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Short Communication

Catalytic hydrogen transfer of ketones over atomic layer deposited highly-dispersed platinum nanoparticles supported on multi-walled carbon nanotubes

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ABSTRACT

Hydrogen transfer of ketones, catalyzed by highly-dispersed platinum nanoparticles supported on multi-walled carbon nanotubes (MWCNTs), was studied. Pt nanoparticles were deposited on gram quantities of non-functionalized MWCNTs by atomic layer deposition (ALD) at 300 °C, using (methylcyclopentadienyl) trimethylplatinum and oxygen as precursors. TEM analysis showed that ~1.4 nm Pt nanoparticles were highly dispersed on MWCNTs. The heterogeneous hydrogen-transfer reactions of acetophenone indicated that an acetophenone conversion of 100% and a 1-phenylethanol selectivity of 99.0% could be obtained with a ketone to Pt mass ratio of 24,690 and a ketone to KOH mass ratio of 22 at 150 °C for 5 h. The selectivity of the Pt/MWCNT catalyst was higher than that of the commercial Pt/C catalyst, due to the highly-dispersed, uniform Pt nanoparticles and the unique porous structures of the Pt/MWCNT catalyst. The high stability of the Pt/MWCNT catalyst was demonstrated by reutilization of the catalyst. The high reactivity and selectivity of this catalyst for hydrogen transfer reduction were also demonstrated for other ketones.

1. Introduction

The reduction of ketones to corresponding alcohols is one of the most important chemical processes in industry and in synthesis-oriented research laboratories. Usually, ketones can be converted into secondary alcohols by reduction reactions involving a number of reducing reagents, including molecular hydrogen, metal hydrides, and dissolving metals [1]. The transfer hydrogenation of organic compounds has attracted much attention, because it is a much safer and more environmentally benign process [1–3]. In addition, the hydrogen donor (e.g., 2-propanol) is cheap and easy to handle, and no elaborate setups (e.g., high pressure reactors) are required. Homogeneous noble metal catalysts, such as Ru complexes [4–6], are known to be effective for these kinds of reactions, but they suffer from difficulties encountered in the recovery and reuse of expensive catalysts, and the necessity for co-catalysts (base and ligand).

Noble metal-based heterogeneous catalysts were also considered because of their advantages in catalyst recovery and recycling. Supported nanoparticle (NP) catalysts, such as Ni [1,7–9] and Pt [10], have been reported to act as effective and reusable catalysts for these kinds of hydrogen transfer reactions. However, such heterogeneous processes need to be improved because usage of the catalysts has been very high (i.e., 10–20 mol% Ni), while the conversion of the reactant and the selectivity of the desired product have been very low. On the other hand, noble metal-based heterogeneous catalysts have normally been prepared by wet-chemical processing. The porous supporting materials were impregnated with an aqueous solution of noble metal precursor, and the noble metal nanoparticles (NPs) were reduced in solution by chemical reducing agents [11]. Although these methods can produce metal particles as small as several nanometers, they cannot precisely control the size of the catalytic NPs and disperse them homogeneously within the porous substrates.

Atomic layer deposition (ALD) is a layer-by-layer process [12,13] that has received increasing attention for the preparation of noble metals such as Pt [14–17], Ru [18,19] and Pd [20–22]. Due to their high cohesive energy, noble metals tend to form via an island growth mechanism (Volmer–Weber mechanism) during the initial stages of the ALD process [23]. This study describes the hydrogen transfer reduction of ketones catalyzed by Pt NPs supported on non-functionalized multi-walled carbon nanotubes (MWCNTs) deposited by ALD.

2. Experimental section

2.1. Materials

(Methylcyclopentadienyl) trimethylplatinum [(MeCp)PtMe$_3$] was purchased from Strem Chemicals, Inc., and the MWCNTs were purchased from US Research Nanomaterials, Inc. All chemicals of the best grade were commercially available (J&K Chemical, Aldrich, Acros, Alfa

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Aesar). 3 wt.% Ru/activated carbon (Ru/C, 50.2% water content, surface area of 789 m^2/g), 3 wt.% Pt/activated carbon (Pt/C, 55.2% water content, surface area of 795 m^2/g), and Raney Ni (50 wt.% slurry in water, active catalyst, surface area of 90–100 m^2/g and pore size of 45 μm) were purchased from Degussa. De-ionized water was used as solvent for the catalytic reactions. All materials were used as received.

2.2. Pt NPs deposited on MWCNTs by ALD

The deposition of Pt NPs by ALD was carried out in a fluidized bed reactor, which is similar to the one previously described in detail [24]. (MeCp)$PtMe_3$ and oxygen were used as precursors. MWCNTs, with a surface area of 360 m^2/g, an outside diameter of 10–20 nm and an inside diameter of 5–10 nm, were used as the catalyst substrate. No surface functionalization was applied for the MWCNTs before Pt ALD. 1.0 g MWCNTs were loaded into the reactor. The experimental details can be found elsewhere [25]. The reaction temperature was 300 °C. Before the reaction, the MWCNTs were degassed at 300 °C for 5 h. Nitrogen gas was fed as flush gas to help remove the unreacted precursor and any by-products formed during the reaction. The dose time of the Pt precursor was 6 min, while the dose time of the oxygen was 15 min, which was sufficient for the reaction. The pressure during dosing was about 4 Torr. The system was pumped down to 50 mTorr prior to the dose of the next precursor. In this study, one cycle of Pt ALD was applied. The ALD-deposited Pt/MWCNT catalyst was directly used in the following catalytic tests without any further treatment.

2.3. Catalytic hydrogen transfer of ketones

The catalytic reactions were conducted in unstirred mini-batch reactors assembled from stainless steel Swagelok® parts. Port connectors, sealed with a cap on both ends, gave a reactor volume of about 5.0 mL. Prior to use in any experiments, the reactors were rinsed with acetone, dried, loaded with water, and conditioned at 300 °C for 30 min to remove any residual materials remaining from the manufacture of the metal parts. In a typical experiment, 0.8 g acetophenone, 37 mg KOH, 4.0 g isopropanol and 0.6 mg Pt/MWCNT were fed into the mini-batch reactor. The reactor was tightly closed, and the mixture was stirred at 150 °C for 5 h. All of the other catalysts had an identical metal mass loading, even though the total mass could have been different due to the different mass fractions of metal in the catalyst support and the different contents of the water. The reutilization of the catalysts was carried out in a 100 mL autoclave. In a typical experiment, 8 g acetophenone, 370 mg KOH, 40 g isopropanol and 6 mg Pt/MWCNT were fed into the autoclave. An identical metal loading was used for the cycling experiment of Pt/C. The reactor was tightly closed, and the mixture was stirred at 150 °C for 5 h. After the reaction, the catalyst was filtered off and dried under vacuum. Every time about 5% fresh catalyst was added to cover the catalyst lost during the filtration process. The filtrate was analyzed using an Agilent gas chromatograph equipped with a flame ionization detector and a Zebron ZB-WAX capillary column (30 m × 0.32 mm × 0.5 μm) with a stationary phase of polyethylene glycol. The column temperature was kept at 80 °C for 3 min, and then increased to 240 °C, at a rate of 8 °C/min. The conversion of ketone and the selectivity to the desired alcohol were calculated as follows: conversion = 100 − (moles of unreacted ketone/moles fed) × 100; selectivity = (moles of desired alcohol/moles of ketone reacted) × 100. Yield = conversion × selectivity/100.

2.4. Catalyst characterization

The Pt mass fraction of the Pt catalysts was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The Pt NPs were visualized with a FEI Tecnai F20 field emission gun, high resolution TEM/STEM. The particle size was measured based on about 200 particles in TEM images. The specific surface area of the particles was calculated by the Brunauer–Emmett–Teller (BET) method from the N_2 adsorption isotherms obtained at −196 °C.

3. Results and discussion

The atomic layer deposited Pt NPs were highly dispersed on the surface of the MWCNTs. As shown in Fig. 1, after one cycle of Pt ALD, the average particle size was 1.4 ± 0.3 nm, and the Pt content on the MWCNTs was 5.4 wt.%, based on ICP analysis. The average inside diameter of the MWCNTs was about 6 nm. The surface area of the MWCNTs decreased from 360 to 320 m^2/g with the addition of 5.4 wt.% Pt. This could have been partly caused by the fact that some Pt nanoparticles blocked the micropores. If the porous structure of the MWCNTs did not change with the addition of Pt, the decrease in the surface area should have been only about 20 m^2/g, which is caused by the addition of 5.4 wt.% Pt to the MWCNTs.

The Pt/MWCNT was employed for a catalytic hydrogen-transfer reaction of acetophenone. The reaction was carried out using isopropanol as a hydrogen donor, at 80–150 °C, in the presence of 4.6–9.2 wt.% of KOH. The main by-product of the liquid phase catalytic hydrogen transfer of acetophenone was ethylbenzene (as shown in Scheme 1). Control experiments indicated that the MWCNTs themselves showed no catalytic activity for the catalytic hydrogen transfer reactions since no reaction could happen in the absence of a catalyst, and there was no reaction in the absence of isopropanol (with tetrahydrofuran as a solvent).

The effects of the reaction temperature on the conversion of acetophenone and the selectivity of 1-phenylethanol with isopropanol as a hydrogen donor were studied by varying the temperature between 80 and 150 °C. As shown in Fig. 2a, the conversion of acetophenone was highly dependent on the reaction temperature. The conversion was lower at a lower reaction temperature. For example, the conversion was 42.8% at 80 °C, after 5 h of reaction, and the conversion reached 100% at 150 °C during the same reaction time. In the following studies, a reaction temperature of 150 °C was chosen. The effect of the quantity of KOH on the hydrogen transfer reduction of acetophenone with isopropanol is shown in Fig. 2. Clearly, the amount of the base was not the key factor for this reaction. The reduction of the base concentration, from 9.2 wt.% to 4.6 wt.%, diminished the conversion of acetophenone by about 0.5%. As shown in Fig. 2b, the effect of the reaction temperature on the selectivity of 1-phenylethanol was very limited. A marginal reduction in the selectivity of 1-phenylethanol was observed when the temperature increased from 80 to 150 °C. The amount of base had little impact

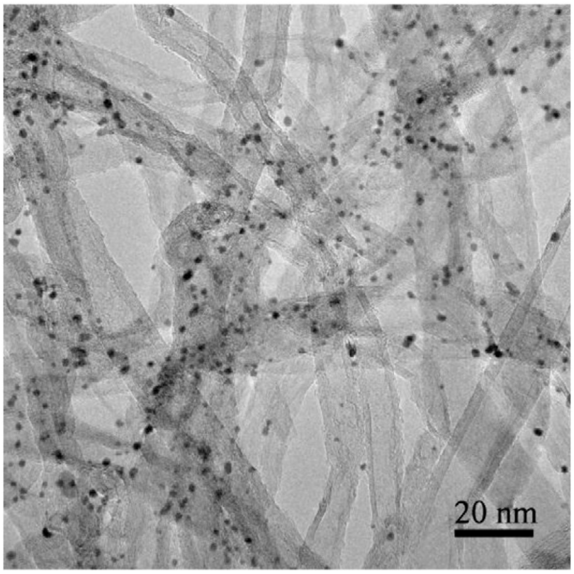
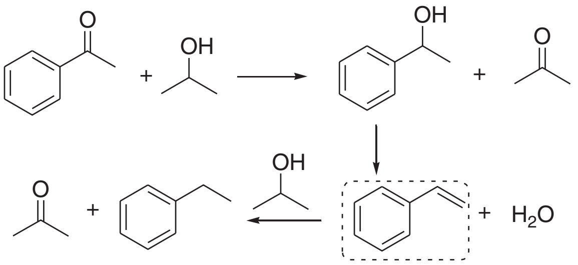


Fig. 1. HRTEM image of Pt nanoparticles deposited on MWCNTs by ALD.



Scheme 1. Hydrogen transfer of acetophenone.

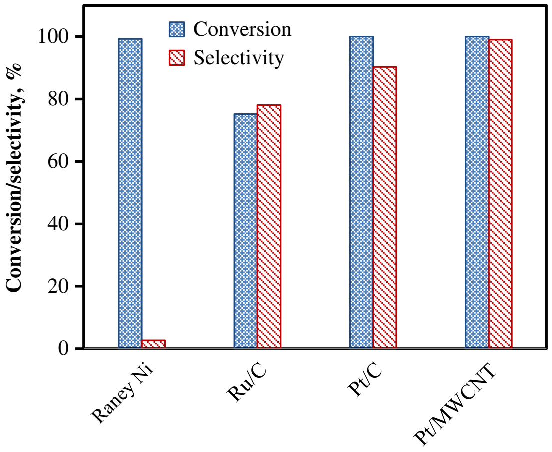


Fig. 3. Hydrogen transfer of acetophenone catalyzed by different catalysts. Reaction condition: 0.8 g acetophenone, 37 mg KOH and 4.0 g isopropanol, 0.6 mg Pt/MWCNT, 150 °C, reaction time 5 h.

on the selectivity of 1-phenylethanol in this reaction. The reaction with 4.6 wt.% of the base at 150 °C reached 100% conversion and 99.0% yield of 1-phenylethanol in 5 h. The results may have been better than the previously reported hydrogen-transfer reaction of acetophenone catalyzed by Pt [10], considering the much larger ratio of acetophenone to Pt catalyst. In the previous studies, an 88% yield of 1-phenylethanol was obtained with a ketone to Pt mass ratio of 80 and a ketone to KOH mass ratio of 2 at 76 °C for 7 h [10]. In the current studies, 99.0% yield of 1-phenylethanol was obtained with a ketone to Pt mass ratio of 24,690 and a ketone to KOH mass ratio of 22 at 150 °C for 5 h. This reaction condition was chosen as a standard condition for further comparisons of studies of other catalysts and other ketones.

For comparison, several commercially available catalysts were evaluated for the same reaction at 150 °C. As shown in Fig. 3, all catalysts were able to reduce acetophenone to 1-phenylethanol with isopropanol as the hydrogen donor. Although Raney Ni reduced acetophenone with a conversion of 99.3%, this led to a hydrogenolysis product with ethylbenzene as the main product. Ru/C was able to reduce acetophenone with an acetophenone conversion of 75.2% and a selectivity of 78.1% to 1-phenylethanol. The Pt/C was able to reduce acetophenone to 1-phenylethanol with 100% conversion and 90.3% selectivity. The ALD-prepared catalyst (Pt/MWCNT), distinctively showed optimum selectivity to 1-phenylethanol (99.0%), with an acetophenone conversion of 100%. Clearly, the Pt/MWCNT catalyst had higher selectivity, as compared to the commercial Pt/C, although they had similar activity for the conversion of acetophenone (Fig. S1). This indicated that the Pt/MWCNT was more efficient in achieving a high yield of 1-phenylethanol, as compared to the commercial Pt/C catalyst. This increase in catalytic performance of the Pt particles was attributed to the high dispersion of the Pt nanoparticles deposited on the MWCNTs by ALD, and the application of MWCNTs, which had unique electronic and textural properties, as a support. The average particle size of Pt/MWCNT was 1.4 ± 0.3 nm, and the commercial 3 wt.% Pt/C had a larger average particle size of 1.8 ± 0.5 nm and a wider particle size distribution (Fig. S2). The MWCNTs had a highly porous structure composed of open-ended meso/macropores, as well as large voids [26]. This unique structure greatly reduced the internal mass transfer resistance, which contributed to faster removal of the product from the Pt surface and the freeing up of more Pt active sites. This explains why the Pt/MWCNT had a higher selectivity than the Pt/C.

The stability of the ALD-prepared Pt catalysts was studied by cycling the catalytic hydrogen transfer of acetophenone at 150 °C, and compared to the commercial Pt/C under the same reaction conditions. The results of the successive experiments of the hydrogen transfer of acetophenone catalyzed by Pt/MWCNT are presented in Fig. 4a. Total 10 cycles were applied, and no noticeable difference of catalytic activity was observed during these 10 cycles. While for the commercial 3 wt.% Pt/C catalyst, total 3 cycles were applied and noticeable deactivation of the catalyst was observed with the increase in the number of cycles, as shown in Fig. 4b. The mass fraction of Pt on MWCNTs and activated carbon support before and after cycling experiments was tested by ICP. For the ALD-prepared Pt/MWCNT, after 10 cycles of reaction, the Pt mass fraction slightly decreased from 5.4 to 5.2% (3.7% Pt leaching). In contrast, the commercial 3% Pt/C lost about 17% of Pt after only 3 cycles of reaction, decreasing from 3.0 to 2.5%. These results indicate that the ALD produced catalysts had higher stability than the commercial Pt/C, and the catalyst can be easily separated by filtration.

The size of Pt NPs after the cycling reaction was also observed by TEM. As shown in Fig. 5, the size of Pt for Pt/MWCNT was 1.4 ± 0.4 nm after cycling for 10 runs. There was almost no particle size change, compared to the as-deposited Pt NPs. In contrast, the size of Pt for commercial Pt/C increased from 1.8 ± 0.5 to 2.2 ± 0.5 nm

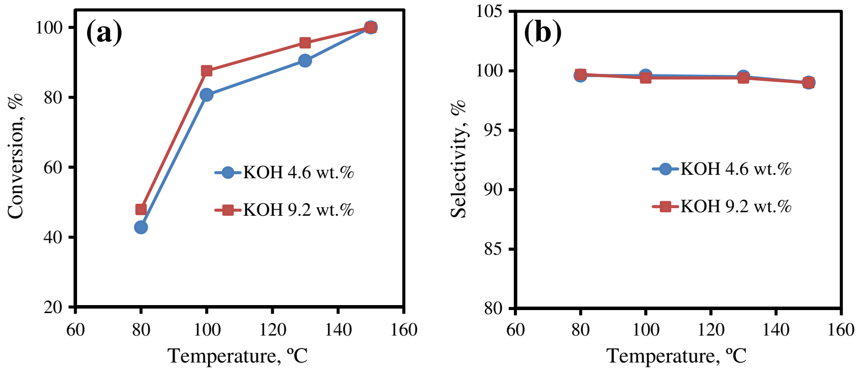


Fig. 2. The effects of reaction temperature and variable amounts of KOH on (a) the conversion of acetophenone and (b) the selectivity of 1-phenylethanol with isopropanol as the hydrogen donor. Reaction condition: 0.8 g acetophenone, 37 mg KOH and 4.0 g isopropanol, 0.6 mg Pt/MWCNT, reaction time 5 h.

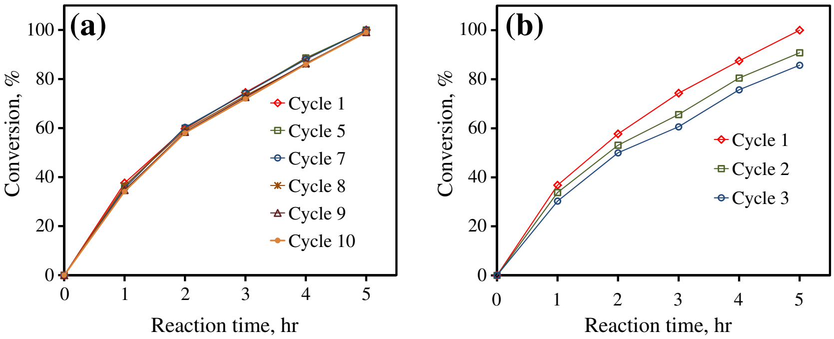


Fig. 4. The conversion of acetophenone in the recycling tests for (a) Pt/MWCNT and (b) Pt/C catalysts. Reaction condition: 8 g acetophenone, 370 mg KOH and 40 g isopropanol, 6 mg Pt/MWCNT or 24 mg Pt/C with 55.2% water content, 150 °C, reaction time 5 h.

after cycling for only 3 runs (Fig. S2). The Pt particles were more firmly supported on the MWCNTs than on the activated carbon. This can be explained by the presence of surface defects on the MWCNTs and the Pt ALD process, since the ALD process would result in the Pt being covalently bonded to the MWCNT support, and thus the stronger metal-support interaction for the ALD-prepared Pt/MWCNT catalysts.

Under optimal reaction conditions, a series of ketone compounds were reduced to corresponding alcohols with modest to good yields, as listed in Table 1. This catalytic hydrogen-transfer reaction was very important, especially for those compounds with halogen on a benzene ring. Normally, halogen is easily removed from the benzene ring in a general experiment. These undesired by-products will still remain as impurities in the reaction system. However, the catalytic hydrogen transfer method can avoid such impurities through the reaction route noted above. As indicated in entries 6–8, the yield of the desired product can be higher than 99%, which is not possible for general hydrogenation reactions. The reduction of the substituted acetophenones was shown to be dependent on the electronic character. In general, the presence of an electron-withdrawing group (entries 4–8) facilitated ketone reduction [7]. On the other hand, acetophenones bearing electron-donating substituents at the para position were more reluctant to react (entries 2 and 3).

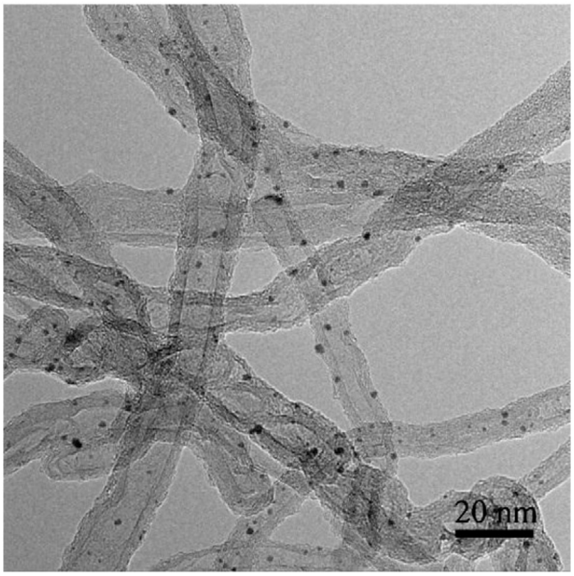
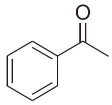
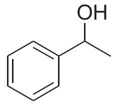
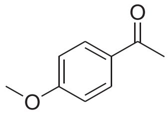
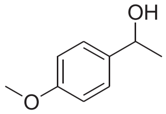
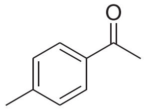
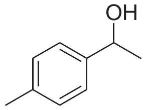
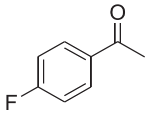
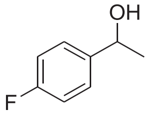
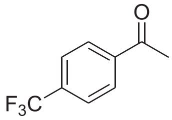
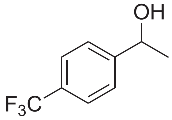
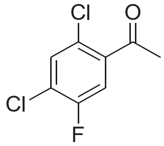
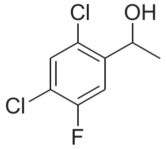
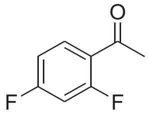
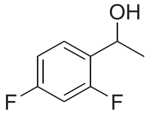
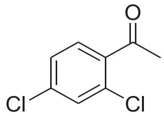
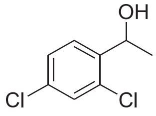


Fig. 5. HRTEM image of ALD-prepared Pt/MWCNT catalyst after 10 cycles of catalytic hydrogen transfer of acetophenone.

4. Conclusions

In summary, high conversion and high selectivity were achieved for the catalytic hydrogen transfer of ketones catalyzed by highly-dispersed platinum NPs deposited on non-functionalized MWCNTs by ALD. HRTEM observation indicated that Pt particles had a narrow size distribution that centered at around 1.4 nm. The ALD-prepared Pt/MWCNT showed the best catalytic performance with 100% conversion of acetophenone and 99.0% selectivity to 1-phenylethanol, as compared to

Table 1
Hydrogen transfer reduction of ketones catalyzed by Pt/MWCNT.

Entry	Ketone	Product	Yield (%)
1			99.0
2			86.7
3			83.8
4			99.2
5			99.3
6			99.6
7			99.1
8			99.3

Reaction conditions: 0.8 g ketone, 37 mg KOH and 4.0 g isopropanol, 0.6 mg Pt/MWCNT, 150 °C, reaction time 5 h.

other commercial catalysts. The high stability of the Pt/MWCNT catalyst was demonstrated by reutilization of the catalyst. This catalyst was employed for heterogeneous catalytic hydrogen transfer reactions of various ketones. The unusual behavior of Pt/MWCNT could be attributed to the high dispersion and high stability of Pt NPs on MWCNTs, as well as to the unique textual and electronic properties of carbon nanotubes.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2013.11.002.

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