Significant morphology dependence on nitrogen proportion in growing carbon nanotubes

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Abstract

To find the possibility in growing carbon nanotubes (CNTs) used as field emitters, different N_2 proportions were mixed with H_2/CH_4 in growing CNTs. It was found that N_2 has significant impact on the growth, diameter and cleanness of CNTs. CNTs with different diameters were grown on the same nickel catalyst particle size with different N_2 proportions. The suppressing CNT growth behavior was observed with 30% N_2 in process gas. The CNTs grown from 47 and 57% N_2 possess smaller diameter and less carbonaceous particles than those grown from 0% N_2. The above phenomena are explained by NH_3 and nickel nitride formation during CNT growth claims proposed by others, together with the authors' proposal: the CNTs are grown selectively on nickel portion instead of the whole catalyst particle constructed by nickel mixed with nickel nitride during CNT growth. This work brings the potential to produce slim and clean CNTs with controlling $N_2/H_2/CH_4$ proportion, which is a requirement for field emitter application.

Key words: nanomaterials, surfaces, carbon nanotubes

1. Introduction

Much attention has been focused on carbon nanotubes (CNTs) since 1991 [1]. A new carbon structure is constructed by graphite-like, seamless, and hollow tubes [2]. The large ratio of tube length to diameter makes CNTs possible to be used as field emitters in display industry [3]. Chemical vapor deposition (CVD) has been usually used to grow CNTs on patterned surfaces, suitable for fabricating field emitters. Plasma enhanced CVD (PECVD) uses heat as well as energetic electrons in plasma to dissociate the reactant and therefore can run at relatively low temperature than traditional thermal CVD. Microwave radiation is a popular high density plasma source applied in PECVD to grow CNTs.

The structure control such as length and diameter of CNTs is specially needed for mastering CNTs' field emission property. Two types of microwave PECVD grown CNTs' structure control have been reported: controlling the morphology of catalyst on which the CNTs are subsequently growing [4-6], or controlling the gas phase reactions during CNTs growth [7,8]. There are reports on the role of nitrogen in growing CNTs. Yang et al [7] reported nitrogen could react with nickel to form nickel nitride. The nitride can efficiently dissolve excess carbon to suppress the passivation of CNT growth. That is, introducing nitrogen will enhance CNT growth. Lee et al [8] proposed nitrogen could combine with hydrogen to form NH_3 when $N_2/H_2/CH_4$ is used as process gas. The NH_3 has much slower etching kinetics to nickel catalyst than that of hydrogen. The diameter of CNTs becomes big when small amount of nitrogen is introduced into the process gas. The diameter gradually decreases with increasing nitrogen proportion.

Different N_2 proportions mixed with CH_4/H_2 have been used to grow CNTs on nickel catalyst in this work. It was observed that significant morphology change of CNTs corresponds to N_2 proportion. The CNT growth is suppressed when N_2 is introduced into the process gas with 30 % proportion. As N_2 is increased to 47%, CNTs are grown with smaller diameter and less carbonaceous particles than those of CNTs grown from 0% N_2. The diameter of CNTs grown from 57% N_2 reduces 56% than that of CNTs grown from 0% N_2. In addition to the NH_3 and nitride formation model mentioned previously, the CNTs grow only on nickel portion instead of whole catalyst composed of nickel and nitride formed during CNT growth. The above mentioned is proposed to explain the whole phenomena.

2. Experiments

Silicon wafer was coated with 2 nm nickel film by a DC sputtering tool. Then, the nickel coated with silicon wafer was put into a 2.45 GHz, maximum power 2 kW microwave plasma system, so called pretreatment, to convert the nickel film into catalyst particles and the following CNT growth. The pretreatment process parameters were fixed as follows: process gas H_2/N_2 =100/33.3 sccm, $2.5X10^3$ Pa process pressure , 450 W microwave power, 250^oC substrate temperature and 20 minutes process time. Independent nickel particles with 28 nm particle size and 12 nm inter-particle distance were obtained after pretreatment from previous study in our laboratory. After pretreatment, subsequent microwave PECVD CNT growth was done with different N_2 proportions. Process gas flow for H_2 and CH_4 was fixed at 80 and 10 sccm respectively. Different N_2 gas flow: 0, 40, 80 and 120 sccm respectively mixed with H_2/CH_4 was produced as the process gas. Different N_2 proportions: $N_2/ (N_2+H_2+CH_4)$ equal to 0, 30, 47 and 57% were tested. Other parameters during CNT growth were fixed: $4x10^3$ Pa process pressure, 800 W microwave power, 600^oC substrate temperature and 15 minutes process time. Surface morphology of the grown CNTs was checked by a field emission scanning electron microscope (SEM, JSM 6700, Jeol). The field emission properties of the grown CNTs were measured in a high vacuum environment at 10^{-4} Pa or less. A positive voltage was applied to the anode and the emission current was measured with an electrometer (Keithly 237). Emission current was measured during voltage ramping up from 0 to 1100 V. The threshold electric field for electron emission is defined as macroscopic electric field needed to produce a current density of 10 μA/cm^2.

3. Results and discussion

Images of CNTs grown from different N_2 proportions are shown in Fig. 1a-d. There are CNTs grown with carbonaceous particles corresponding to 0% N_2 shown in Fig.1a. The CNTs cannot grow with respect to 30% N_2 seen in Fig.1b. As N_2 proportion is increased to 47%, the CNTs can grow again with smaller tube diameter and less carbonaceous particles than those of CNTs grown from 0% N_2 observed from Fig.1c. The diameter of CNTs grown from 57% N_2 is much smaller than that of CNTs grown from 0% N_2 observed from Fig.1d. The diameters and field emission properties of CNTs grown from different N_2 proportions are summarized in table 1. The CNT threshold electric field reduces with diameter of CNTs. The current density of CNT field emission with anode biased at 1100V corresponding to 0% N_2 is about 10 and 20 times smaller than that corresponding to 47 and 57% N_2 respectively.

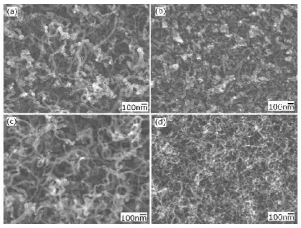
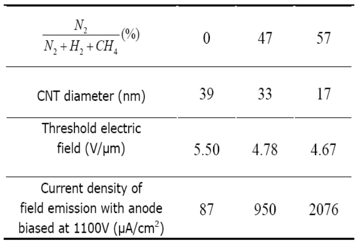


Fig. 1 SEM images of CNTs grown from different $N_2/N_2+H_2+CH_4$ proportions: (a) 0% (b) 30% (c)

47% (d) 57%.

Table 1 Diameters and field emission properties of CNTs grown from different $N_2/N_2+H_2+CH_4$ proportions



$\frac{N_2}{N_2+H_2+CH_4}(\%)$	0	47	57
CNT diameter (nm)	39	33	17
Threshold electric field (V/μm)	5.50	4.78	4.67
Current density of field emission with anode biased at 1100V (μA/cm^2)	87	950	2076

Some reports discuss that N_2 play a significant role in process gas to grow CNTs [7,8]. Results in Fig.1 support this statement. But there is difference between Lee et al. and ours. Lee et al. [8] reported that the diameter of CNTs becomes larger when 33% N_2 or below is introduced into the process gas $N_2/H_2/CH_4$ than that of CNTs grown from 0% N_2; and the diameter of CNTs decreases with increasing N_2 proportion. Our results do not indicate that the diameter of CNTs becomes larger when N_2 is mixed into process gas. Our findings indicate that the CNTs growth is suppressed corresponding to 30% N_2 observed in Fig.1b. This is different from results of Lee et al. The suppression behavior could be explained as follows. Tsang et al [9] reported NH_3 can be formed when N_2 is introduced to H_2/CH_4 plasma system. The nitrogen catches hydrogen atoms to form NH_3. The amount of free hydrogen molecules or atoms in the process gas required for growing CNTs will therefore decrease if NH_3 reaction occurs. The purpose of adding hydrogen during CNT growth is to etch the growing amorphous carbon for avoiding CNT suppression [5]. Adding N_2 to process gas reduces the amount of free hydrogen, so the CNT suppression cannot be avoided. This claim could explain the CNT suppression shown in Fig.1b. There is also another possible reaction for the ionized nitrogen proposed by Yang et al [7]. Yang et al found the formation of a nickel nitride phase, which was checked by X-ray diffraction for nickel film after N_2 included plasma treatment. The nitrogen ion reacts with nickel catalyst to form nickel nitride. The formed nickel nitride does not reverse back to nickel easily due to its strong ionic bond. The nitride can dissolve the excess carbon sufficiently, so the suppression behavior can be prevented by nickel nitride. Based on our results, we infer both NH_3 and nitride formation could happen during the introduction of nitrogen. N_2 reacts with H_2 first during gas mixing procedure and the latter faces the nickel catalyst. The reaction priority is NH_3 rather than nickel nitride. When the N_2 proportion is not large enough like 30% in our work, NH_3 formation will dominate. In such case, the CNT suppression originally prevented by free hydrogen will take place. The NH_3 formation could be saturated as N_2 proportion is over some point like 47% in our work. Formation of nickel nitride becomes the main nitrogen reaction. The CNTs can grow again with excess carbonaceous particles dissolved by nickel nitride. This can explain the clean morphology of CNTs grown from 47 and 57% N_2 as shown in Fig.1c and 1d respectively.

The diameter of CNTs reduces with increasing N_2 proportion reported in this work. We propose CNTs grow selectively on nickel portion instead of whole nickel mixed with nickel nitride. The general CNT formation mechanism is that hydrocarbon containing gas decomposes on catalyst to grow CNT. The hydrocarbon gas adsorbs on catalyst is the first step in CNT formation. Nickel possesses metal bond with high electrical conductivity: high free electron concentration. The free electrons of nickel move easily from their original charge balance positions when the hydrocarbon gas is nearby to form attractive dipoles. This makes catalyst's nickel portion easily attract the hydrocarbon gas with van der Waals force. Nickel nitride, produced from the reaction between nickel and nitrogen during CNT growth, displays ionic bond and bound electrons. It is hard to attract the hydrocarbon gas. As N_2 is increased during CNT growth, much nickel nitride is formed and thus less nickel is left. The CNTs are grown on the remaining nickel portion instead of whole nickel mixed nickel nitride.

The current density of CNTs' field emission corresponding to 47 and 57% N_2 increases much higher than that of CNTs' field emission corresponding to 0% N_2 observed in table 1. It is also a hint for clean morphology of CNTs grown from 47 and 57% N_2. Comparing CNTs grown from 0% N_2 with those grown from 47%, there is only 15% decrease in diameter; however, there is more than 10 times increase in current density of field emission with anode biased at 1100 V. One of the reasons for high current density attributes to obstacles like much fewer carbonaceous particles on CNTs grown from 47 and 57% N_2 than those of CNTs grown from 0% N_2, to interfere emitting electrons of CNTs during field emission test.

4. Conclusions

To evaluate the possible method in growing CNTs applied as field emitters, different N_2 proportions mixed with H_2/CH_4 microwave plasma have been used in growing CNTs. The N_2 proportion has significant impact on the growth, diameter and cleanness of CNTs. Slim and clean CNTs can be obtained with appropriate N_2 proportion. These phenomena can be explained by NH_3 and nickel nitride formation during CNT growth proposed by others, and CNTs grown selectively on nickel portion instead of whole nickel mixed with nickel nitride proposed by us. This work contributes the opportunity to apply $N_2/H_2/CH_4$ in producing clean and slim CNTs suitable to be used as field emitters.

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Figure 1a

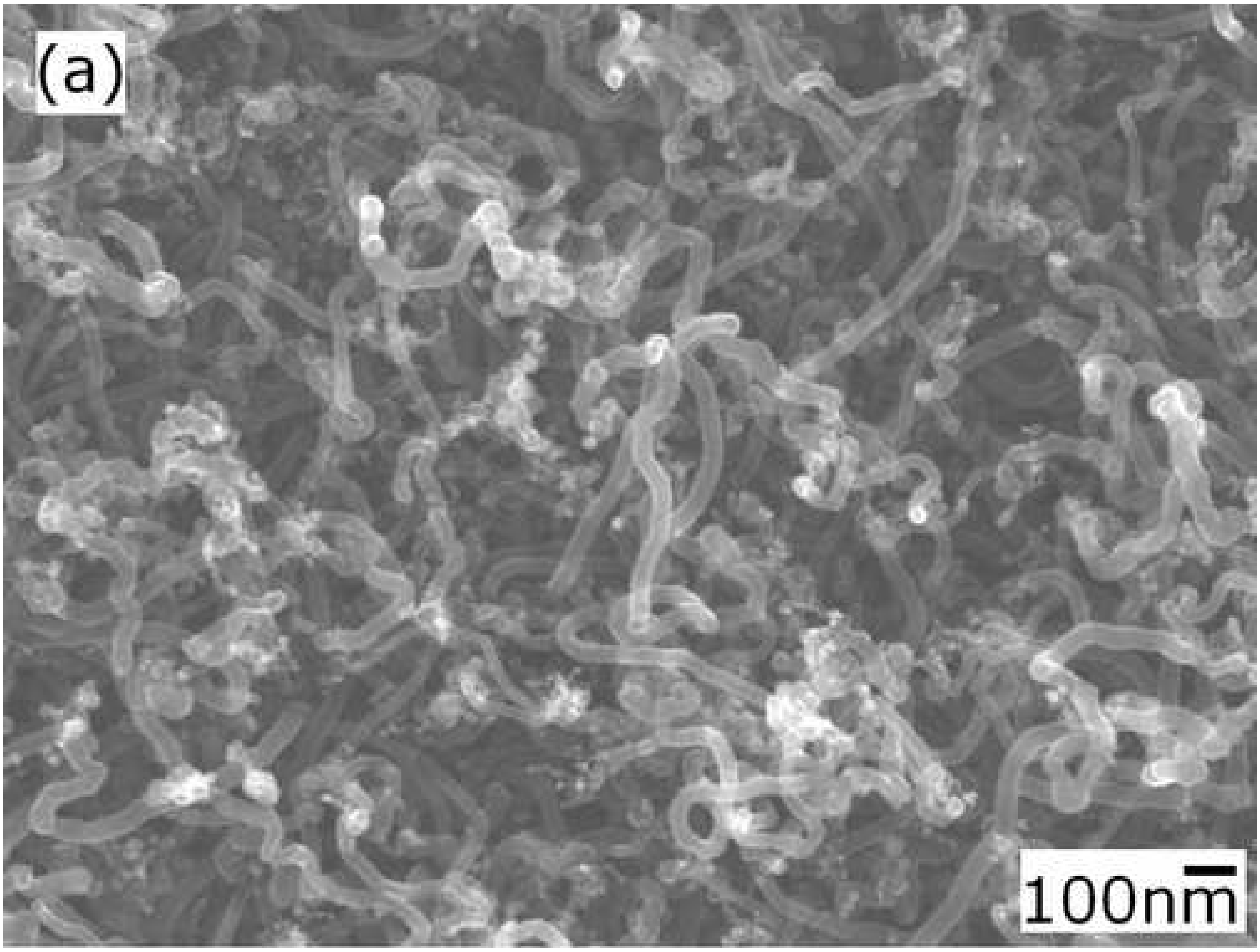

Figure 1b

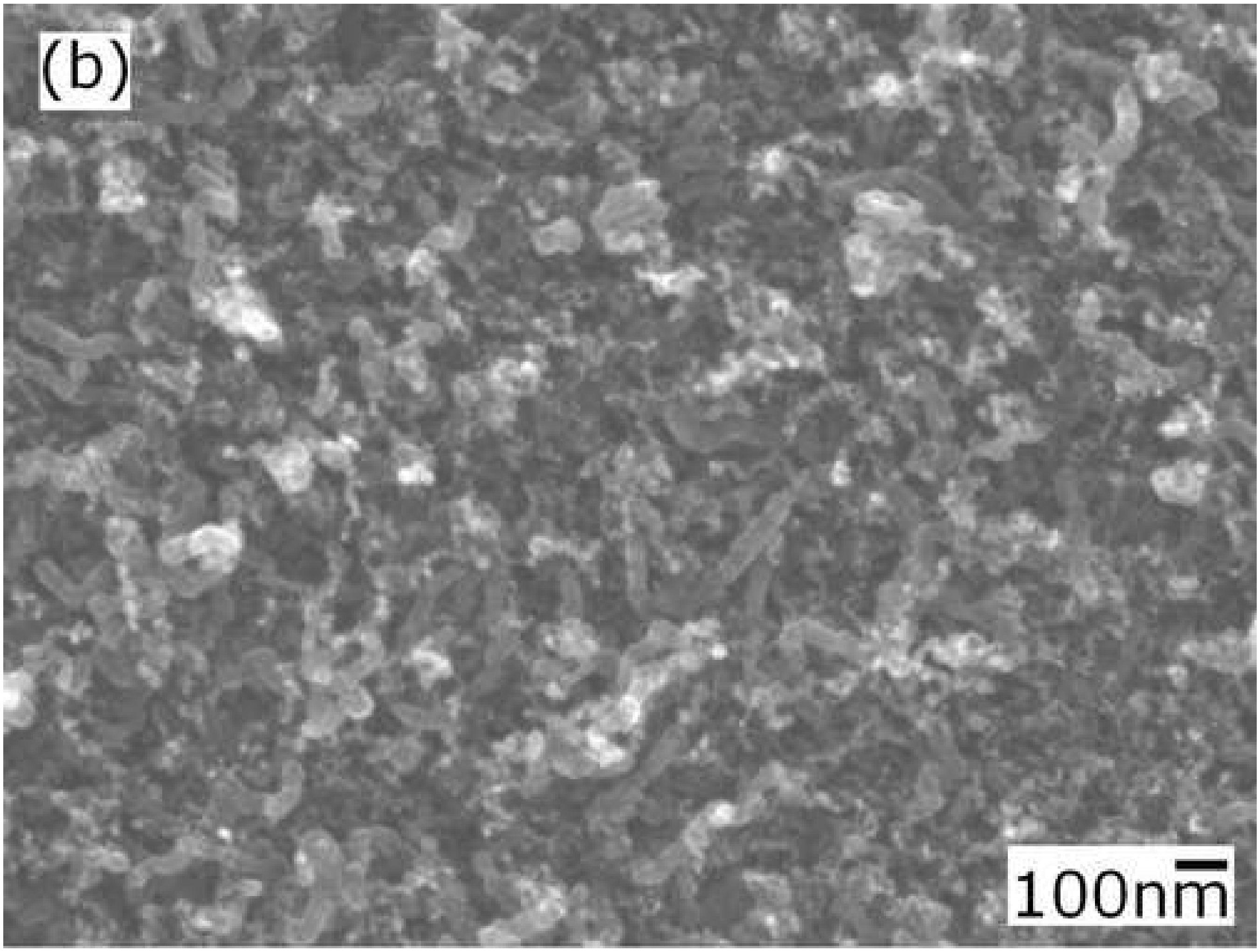

Figure 1c

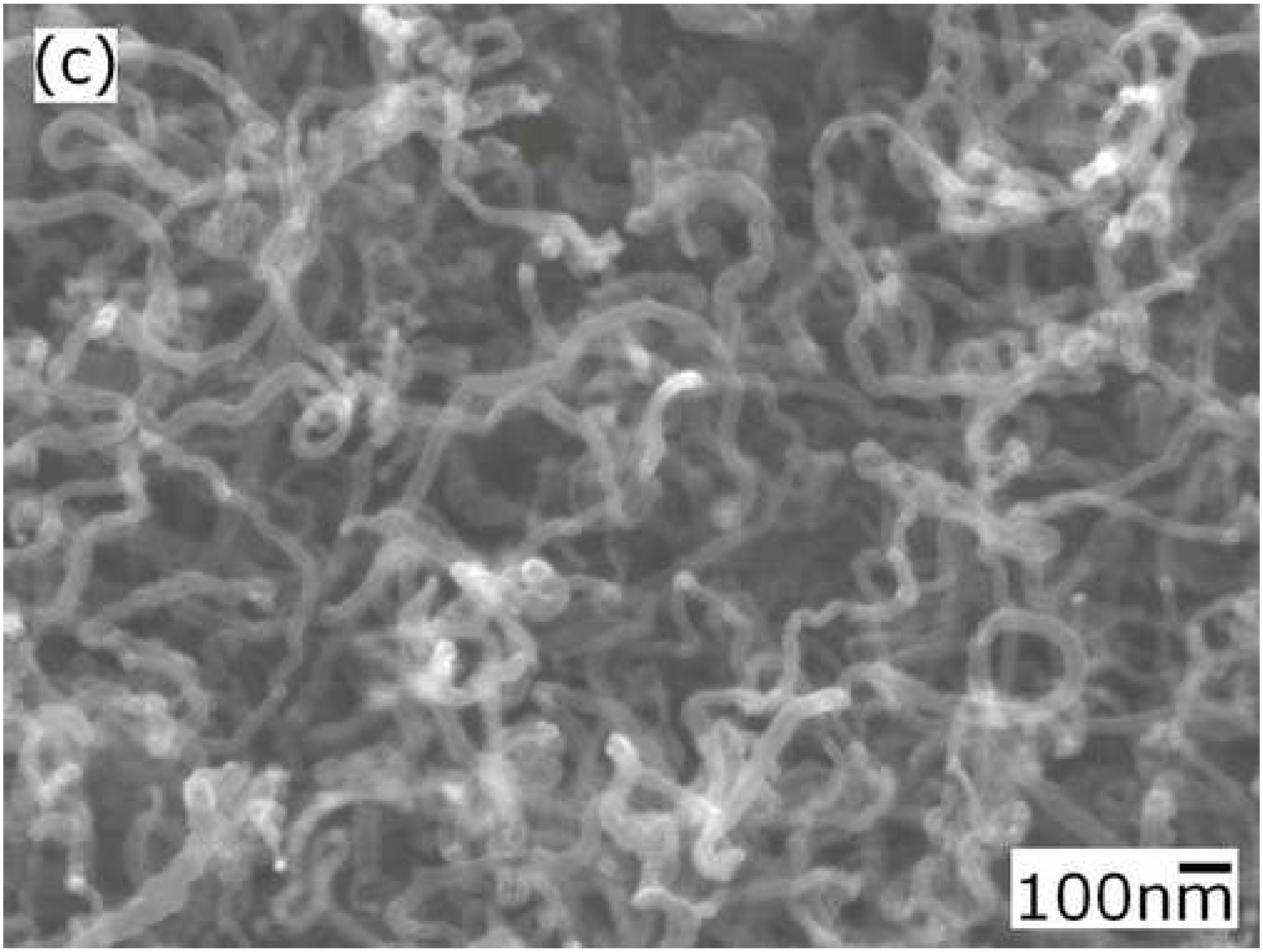

Figure 1d

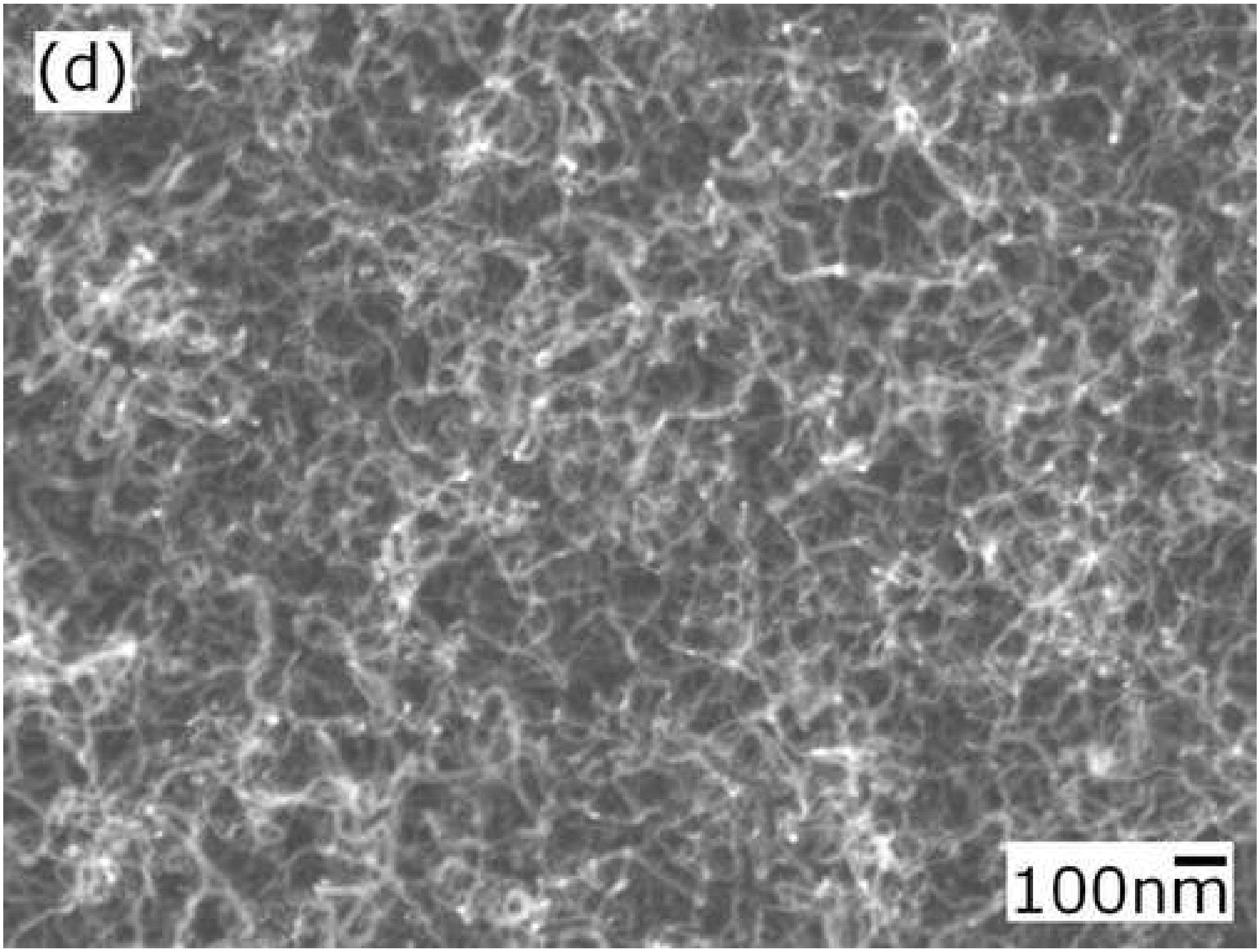

Table1

$\frac{N_2}{N_2+H_2+CH_4}(\%)$	0	47	57
CNT diameter (nm)	39	33	17
Threshold electric field (V/μm)	5.50	4.78	4.67
Current density of field emission with anode biased at 1100V (μA/cm^2)	87	950	2076