Title	Fabrication of carbon nanotube film directly grown on conductive stainless steel film and application to dielectrophoretic nanoparticle capture
Author(s)	Sano, Noriaki; Nakamura, Tamon; Tamon, Hajime; Suntornlohanakul, Tatporn; Poonjaremsilp, Chantamanee; Charinpanitkul, Tawatchai
Citation	Journal of Applied Physics (2014), 115(15)
Issue Date	2014-04-21
URL	http://hdl.handle.net/2433/187914
Right	© 2014 AIP Publishing LLC.
Type	Journal Article
Textversion	publisher

Fabrication of carbon nanotube film directly grown on conductive stainless steel film and application to dielectrophoretic nanoparticle capture

Noriaki Sano, Tamon Nakamura, Hajime Tamon, Tatporn Suntornlohanakul, Chantamanee Poonjarernsilp, and Tawatchai Charinpanitkul

Fabrication of carbon nanotube film directly grown on conductive stainless steel film and application to dielectrophoretic nanoparticle capture

Noriaki Sano,[1,a)] Tamon Nakamura,[1] Hajime Tamon,[1] Tatporn Suntornlohanakul,[1,2,3] Chantamanee Poonjarernsilp,[1,4] and Tawatchai Charinpanitkul[2]

[1]*Department of Chemical Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan*
[2]*Center of Excellence in Particle Technology, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Patumwan, Bangkok 10330, Thailand*
[3]*International School of Engineering, Faculty of Engineering, Chulalongkorn University, Patumwan, Bangkok 10330, Thailand*
[4]*Department of Chemical Engineering, Faculty of Engineering, Rajamangala University of Technology Krungthep, 2 Nanglinchee Road, Sathorn, Bangkok 10120, Thailand*

Multi-walled carbon nanotubes (CNTs) were synthesized directly on stainless steel film thermally deposited on an alumina plate. To activate the growth of CNTs, the stainless steel film was reduced in H_2 stream without oxidation step. The electrical resistivity of the CNT film synthesized by this way turned to be 1/190 of CNT film synthesized by a conventional way using catalyst preparation method with magnetron sputtering. Dielectrophoretic (DEP) particle capture was demonstrated using the patterned CNT film synthesized on stainless steel film, and it was observed that carbon nanohorns (CNHs) dispersed with Pd nanoparticles (Pd-CNHs) and Pd-Au alloy nanoparticles (Pd/Au-CNHs) were captured at the CNT electrodes due to the high electric field strength there. In this DEP capture, Pd-CNHs were enriched in the present condition. The temperature to deposit stainless steel film and the influence of oxidation step were also investigated for the growth of CNTs. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4870856]

I. INTRODUCTION

Carbon nanotubes (CNTs)[1] have variety of unique properties, and new applications have been developed for many fields. So far, there are considerable number of literatures about applications of CNTs, for example, electromagnetic composite materials,[2] chemical/physical sensors,[3,4] low-voltage field emission devices,[5,6] and so forth. In addition to these applications for electronics, the structure of CNTs having high surface area and high chemical stability enable ones to use CNTs for some energy applications, for example, high performance super capacitors[7,8] and fuel cell electrodes.[9,10] In spite of these many applications reported so far, still one can try to develop novel applications using CNTs. In the present study, an application of CNTs for dielectrophoretic (DEP) particle capture is newly proposed.

The synthesis of CNTs on solid surfaces is necessary for some applications. For such synthesis, it is common to synthesize CNTs by catalytic growth in chemical vapor deposition (CVD) process. For the CVD synthesis, it is necessary to prepare catalyst nanoparticles on the surfaces for the growth of CNTs, and there are several ways for catalyst preparation, for example, magnetron sputtering, dip coating, attaching pre-fabricated nanoparticles, etc. Fe, Ni, and Co seem to be the most common catalyst components for the CNT growth. After preparing the catalytic nanoparticles, gases containing carbon are fed to the surfaces on which the catalyst nanoparticles are dispersed, and CNTs are synthesized on catalyst nanoparticles.

When blush-like CNT film is synthesized on a solid surface, the CNTs are grown independently from each discrete catalyst nanoparticle. Therefore, the electric sheet resistance of CNT film can be mainly determined by contact resistance between CNTs, and the sheet resistance can be high although each CNT can have a very high electric conductivity. However, it is necessary to reduce the sheet resistance of CNT film for some applications. To realize to fabricate the CNT film of low sheet resistance, CNTs must be electrically connected one another effectively. In the present study, a method is proposed in which a conductive stainless steel film is prepared on the solid surface and CNTs are directly synthesized on it. By this way, CNTs will be electrically connected at their bottoms, so that CNT film having low sheet resistance can be fabricated. Here, a patterned CNT film was fabricated by this way, and a DEP particle capture was demonstrated using this CNT film as an electrode.

II. EXPERIMENTAL

A. Synthesis of CNT film on stainless steel film

High quality multi-walled CNTs (MWCNTs) can be synthesized directly on stainless steel surface when the surface is properly treated.[11–19] This surface treatment involves an oxidation followed by a mild reduction. In the previous studies reported, CNTs were synthesized on the surfaces of stainless steel of bulk forms. In the present study, CNTs are synthesized on a conductive stainless steel film deposited on

a)Author to whom correspondence should be addressed. Electronic mail: sano@cheme.kyoto-u.ac.jp. Fax: +81 75 383 2654.

an insulate alumina plate. This layered structure can be useful for some applications as electrodes.

A flake of a stainless steel, type SUS316, of a size about 3 mm × 5 mm × thickness 0.5 mm was put on a graphite plate (thickness = 1 mm) placed in a vacuum chamber, and the electric current was supplied to the graphite plate to raise its temperature up to 1500 °C. When the temperature became above the melting point of the stainless steel, the flake of the stainless steel was melted and its vapor was generated. An alumina plate (thickness = 1 mm) was placed in parallel to the graphite plate with a distance about 8 mm. The vaporized stainless steel was condensed on the surface of the alumina plate. The temperature of the stainless steel flake was measured by a radiation thermometer (Land Corp., CYCROPS100B).

When the stainless steel film on the alumina plate was patterned to fabricate the DEP electrodes, a patterning was conducted by photolithography. A photosensitive resin (Fujiyakuhinkogyo Co., Ethylene glycol monoethyl ether) was coated on the stainless steel film, and a light from a casual fluorescent lamp was radiated to it through a mask sheet. After this photosensitizing step, the area on the resin which received the light was removed by a developing liquid (Fujiyakuhinkogyo Co, FPPR-B), and exposed area of stainless steel film was dissolved by 1 mol/l HCl aq. The patterned stainless steel film was obtained after the remaining resin was washed by ethanol.

When CNTs were synthesized, the alumina plate on which the stainless steel film was patterned was oxidized at 800 °C in air for 30 min as a first step. Next, it was placed in H_2 environment in a tubular furnace (H_2 flow rate = 200 cc/min) and its temperature was controlled at 750 °C for 30 min. After this reduction step, the gas components were switched to ethylene (C_2H_4) mixed with H_2 (C_2H_4 flow rate = 120 cc/min, H_2 flow rate = 200 cc/min), and the temperature was kept 750 °C for 30 min. After this CVD process, the products were sent to structural analyses. It should be noted that the oxidation step could be omitted to synthesize CNT film in the present study as explained later.

A transmission electron microscope (TEM) (JEOL, JEM1010) and a scanning electron microscope (SEM) (Technex Lab Co., Tiny-SEM1710) were used to observe the structure of the products. A Raman spectroscopy (Ramda Vision, MicroRAM-3000L) also was used to analyze the structure. An energy dispersive X-ray (EDX) (Technex Lab Co., Tiny-EDX(LE)-α) mounted on the SEM was used to analyze the components in the stainless steel film fabricated here. The same EDX instrument was used when the DEP particle capture using the patterned CNT film was evaluated.

B. DEP particle capture

When particles are electrically polarized in non-uniform electric field, the particles may receive DEP force.[20–24] When particles receive such force in liquid, they may move toward areas which have high electric field strength. It is known that this force can be, in principle, proportional to the cube of the particle diameter. Thus, it is difficult to capture nano-size particles by DEP force. Nevertheless, it is

desirable to develop DEP particle capture system for nanoparticles because conventional methods such as sedimentation and filtration[25–29] also have drawback to separate nanosize particles. It can be expected that nanoparticles having different dielectric properties can be separated by DEP separator if it is properly developed.

In the experiment, AC voltage of 200 V amplitude with 50 kHz frequency was applied on the patterned CNT film to generate DEP force. The AC voltage was generated by a power generator (NF Co., BA4825) that can amplify signals from a function generator (NF Co., DF1906). Target particles for the DEP particle capture were carbon nanohorns (CNHs) dispersed with Pd nanoparticles (Pd-CNHs) and CNHs dispersed with Pd-Au alloy nanoparticles (Pd/Au-CNHs), which were synthesized by gas-injected arc-in-water (GI-AIW) method. The detail of this method to synthesize metal-dispersing CNHs can be referred elsewhere.[30,31] These particles were mixed and dispersed in ethanol by sonication prior to the DEP particle capture experiment. The weights of Pd-CNHs and Pd/Au-CNHs were almost even in mixing, and the total particle concentration in ethanol was 0.2 wt. %. The ethanol containing these particles was dropped on the area of the CNT-film electrodes to realize DEP particle capture there.

III. RESULTS AND DISCUSSION

A. Synthesis of CNT film on stainless steel film deposited on alumina plate

When the stainless steel was evaporated by approximately 1500 °C, a shiny metallic film was fabricated on the alumina plate. CNT film was formed by the process explained in the Experimental section. In addition, CNT film was formed even when the oxidation step was omitted. There was no significant difference between these CNT films by visual observation.

Fig. 1 shows a SEM image of the cross-section of the alumina plate on which the CNT film was synthesized. This CNT film was obtained without the oxidation step. The schematic image of the multi-layer structure on the alumina plate is also shown in this figure. A stainless steel film was deposited on the surface of alumina plate, and blush-like CNT film was formed on the stainless steel film layer. A TEM image of the CNTs synthesized here is shown in Fig. 2. It is shown that the structure of the CNTs is multi-wall, and the
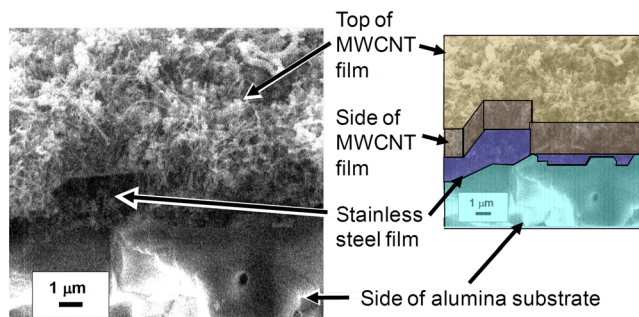

FIG. 1. SEM image of CNT film synthesized on stainless steel film deposited on alumina plate.
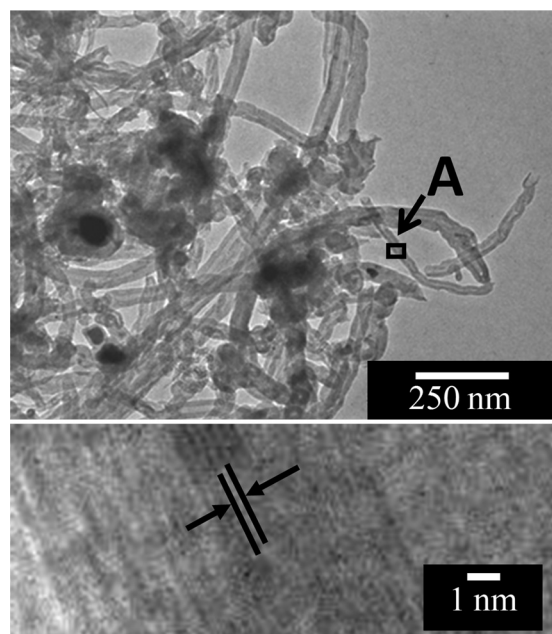
FIG. 2. TEM image of CNTs synthesized on the stainless steel film. The high magnification image corresponds the square mark pointed by "A" in the low magnification image.

inter-layer distance in each wall is approximately 0.35 nm, which is equivalent to the inter-layer distance in graphite structure. One can consider that each CNT is electrically connected by the stainless steel film at their bottoms. The electric surface resistivity was analyzed (Sanwa Co, PC5000) in several places on the CNT film. As a result, the surface resistivity turned to be around 25 Ω/sq in average. The stainless steel film was so thick that the stainless steel film remained as conductive even after the CNTs are grown thereon. It was impressed that the growth mechanism of CNTs is root growth because most of CNTs did not contain catalytic particles in their tips in TEM observation.

For comparison, the CNT film was fabricated by a conventional method with a catalyst preparation using a magnetron sputter (JEOL, JEC-3000FC).[32] In this method, Fe was deposited by 40 mA for 200 s as main catalyst component, and Mo was also deposited on Fe layer by the same ion current for 1 s to enhance the CNT growth. From this catalyst preparation, CNT film which seemed similar to that synthesized by the present method was obtained on the alumina plate. In this case, the metallic layer (Fe, Mo) was so thin that this layer can be transformed to discrete nanoparticles dispersing on the surface on an alumina plate. Then, each CNT can be grown on these nanoparticles. From this structure, the sheet resistance of CNT film must be very high. As a result, the surface resistivity of this CNT film was approximately 4700 Ω/sq. From this result, the resistivity in CNT film became 1/190 times by introducing the stainless steel deposition under the CNTs by the present synthesis method.

B. Influence of pretreatment conditions on CNT growth

A previous report about the influence of the temperature in the oxidation step suggested that the higher the oxidation step temperature could lead to the faster growth of CNT.[19] However, the tendency seen at this time seems different from such previous case. The SEM images of CNTs synthesized without the oxidation step was similar to the case with the oxidation step. Nevertheless, as seen in Fig. 3, there was some difference observed in Raman spectra between in the CNT film synthesized with oxidation step and without it. One can see two peaks indicating graphite structure (G-peak) at about 1570 cm^{-1} and disorder structure (D-peak) at about 1340 cm^{-1} in the both films. However, it should be noticed that the intensity of G peak seems similar to that of D peak in the case of the CNT film synthesized with oxidation step, while G peak is apparently more prominent than G peak in another case without oxidation step. It could be interpreted that CNTs synthesized with oxidation step would have less crystallinity than the others. Thus, CNT film synthesized without oxidation step was employed for the DEP particle capture experiment.

Note that the purity of CNTs synthesized in this study was evaluated to be high by microscopic observations. It must be also noted that CNTs synthesized by any thermal CVD do not have perfectly straight structure with extremely high crystallinity because they tend to become aligned vertically to the substrate surface by being supported by CNTs one another, and they are not free standing. So, multiwalled CNTs synthesized by thermal CVD are always curling and look like Fig. 2. Therefore, CNT synthesized by thermal CVD can exhibit D-peak which is comparable to G-peak even when their purity is high. Because the perfectly straight structure of MWCNTs is not necessary to realize DEP capture of nanoparticles by use of CNTs, the quality of CNTs synthesized here should be fine for our purpose.

It was found that the temperature used to evaporate stainless steel flake to deposit stainless steel film on alumina plate was critically important. When the temperature was raised to a melting point of stainless steel at approximately 1500 °C, the stainless steel flake was melted and it turned to be liquid. After its liquidization, the temperature of the melted liquid turned to become a supercooling temperature about 1200 °C keeping its liquid phase. The metallic film can be formed on the surface of the alumina plate during the
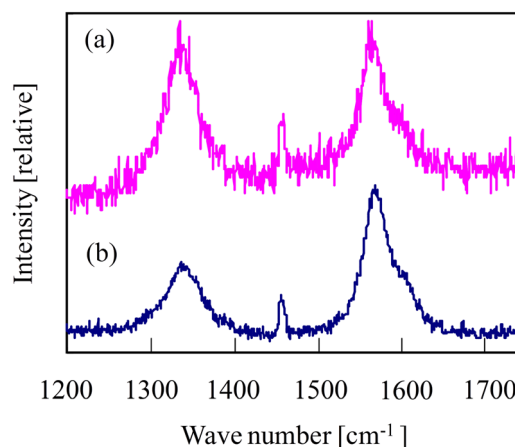

FIG. 3. Raman spectra of (a) CNT film synthesized with oxidation step, and (b) without oxidation step.

stainless steel was evaporated at this temperature. However, the growth of CNT was rarely seen on the film prepared at this temperature. Instead, CNT film was obtained when the stainless flake was evaporated at 1500 °C, as explained above. The metallic films formed by the evaporation temperatures 1200 °C and 1500 °C were analyzed by EDX as shown in Fig. 4. When the evaporation temperature was 1200 °C, the main components of the resulted film became Mn as shown in Fig. 4(a). This component is not the main component of stainless steel but considered impurity. Mn was concentrated in the deposited film because the vapor pressure of the main components in stainless steel, Fe and Cr, should be significantly lower than that of Mn in this condition. When the evaporation temperature was as high as 1500 °C, the components in the deposited film became similar to the original stainless steel as shown in Figs. 4(b) and 4(c).

C. DEP particle capture experiment using patterned CNT film

In the present study, DEP particle capture experiment was demonstrated using the CNT-film electrodes patterned on the alumina plate. The dimensions of the electrodes are described in Fig. 5. As seen here, comb-like shape electrodes were prepared by the CNT growth without the oxidation step on the stainless steel film patterned by the photolithography.
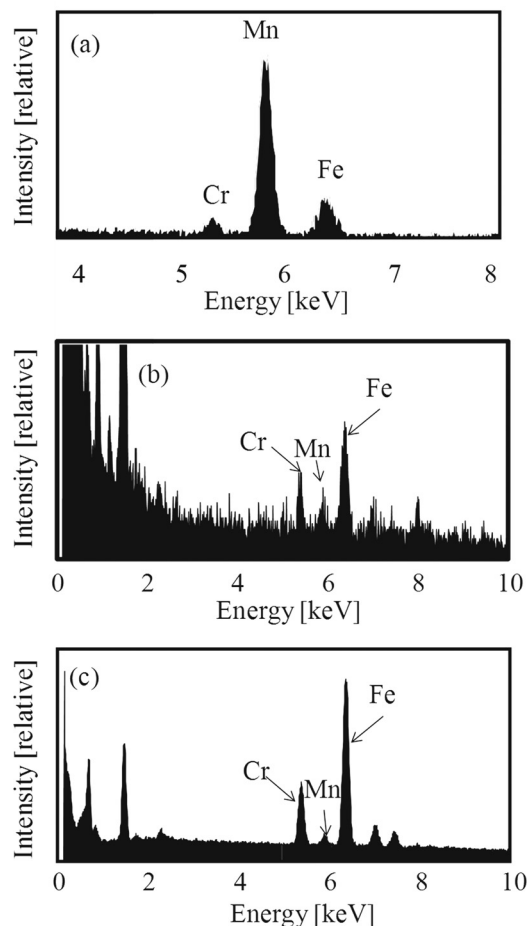

FIG. 4. EDX spectra of (a) stainless steel film deposited at 1200 °C, (b) deposited at 1500 °C, and (c) initial stainless steel.
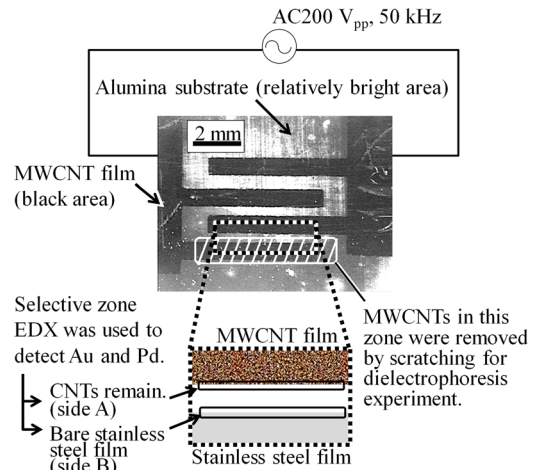

FIG. 5. Dimensions of CNT electrodes used for DEP particle capture experiment.

As explained in the Experimental section, AC voltage was applied on the electrodes for DEP particle capture. During the AC voltage was applied on the electrodes, the ethanol containing the particle mixture prepared by the procedure explained in the Experimental section was dropped onto the alumina plate on which the patterned CNT film was fabricated. An example of TEM image of the target particles is shown in Fig. 6. It was observed that the average diameter of the metallic particles dispersing in CNHs were 2.6 nm and 5.0 nm in Pd/Au-CNHs and Pd-CNHs, respectively. After the ethanol was dried from the alumina plate, its surface was directly analyzed by the selective-area EDX.

The role of CNT in the DEP particle capture is depicted in Fig. 7. As mentioned in the Experimental section, the DEP particle capture should be difficult if the particle size is nano. Nevertheless, DEP force on small particles should become extremely strong when the electric field strength is significantly enhanced in a localized zone near a micro-size electrode. CNTs should be the preferable electrode materials to realize such a condition. Namely, the electric field at the CNTs should be extremely large due to the CNTs' curvature radius of nanometer scale. It can be estimated that the electric field strength at MWCNT can reach 6–7×10^9 V m^{-1} level at similar applied voltage,[33] which cannot be achieved
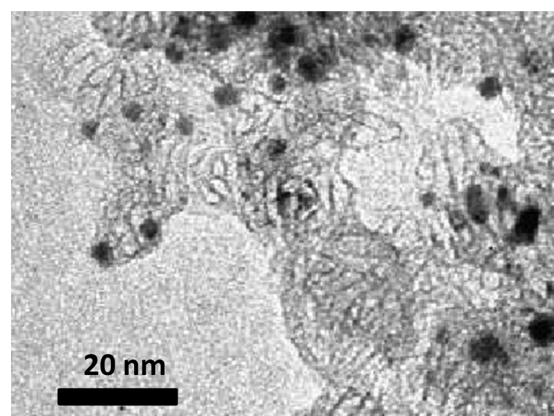

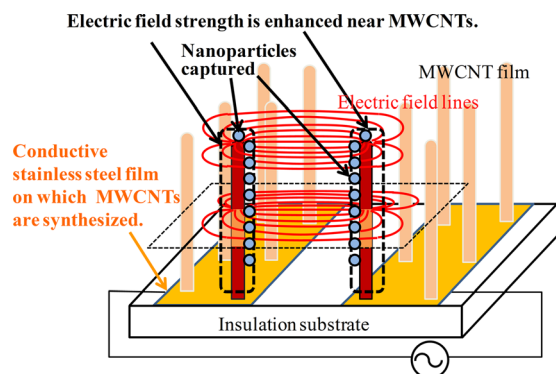FIG. 6. TEM of Pd/Au-CNHs used in DEP particle capture experiment.

FIG. 7. Schematic image explaining the role of CNTs in DEP particle capture.

by use of conventional electrodes. The nanoparticles can be attracted by top of MWCNTs and also by side of MWCNTs that is exposed to liquid. The side of MWCNTs facing the inter-MWCNT spaces may not attract the nanoparticles by dielectrophoresis because the concentrated electric field is not formed there.

In the present study, a part of CNT film was removed to clarify the effect of CNTs. As shown in Fig. 5, one edge of an electrode pair was scratched out. Then, one side in the electrode pair keeping CNTs (side A) should exhibit the effect of CNTs, and other side whose CNTs were removed (side B) should correspond the conventional DEP particle capture without CNTs.

EDX spectra obtained at the side A and the side B are shown in Fig. 8. On the side A, there are the peaks indicating Pd and Au at 2.85 keV and 2.15 keV. In contrary, these peaks are not prominent on the side B. This result suggests that the target particles could be captured due to the large electric field strength induced by CNTs.

It should be informed that the weight ratio Pd/Au in the captured particles detected by EDX analysis changed by the DEP particle capture. The weight ratio Pd/Au detected in the
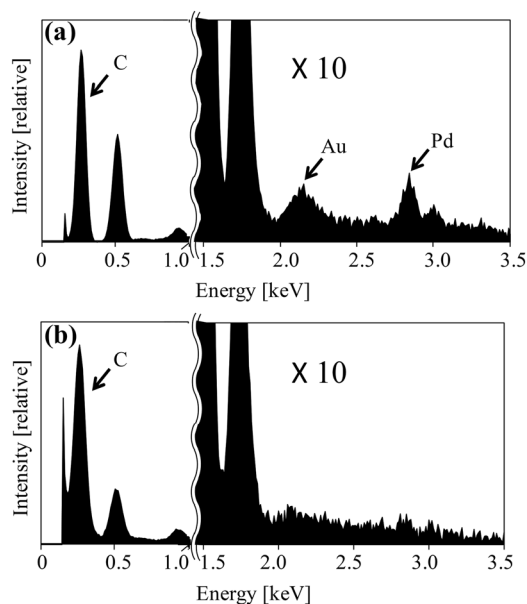
initial particle mixture before the DEP capture was approximately 1.0. The weight ratio Pd/Au in the particle mixture captured by CNT electrode was approximately 1.4. It means that Pd-CNHs were enriched by this DEP capture. It could be speculated that this enrichment occurred because the diameter of Pd nanoparticles dispersed in Pd-CNHs is larger than Pd-Au alloy nanoparticles in Pd/Au-CNHs as mentioned above. This result would indicate the feasibility of application of CNT electrode to purify specific metal-dispersing carbon nanoparticles according to the dispersion of the metals. The effort to raise the purification extent should be pursued in future.

IV. CONCLUSIONS

Multi-walled CNTs were synthesized directly on the stainless steel film deposited on an alumina plate to electrically connect CNTs at their bottoms. It can be expected that CNT film synthesized in this way can have low electric resistance so that the patterned CNT film can be used for electrode applications. In the present experiment, the DEP particle capture experiment was demonstrated. Making layered stainless steel film for MWCNT growth is one of the remarkable points because DEP particle separator cannot be fabricated without it. It must be noted that currently both electro and electroless plating of stainless steel is not technically available. Under such situation, the method to deposit stainless steel film applied in this study (thermal vacuum coating) is the simplest technique to fabricate stable stainless steel film of low electrical resistance on a insulate substrate. An important information is obtained that the temperature to deposit stainless steel must be high enough (1500 °C) to active the growth of CNTs thereon. Regarding CNT growth, it was found that oxidation step in pretreatment on stainless steel is not necessary.

As a result, the electric resistivity in the CNT film fabricated by the present method became 1/190 of that in CNT film, which was synthesized by a conventional catalyst preparation method using magnetron sputtering. A patterned CNT film was fabricated by photolithography for patterning the stainless steel film, and this CNT film was used for DEP electrode. It was observed that CNHs dispersed with Pd and Pd-Au alloy nanoparticles can be captured by a high electric field induced by CNTs, and CNHs dispersed with Pd nanoparticles were enriched by this DEP capture. It can be emphasized that new application of CNT film layered with deposited conductive stainless steel film based on DEP force may enable ones to purify nanoparticles, which are hardly separated by other methods.

FIG. 8. EDX spectra of (a) side A and (b) side B on an electrode pair in Fig. 5.

[1]S. Iijima, M. Yudasaka, R. Yamada, S. Bandow, K. Suenaga, F. Kokai, and K. Takahashi, Chem. Phys. Lett. **309**, 165 (1999).

[2]A. P. Singh, B. K. Gupta, M. Mishra, Govind, A. Chandra, R. B. Mathur, and S. K. Dhawan, Carbon **56**, 86 (2013).

[3]M. A. Cullinan and M. L. Culpepper, Carbon **51**, 59 (2013).

[4]N. Hu, T. Itoi, T. Akagi, T. Kojima, J. Xue, and C. Yan, Carbon **51**, 202 (2013).

[5]M. Shahi, S. Gautam, P. V. Shah, P. Jha, P. Kumar, J. S. Rawat, P. K. Chaudhury, Harsh, and R. P. Tandon, J. Appl. Phys. **113**, 204304 (2013).

[6]S. X. Lim, S. L. Chang, F. C. Cheong, E. S. Tok, Z. Zhang, C. T. Lim, and C.-H. Sow, J. Phys. Chem. C **117**, 14408 (2013).

[7]C. Huang, N. Grobert, A. A. R. Watt, C. Johnston, A. Crossley, N. P. Young, and P. S. Grant, Carbon **61**, 525 (2013).

[8]M. Noked, S. Okashy, T. Zimrin, and D. Aurbach, Carbon **58**, 134 (2013).

[9]A. Varga, M. Pfohl, N. A. Brunelli, M. Schreier, K. P. Giapis, and S. M. Haile, Phys. Chem. Chem. Phys. **15**, 15470 (2013).

[10]T. Fujigaya and N. Nakashima, Adv. Mater. **25**, 1666 (2013).

[11]N. Sano, T. Kodama, and H. Tamon, Carbon **55**, 365 (2013).

[12]N. Hordy, N.-Y. Mendoza-Gonzalez, S. Coulombe, and J.-L. Meunier, Carbon **63**, 348 (2013).

[13]M. Hashempour, A. Vicenzo, F. Zhao, and M. Bestetti, Carbon **63**, 330 (2013).

[14]M. He, P. V. Fedotov, E. D. Obraztsova, V. Viitanen, J. Sainio, H. Jiang, H. Jiang, E. I. Kauppinen, M. Niemelä, and J. Lehtonen, Carbon **50**, 4294 (2012).

[15]A. V. Gaikwad, T. K. Rout, D. Van der Plas, R. V. Dennis, S. Banerjee, S. P. Benito, and L. Lefferts, Carbon **50**, 4722 (2012).

[16]V. Martínez-Hansen, N. Latorre, C. Royo, E. Romeo, E. García-Bordejé, and A. Monzón, Catal. Today **147**, S71 (2009).

[17]C. E. Baddour, C. Upham, and J.-L. Meunier, Carbon **48**, 2652 (2010).

[18]C. E. Baddour, F. Fadlallah, D. Nasuhoglu, R. Mitra, L. Vandsburger, and J.-L. Meunier, Carbon **47**, 313 (2009).

[19]N. Sano, Y. Hori, S. Yamamoto, and H. Tamon, Carbon **50**, 115 (2012).

[20]H. A. Pohl, *Dielectrophoresis: The Behavior of Neutral Matter in Nonuniform Electric Fields* (Cambridge University Press, Cambridge, UK, 1978).

[21]M. Hughes, Electrophoresis **23**, 2569 (2002).

[22]T. B. Jones, *Electromechanics of Particles* (Cambridge University Press, Cambridge, UK, 1995).

[23]N. Sano, K. Iwase, and H. Tamon, J. Chem. Eng. Jpn. **46**, 535 (2013).

[24]N. Sano, B. Matsukura, Y. Ikeyama, and H. Tamon, Chem. Eng. Sci. **84**, 345 (2012).

[25]S. Kanemaru, T. Oshima, and Y. Baba, J. Chem. Eng. Jpn. **45**, 816 (2012).

[26]J.-Y. Lee, B.-K. Choi, S.-K. Maeng, K.-H. Ahn, and K.-G. Song, J. Chem. Eng. Jpn. **46**, 127 (2013).

[27]Y. Shimada, D. Bi, H. Habaki, and R. Egashira, J. Chem. Eng. Jpn. **46**, 376 (2013).

[28]T. Yoshioka, H. Nagasawa, M. Kanezashi, and T. Tsuru, J. Chem. Eng. Jpn. **46**, 659 (2013).

[29]D.-Q. Cao, E. Iritani, and N. Katagiri, J. Chem. Eng. Jpn. **46**, 593 (2013).

[30]C. Poonjarernsilp, N. Sano, T. Charinpanitkul, H. Mori, T. Kikuchi, and H. Tamon, Carbon **49**, 4920 (2011).

[31]N. Sano, T. Ishii, H. Mori, Y. Ikeyama, and H. Tamon, J. Appl. Phys. **112**, 044301 (2012).

[32]N. Sano, S. Ishimaru, and H. Tamaon, Mater. Chem. Phys. **122**, 474 (2010).

[33]J.-M. Bonard, F. Maier, T. Stockli, A. Chatelain, W. A. de Heer, J.-P. Salvetat, and L. Forro, Ultramicroscopy **73**, 7 (1998).