Application of dielectrophoresis to fabrication of nanomaterial-based sensors

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Abstract-Dielectrophoresis (DEP) is electrokinetic motion of dielectrically polarized materials in non-uniform electric fields. DEP has been successfully applied to manipulation of nanomaterials including CNTs, metallic nanoparticles and semiconducting nanowires. Under positive DEP force, which attracts nanomaterials toward the higher field region, nanomaterials are trapped in the electrode gap and automatically establish good electrical connections between them and the external measuring circuit. This feature allows us a fast, simple and low-cost fabrication of nanomaterial-based sensors based on a bottom-up basis. This paper firstly presents a theoretical background of DEP phenomena and then reviews recent works of the present author, which were aimed to develop nanomaterial-based sensors, such as a carbon nanotube gas sensor and a ZnO nanowire photosensor, using DEP fabrication technique.

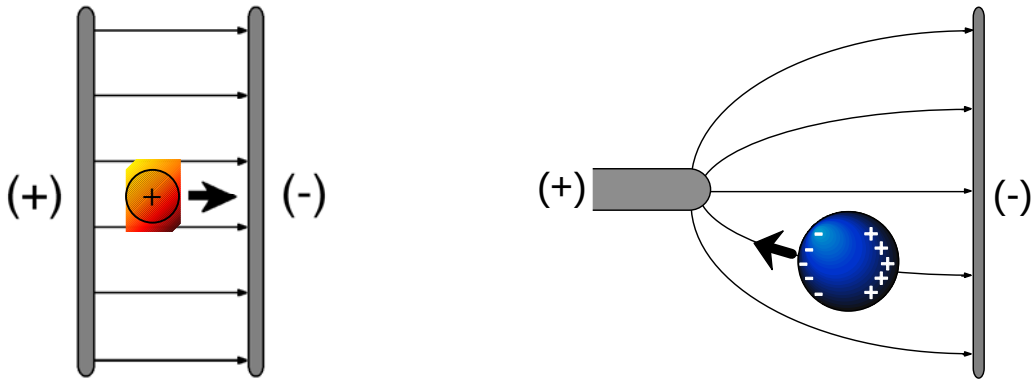
I. Introduction

For the past several years, great interest has been paid to nanosized materials of various compositions and structures. For example, carbon nanotubes (CNTs) and other related families of one-dimensional nanostructures (nanowires) are promising for a variety of potential applications. Precise and reliable handling of these nanomaterials is important for bottom-up assembly of nanodevices, and enormous efforts employing a variety of approaches have been made and reported. Dielectrophoresis (DEP) is electrokinetic motion of dielectrically polarized materials in non-uniform electric fields. The polarized material is driven towards or away from the high field region depending on the complex dielectric permittivity of the particle and its surrounding medium. DEP has found many useful biotechnological applications including separation, detection and characterization of microscale biological cells [1]. Recent rapid advance in the fabrication of integrated semiconductor devices has been successfully transferred to microelectrode structures for DEP and has enhanced flexibility of the technique. The smaller electrodes, which can generate higher intensity electric field gradients without the need for large electrode potentials, offer the advantage of manipulating of smaller sized biological materia such as deoxyribonucleic acid (DNA) or protein as well as nanomaterials including CNTs, metallic nanoparticles and semiconducting nanowires. The present author has demonstrated that the DEP manipulation could provide a way to trap and retain CNTs [2-6], carbon nanohorns (CNHs) [7], zinc oxide (ZnO) nanowires [8] and palladium (Pd) nanoparticles [9,10] on metallic microelectrodes and that these DEP-trapped nanomaterials could serve as sensing elements. One advantage of the DEP fabrication technique is that one can quantify the amount of trapped nanomaterials on a real time basis by monitoring electrical impedance of the sensor. This feature enables one to precisely control and calibrate the response of the nanomaterial-based sensors. Another advantage is that various combinations of nanomaterials and metallic microelectrodes can be obtained because two processes of nanomaterial synthesis and sensor fabrication are separated. This paper firstly presents a principle of DEP phenomena and then reviews recent works of the present author, which were aimed to develop nanomaterial-based sensors using DEP fabrication technique.

II. Principle of DEP

Fig. 1 shows two types of electrokinetic phenomena, which are potentially applicable to manipulation of nanomaterials. Electrophoresis (EP) is the well-known coulombic force due to the net charge of a particle placed in an external electric field. Dielectrophoresis (DEP) refers to the action of a dielectrically polarized particle in non-uniform electric fields. The DEP force acting on a spherical particle of radius a suspended in a medium of absolute permittivity ε_{m} is given by [1]

$$\boldsymbol{F}_{\mathrm{D}} = 2\pi a^3 \varepsilon_{\mathrm{m}} \mathrm{Re}\left[\boldsymbol{K}(\omega)\right] \nabla \left|\boldsymbol{E}\right|^2 \qquad (1)$$



(a) (b)

Figure 1. Electrokinetic phenomena. (a) Electrophoresis (EP). (b) Dielectrophoresis (DEP).

where $|\boldsymbol{E}|$ is the magnitude (RMS) of the applied field and $\mathrm{Re}[\boldsymbol{K}(\omega)]$ is the real component of the Clausius-Mossotti factor given by

$$\boldsymbol{K}(\omega)=\frac{\varepsilon_{\mathrm{p}}^{*}-\varepsilon_{\mathrm{m}}^{*}}{\varepsilon_{\mathrm{p}}^{*}+2\varepsilon_{\mathrm{m}}^{*}} \qquad (2)$$

where $\varepsilon^{*}_{\mathrm{p}}$ and $\varepsilon^{*}_{\mathrm{m}}$ are the complex permittivity of the particle and surrounding medium respectively. For a real dielectric, the complex permittivity is defined as $\varepsilon^{*}=\varepsilon-j(\sigma/\omega)$, where ε is the permittivity and σ is the conductivity of the dielectric and ω is the angular frequency of the applied electric field. Eq.(1) implies that direction of DEP forcec is not dependent on that of external field. Due to this feature, a dielectric particle can be driven to one direction even under an AC electric field. This is a great advantage for electrokinetic handling of bilogical particles and nanomaterials, which are usually suspended in an aqueous medium for handling, because unfavorable electrochemical reactions can be suppressed under AC field. For $\mathrm{Re}[\boldsymbol{K}(\omega)]>0$, the polarized particle is driven towards the high field region (positive DEP), or away from the high field region for $\mathrm{Re}[\boldsymbol{K}(\omega)]<0$ (negative DEP). Eq.(1) also indicates that DEP force linearly increases with the strenght and gradient of the external electric field. A micro-scaled electrode, which is made of thin metal film and patterned by photolithograpy, can produce strong DEP force and has been widely employed for a platform for DEP handling of biological particels and nanomaterials. Eqs.(1) and (2) mean that DEP force is influeced by dielctric properties of nanomaterials and the surrounding medium as well as the field frequency. This feature realizes a selective handling of dielectric materials due to their permittivity and conductivity [1]. Fig. 2 depicts an example of theoretically calculated frequency dependency of $\mathrm{Re}[\boldsymbol{K}(\omega)]$ of a biological cell (yeast).

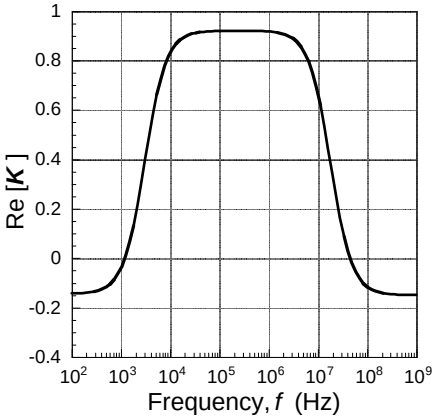


Figure 2. Frequency dependency of parameter $\mathrm{Re}[\boldsymbol{K}(\omega)]$ for yeast cells.

III. Manipulation of nanomaterials using dielectrophoresis

A typical fabrication system for a nanomaterial-based sensor is schematically depicted in Fig. 3 [2]. The equipment is based on the dielectrophoretic impedance measurement (DEPIM) system, which has been developed by the author for electrical inspection of bacteria or micro-organisms [11]. An interdigitated microelectrode of thin metallic film is patterned on a glass substrate by the photolithography technique (Fig. 4a). The electrode has a castle-wall pattern in order to form high and low electric field regions periodically. Each electrode finger has a 5 mm length and 5 μm minimum

clearance. The castellations are squares with sides of 50 μm. The 20 electrode fingers form 19 castellated gaps. As shown in Fig. 4b, nanomaterials are trapped around the electrode corner where the field strength becomes higher as predicted by the theoretical field calculation shown in Fig. 5. The castle wall electrode is surrounded by a silicon rubber spacer to form a sealed chamber (15 μl capacity) in which nanomaterial suspension is stored. Most of commercially available nanomaterials are stored and supplied as aggregated powder. Before DEP manipulation, these aggregations must be well dispersed and suspended in an aqueous medium. Ultrasonication is widely used to obtain uniformly dispersed nanomaterial suspension. Undispersed large particles should be removed by centrifuging or filtration. The nanomaterial suspension is continuously fed into the microelectrode chamber from a reservoir by a peristaltic pump. The DEP trapping of nanomaterials on the microelectrode is performed with an AC voltage of appropriate amplitude and frequency (typically 100 kHz frequency and 10 V peak-to-peak amplitude for CNT, for example). This AC voltage can be also used to simultaneously measure the electrode impedance so that the amount of DEP-trapped nanomaterial can be quantified and controlled [4]. After a desired period of time, the DEP process is stopped and the aqueous medium is gently evaporated at room temperature so that one can obtain a nanomaterial retaining microelectrode.

IV. Fabrication and characterization of nanomaterial-based sensors

There are three types nanomaterial-based sensors, which can be fabricated by DEP fabrication method. Type A sensor has a simple basic structure composed of a DEP-trapped nanomaterial and a metallic microelectrode. The nanomaterial serves as a sensing transducer, while the microelectrode merely provides an electrical connection to the external measurement instrumentations. Type B sensor takes advantages of electronic or chemical interactions obtained at interfaces between nanomaterials and the microelectrode. Type C sensor has a higher order structure composed of several different kinds of nanomaterials so that chemical or physical functionalization of a main nanomaterial can improve the sensor performance.

A. Type A sensor - basic structure

Fig. 6 shows a scanning electron microscope (SEM) image of multi-walled CNTs (MWCNTs), which were trapped on the Cr microelectrode. MWCNTs were trapped around the electrode corner, where the electric field became higher as depicted in Fig. 5, indicating positive DEP is dominant for the MWCNT trap [2]. Since the MWCNTs were longer than the electrode gap, the trapped MWCNTs bridged the gap and established electrical connection between the electrodes. During the DEP process, the electrode

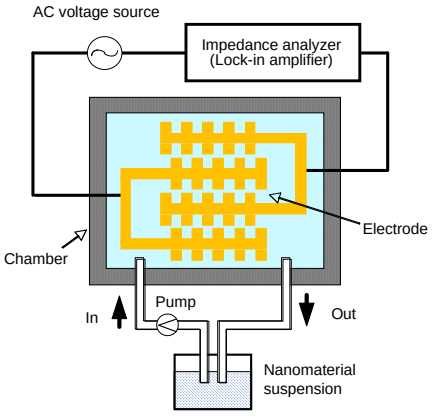
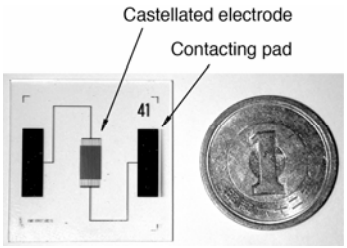
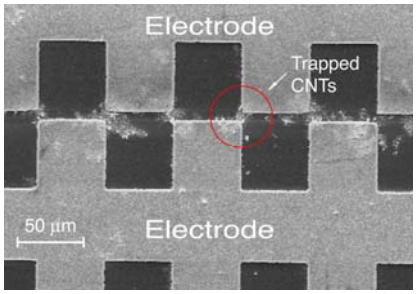


Figure 3. DEP fabrication set-up for nanomaterial-based sensor.



(a)



(b)

Figure 4. (a) Entire view of a microelectrode. (b) SEM image of the DEP-trapped CNT in the castellated gap.

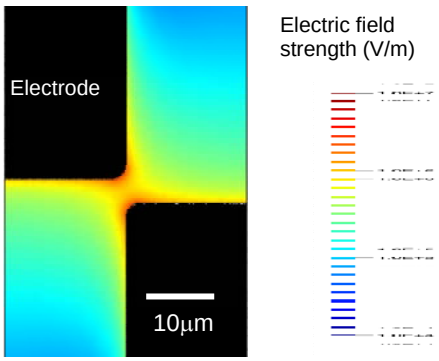


Figure 5. A numerically calculated of field distribution in a castellated microelectrode for applied voltage of 10 V (FEMLAB).

conductance increased with elapsed time, namely, with more MWCNTs trapped onto the electrode. The conductance increment from the initial value represents the total conductance DEP-trapped MWCNTs. DEPIM, which was originally developed to enrich and detect micron-sized bacteria suspended in water [11], could provide a way to quantify the amount of nanomaterials on a real-time basis. It is known that CNT is sensitive to oxidative or reducing gases. Fig. 7 shows responses of a DEP-fabricated MWCNT gas sensor to NO_2 (oxidative) and NH_3 (reducing) gases obtained at room temperature. The electrical conductance of MWCNT sensor increased or decreased upon exposure to ppm-level NO_2 and NH_3, respectively. The sensor responses were attributed to p-type semiconducting behavior of MWCNT. Similar results have been obtained for a DEP-fabricated single-walled CNT (SWCNT) sensor. The initial conductance dependency of the MWCNT and SWCNT sensor responses for 1 ppm NO_2 is summarized in Fig. 8 [4]. The initial conductance G_0 is the conductance just before NO_2 exposure. The sensor response ΔG increased almost proportionally with G_0. This implies that the sensor response normalized by the initial conductance, $\Delta G/G_0$, can be a measure for intrinsic sensitivity of the CNT gas sensor. The normalized sensitivity of the SWCNT sensor was higher than that of the MWCNT sensor probably because SWCNTs contained more semiconducting tubes. The DEP fabrication and impedance monitoring can effectively control the initial conductance of the CNT sensor and can improve reproducibility and uniformity of the sensor response. Single-walled carbon nanohorn (SWCNH), which is a new member of carbon nanostructure family and attracting much attention because of large surface area and high gas-absorption capacity, can be also manipulated by DEP [7]. The DEP-fabricated SWCNH gas sensor had similar NO_2 and NH_3 responses to CNT gas sensors. Fig. 9 depicts a SEM image of DEP-trapped ZnO nanowires, which also have one-dimensional nanostructure similar to CNTs [8]. In recent years, wide-gap semiconductors such as ZnO, TiO_2 and SnO_2 have been drawing increased attention due to the UV photoresponse and optical transparency in the visible light wavelength. In particular, wide-gap semiconductors with nanostructures such as nanoparticles, nanorods, and nanowires are promising as a new type of UV photosensor. ZnO nanowires are expected to have good UV response due to their large surface area to volume ratio, and they might enhance the performance of UV photosensors. When the DEP-fabricated ZnO nanowire photosensor was illuminated by 365 nm UV light, the conductance exponentially increased with a time constant of a few minutes and then gradually saturated as depicted in Fig. 10. The slow UV responses of the ZnO nanowire photosensor were similar to those observed for ZnO thin film and might be attributed to adsorption and photodesorption of ambient gas molecules such as O_2 or H_2O. The ZnO nanowire photosensor could detect UV down to the 10 nW/cm^2 range [8].

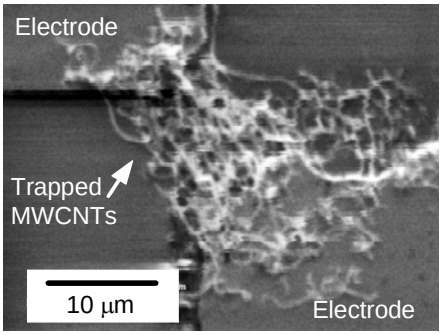


Figure 6. A SEM image of DEP-trapped MWCNTs.

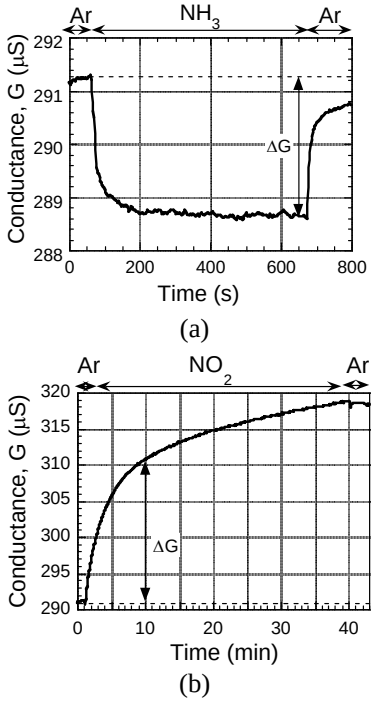


Figure 7. Conductance responses of a DEP-fabricated MWCNT gas sensor to (a) 10 ppm NH_3 and (b) 1ppm NO_2 at

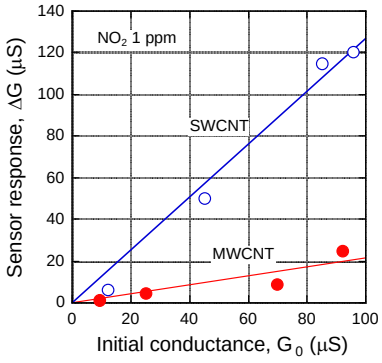


Figure 8. A linear relationship between the initial conductance G_0 and CNT sensor response ΔG to 1 ppm NO2.

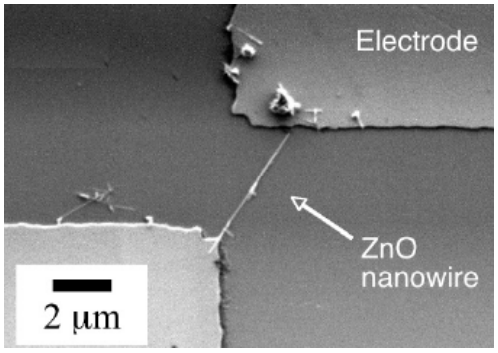


Figure 9. A SEM image of DEP-trapped a ZnO nanowire.

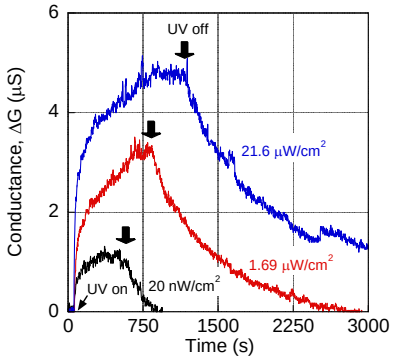


Figure 10. Responses of the DEP-fabricated ZnO nanowire photosensor to 365 nm UV light.

B. Type B sensor - interface between nanomaterials and microelectrode

One advantage of DEP fabrication technique is that the microelectrode made of various metallic materials can be employed because two processes of the nanomaterial synthesis and the sensor fabrication are separated. Preformed nanomaterials can be integrated onto the microelectrode by the electrokinetic process without damage by heating or chemicals, which may be caused by substrate heating, plasma or arc discharges used for the nanomaterial production process. Fig. 11 depicts the NO_2 responses of three CNT gas sensors, which use three different metal electrodes (Pd, Cr and Al) [5]. The sensor response to NO_2 showed a clear dependency on the electrode material. For Pd and Cr electrodes, the sensor resistance gradually decreased after NO_2 exposure. On the contrary, the resistance of the Al/CNT sensor abruptly increased at the moment of NO_2 exposure, but turned to decrease in seconds. The fact that the CNT sensor response was influenced by the metal electrode material suggested that the interface between the CNT and the metal electrode might play an important role in the gas detection process. The Al/CNT sensor response could be interpreted as a superposition of the Schottky contact resistance and the CNT resistance, which were differently influenced by the NO_2 adsorption. The Schottky response of the Al/CNT sensor was approximately one order of magnitude faster than the CNT response obtained using the other metal electrodes. According to the basic theory of metal/semiconductor interface, the p-type semiconducting CNT can form an ohmic contact with a metallic electrode when $\rangle_M > \rangle_S$, where $\rangle_M$ and $\rangle_S$ are the work functions of the metallic electrode and the semiconducting CNT, respectively. On the other hand, a metallic electrode having a lower work function than $\rangle_S$ may form a Schottky barrier at the metal/CNT contact. Among these metals, Al has the lowest value of $\rangle_M$ (4.28 eV). It has been reported that the work function of CNT was almost equal to that of graphite (4.5 eV). Al, which has the lowest work function among tested metals, can form the Schottky barrier with contacting CNT. These experimental findings may open the way to a new type of molecular controlled CNT device, which has an adjustable energy barrier at the interface with metallic electrodes.

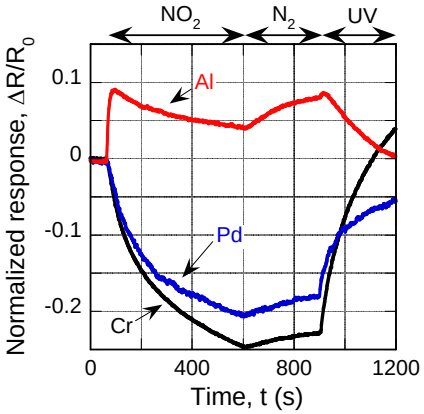


Figure 11. Response of three CNT gas sensors (fabricated onto Cr, Pd, or Al electrodes) to 1 ppm NO_2.

C. Type C sensor - interface between various nanomaterials

DEP fabrication technique realizes a higher order structure composed of several different kinds of nanomaterials. The composite nanostructure can be readily obtained by simultaneous DEP trapping of various nanomaterials mixed and suspended in an aqueous medium. A more controlled structure may be realized by DEP trapping these nanomaterial, which are separately suspended and individually DEP trapped using a multi-flow system. Shown in Fig 12 is a SEM image of a DEP-fabricated nanocomposite sensor for hydrogen gas detection [10]. This sensor was fabricated by simultaneously trapping CNTs and Pd nanoparticles under action of the positive DEP. Pd thin films or fine particles

have been widely employed for the conventional hydrogen sensors due to the catalytic nature. Thus far, Pd has been successfully incorporated also with the CNT gas sensors using electron-beam evaporation or RF magnetron sputtering in order to realize hydrogen gas sensing. It is expected that the DEP technique, which does not need costly equipments such as electron-beam evaporator or RF magnetron sputtering apparatus for the Pd functionalization of CNTs, can provide an alternative way for the CNT/Pd interface fabrication. It was found that hydrogen detection was possible only when Pd nanoparticles were incorporated with CNT, showing that Pd played an important role in the H_2 sensing mechanism. Besides application to the hydrogen gas sensing, the proposed DEP fabrication technique may open the way to a new type of CNT device, which is incorporated with catalytic nanomaterials to realize selective detection of gas molecules. The DEP- fabricated CNT/catalyst arrays may enable selective sensing of a wider variety of detectable gases on a single chip basis.

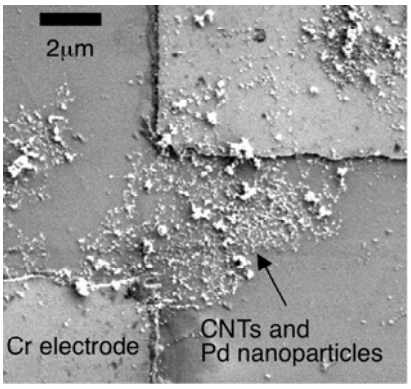


Figure 12. A SEM image of DEP-trapped a CNTs and Pd nanoparticles.

V. Conclusions

In conclusion, DEP has been successfully applied to bottom-up fabrication of chemical and physical sensors composed of various nanomaterials. The DEP manipulation can realize a simple, fast and low cost assembly of nanosensors, which have many advantages such as higher sensitivity and wider range of detection capabilities over conventional sensors composed of thin films or bulky material. Especially, a multi-functional sensing chip, on which various nanomaterials are trapped and integrated by DEP, seems to be promising as a new type of sensor for environmental assessment.

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