nanotube forests. The Raman spectrometer used in this study had a laser at 633 nm spectral detection.

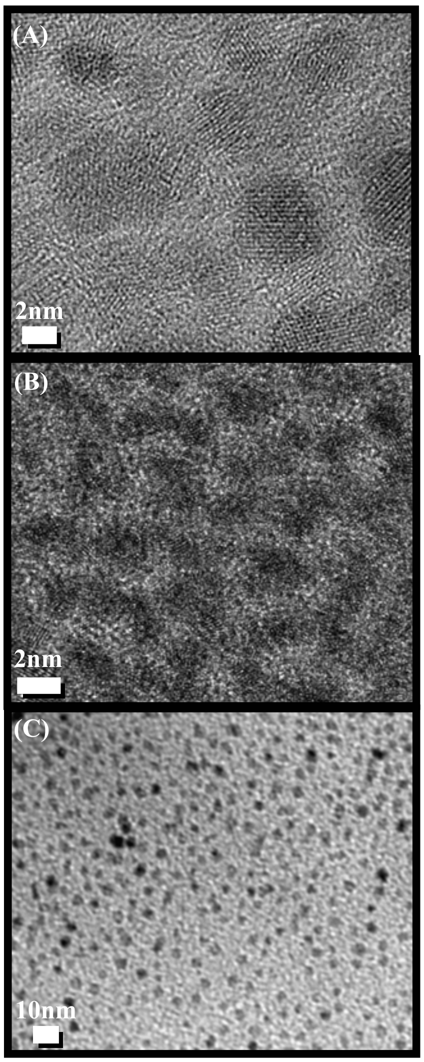

Fig. 1. TEM Images of nanoparticles (A) Fe NPs, (B) Fe-Pt NPs, (C) Fe-Co NPs

3 RESULTS AND DISCUSSION

3.1 Imaging - Nanoparticles

The ability to control composition and size in the synthesis of bimetallic Fe-Pt and Fe-Co nanoparticles is important for the exploitation of their catalytic properties. The Fe, Fe-Pt, and Fe-Co nanoparticles used in the process were examined under TEM and found to have an average diameter of 2~3nm (Fig. 1).

EDS analysis reveals the composition of bimetallic nanoparticles. The molar ratio of iron to platinum and iron to cobalt is 4:1 and 1.2:1, repectively. This composition of iron to platinum in a 4:1 ratio is important for the growth of carbon nanotubes, as both 1:1 and 2:1 molar ratios resulted in no growths. The effects of the composition of the nanoparticles may be related to their ability to dissolve carbon atoms and form nanotubes [7, 14].

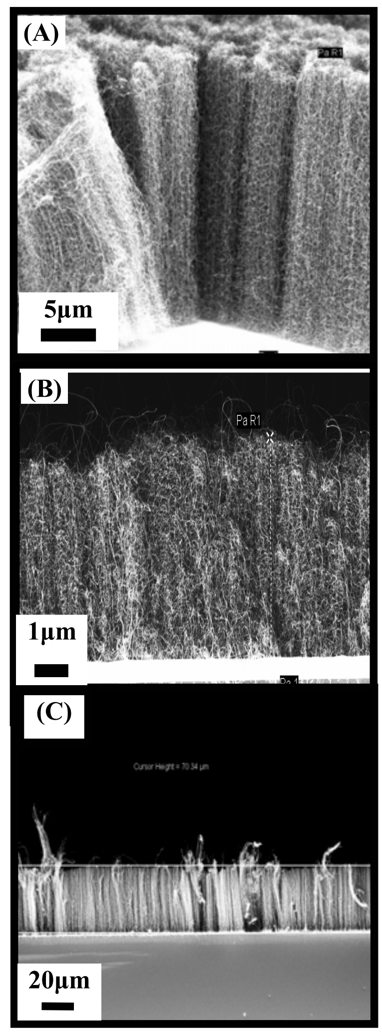

Fig. 2. The SEM Images of the MWCNTs grown on (A) the Fe nanoparticles, (B) the Fe-Pt nanoparticles and (C) the Fe-Co nanoparticles.

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3.2 Imaging – Growths in PECVD

Growths were performed, using the atmospheric plasma jet as previously described, at 680^{o}C for 3min.

Fig. 2. showes MWCNT forests which were dense, uniform, and well-aligned on Fe, Fe-Pt and Fe-Co nanoparticles, respectively. The forest's height varied from 30 µm for Fe to 5 µm for Fe-Pt and 80~100 µm for Fe-Co nanoparticles. The MWCNT forests produced on Fe-Co particles was taller than those grown on Fe and Fe-Pt nanoparticles. We think that the advantages of using Fe-Co nanoparticles over Fe alone is the increase in the MWCNT forest's height from 30 µm to 80~100 µm. The addition of Co prevents the catalyst from poisoning and enhance the growth of the MWCNT forests. But Pt does not improve the catalytic properties.

Fig. 3. is the TEM Images of MWCNTs grown on different particles (Fe, Fe-Pt, and Fe-Co). According to TEM results, the diameter of MWCNTs grown on Fe, Fe-Pt, and Fe-Co is in the range 10~25nm, 7~22nm, and 7~23nm respectively. This result indicates that bimetallic nanoparticles decrease diameter of MWCNTs slightly, as compare to the MWCNTs grown on Fe NPs.

3.3 Spectroscopy

Raman spectroscopy was performed on separate samples to provide another measure of the quality of the carbon nanotubes. Three scans reveal similar spectroscopic profiles. Fig. 4. showed Raman spectra in the range from 1200 cm^{-1} to 1700 cm^{-1} for MWCNTs grown on different nanoparticles. As shown Fig. 4, D and G peaks appeared at 1321 cm^{-1} and 1573 cm^{-1} for Fe nanoparticles, 1327 cm^{-1} and 1580 cm^{-1} for Fe-Pt nanoparticles, and 1324 cm^{-1} and 1577 cm^{-1} for Fe-Co nanoparticles, respectively. The D peak is generally caused by defects in the curved graphite sheet and by the finite sizes of graphite crystallites. The G peak corresponds to the tangential stretching mode of graphite and indicates the presence of a crystalline graphitic structure for MWCNT forests.

The quality of carbon nanotubes can be estimated as the G/D peak ratio in the Raman spectra.

The G/D peak ratio of the MWCNTs grown on Fe-Co nanoparticles is 1.16. In case of MWCNT forests grown on Fe and Fe-Pt catalysts are 0.99 and 0.92, respectively. From the Raman results, the quality of the MWCNT forests grown on the Fe-Co nanoparticles as a catalyst is ~17% better.

4 CONCLUSION

We demonstrate bimetallic nanoparticles using simple and efficient ways of producing bimetallic nanoparticles that can be used as catalysts for the continuous growth of MWCNTs forests by APPECVD. MWCNTs have been successfully grown on catalyst nanoparticles at atmospheric pressure using an atmospheric pressure plasma jet (APPJ) system. Bimetallic nanoparticles decrease the diameter of MWCNTs compared with monometallic nanoparticles. Although the height of the forests on Fe-Pt is less than that of the forests on Fe, the Fe-Co nanoparticles increase the forests height significantly. In addition, Raman G/D peak ratio of MWCNTs grown on Fe-Co indicate that the quality of forests is better than that of Fe and Fe-Pt. The results from these CNT growths on bimetallic particles are promising for large scale production with controllable nanotube features. Careful study of bimetallic nanoparticles which offer ease in both synthesis and dissemination, and how they catalyze carbon nanotube growth, promises development toward superior and reliable results [15, 16]. Further detailed studies are under way to fully understand the catalytic activity of the iron platinum nanoparticles and to elucidate the mechanism of the carbon nanotube growths from these particles.

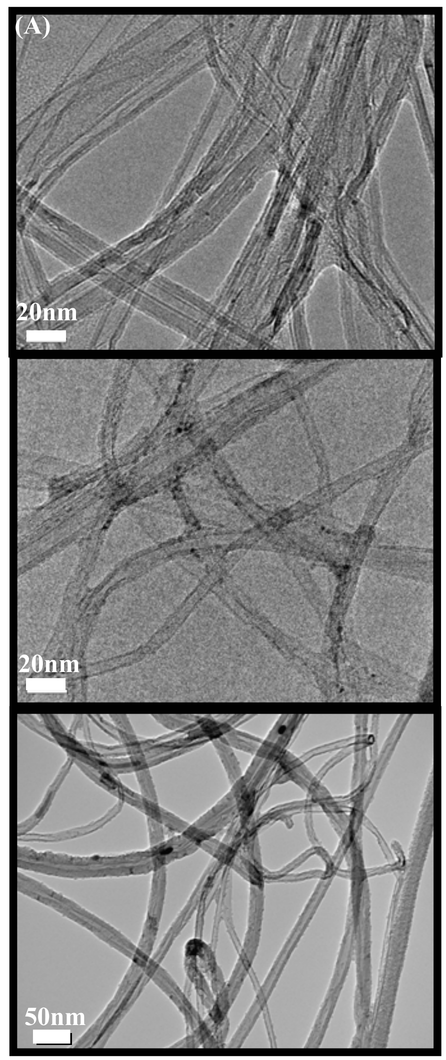

Fig. 3. The TEM Images of the CNTs grown on (A) the Fe nanoparticles and (B) the Fe-Pt nanoparticles, and (C) Fe-Co nanoparticles

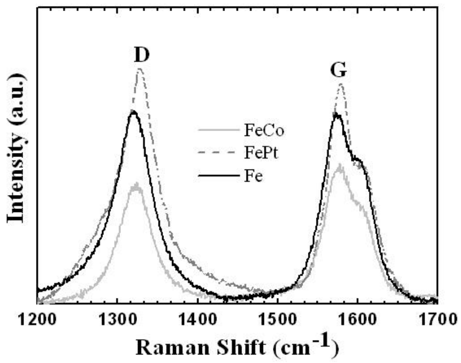

Fig. 4. Raman spectra of MWCNTs grown on Fe, Fe-Pt, and Fe-Co nanoparticles

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