Alignment of carbon nanotubes by magnetic fields and aqueous dispersion

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Abstract. Homogeneous dispersion of multi-walled carbon nanotubes (CNTs) in aqueous solution was achieved using several dispersants. The most efficacious dispersant was Polyethyleneimine (PEI). Stable CNT dispersions are found to have higher zeta potentials compared to poorly dispersed suspensions. Application of a strong magnetic field of 12 T to CNT to align in the direction of the magnetic field. Well-aligned CNTs according to direction of magnetic field were obtained.

1. Introduction
Carbon nanotubes (CNTs) have attracted great interest because of their unique structural, electronic, physical and thermal properties, such as high electrical conductivity, thermal conductivity and elastic modulus. Consequently, CNTs have been widely studied as additives or reinforcing materials in advanced composites, including epoxy, metal, ceramic and nano-composites [1-5].

It is well known that CNTs with high aspect ratios easily form aggregates or bundles owing to very strong van der Waals interactions between them [6]. It is therefore difficult to prepare stable dispersions of CNTs in aqueous or organic solution [7, 8]. However, the alignment of CNTs and formation of stable dispersions is necessary to optimize the properties of technologically useful materials, e.g., reinforced composites, electronic components and optical materials, so considerable effort has been expended in finding ways of forming stable dispersions of well-aligned CNTs.

To date, several methods have been reported that produce stable dispersions of CNTs in aqueous or organic solution, such as use of dispersing agents [9-11], colloidal surfactants [12] and chemical treatments [13, 14]. The use of an appropriate dispersing agent is particularly attractive as it minimizes the chemical damage or modification of CNT surfaces compared with the other methods.

In addition, methods for aligning CNTs include use of templates [15,16], self-standing geometries [17], and electric fields [18]. However, these methods have not been investigated in detail. There are still some challenges that need to be overcome to enable fully controlled alignment of CNTs. It has been reported that high magnetic fields are useful for producing a controlled texture in anisotropic ceramics such as Al₂O₃, AlN and hydroxyapatite [19, 20]. Therefore, we focus on the use of high magnetic field for alignment of CNTs [21]. The purpose of this work is to investigate the dispersion of multi-walled CNTs and alignment of CNTs using high magnetic field in aqueous solution.
2. Experimental

2.1. Preparation of CNT suspensions
Commercial multi-walled CNT powders (IlJin Co. Korea) that were synthesized by catalytic chemical vapor deposition (CVD) were used in this study. The properties of the pristine CNT powders are listed in Table 1; the powders were found to be 95 wt% pure. Polyethyleneimine, ammonium hydroxide (NH₄OH) and sodium hydroxide (NaOH) were used as dispersing agents in aqueous solution in this study. 1~5 mg of CNTs and 50~500 μl of each dispersant were added to 30 ml of distilled water. Ultrasonication was used to help to break up the agglomerates by providing sufficient energy to overcome the attractive van der Waals forces between nanotubes [22,23]. Ultrasound generator was input into each suspension vials and the mixture was simultaneously stirred using a magnetic bar under ultrasonication for 10~30 mins to disperse and to break the bundle or agglomerates of the CNTs.

2.2. Characterization
Particle size distributions of the CNTs were measured using a laser particle analyzer (Otsuka Electronics, LSPZ-100). Phase analysis of the CNTs was also performed by X-ray diffraction (Jeol, JDX-3500) using CuKα radiation. The zeta potential of each dilute suspension was measured with a zeta potential analyzer (Otsuka Electronics, LSPZ-100 series). Each sample was ultrasonicated for 10 mins prior to measurement. The ionic strength was maintained using a 10 mM NaCl solution. The zeta potentials (ζ) were calculated from [24]

\[ \zeta = \frac{V_S}{\Delta \rho} \cdot \frac{\eta}{\varepsilon \varepsilon_0} \cdot \frac{L}{A} \cdot \frac{1}{R} \]  

where VS is the streaming potential, Δρ the hydrodynamic pressure difference across the sample, η is the viscosity and ε the permittivity of the liquid, ε₀ the permittivity of free space, L and A are the length and cross sectional area of the sample, respectively, and R is the electrical resistance across it. After ultrasonication, a drop of each suspension was carefully placed on a silicon wafer using a micropipette for microstructural analysis. The suspension was dried at room temperature for 24 hrs. The morphology and conformation of the CNTs was characterized by digital microscopy (Keyence, VHX-600) and scanning electron microscopy (SEM) (Jeol, JSM-6500).

2.3. Application of a high magnetic field
A strong magnetic field of 12 Tesla was applied to the suspensions to seek to align the CNTs. The droplets of the CNT suspensions on silicon wafers were carefully placed within the magnetic generator equipment at the (horizontal) center of the magnetic field for 1~10 hrs as illustrated in Fig.1.

| Property     | Value     |
|--------------|-----------|
| Diameter (nm) | 10~15     |
| Length (μm)  | 10~20     |
| Purity (%)    | > 95      |
| Surface area (m²/g) | 200     |
| Bulk density (g/cc) | 0.1     |

Table 1. Properties of CNT powders.

Figure 1. Schematic diagram of setting of sample in magnetic field generator.
3. Results and discussion

3.1. Dispersion of CNTs

Fig. 2 shows typical micrographs of raw powders of CNTs. The CNTs appear to be solid particles (Fig. 2(a)). This indicates that the nanotubes have agglomerated/flocculated to form particle-like bundles because of the relatively strong van der Waals interactions between CNTs. The surfaces of the CNT bundles have the appearance of soft cotton or fine hair (Fig. 2(b)). The laser particle analyzer gave particle sizes of about 272 nm.

A typical XRD pattern of the CNT powders is shown in Fig. 3. This confirms that the observed phase is pure carbon, with the main peak at $2\theta = 25.6$ degrees [25].

Fig. 4 shows photographs of vials containing 0.1 mg CNT dispersions after mixing by ultrasonic agitation. Samples A, B and C are inhomogeneous, with considerable sedimentation towards the bottom of the vials, resulting in the rest of the dispersion being more-or-less completely transparent. CNTs of their suspensions were insoluble even after ultrasonication. This flocculation is a result of the significant van der Waals interaction between the sidewalls of the CNTs.

Fig. 3. XRD pattern of CNT powders.
However, sample D corresponded to a homogeneous, well-dispersed CNT suspension black in appearance and with no observable precipitation. The CNTs remained in the dispersed state for over one year. This result demonstrates that PEI is an effective dispersant for CNTs. The strong electrostatic repulsion introduced between the nanotubes by the organic molecules successfully separate the nanotubes for long periods of time.

To investigate the dispersion behavior of CNTs in aqueous solutions, zeta potentials were measured. The zeta potential and pH values of each sample are listed in Table 2. The first three samples have negative zeta potentials varying around -15 mV, whereas sample D has a zeta potential of +20 mV. It is known that pristine CNT suspensions without dispersants have a minus charge at pH of 8.5. In addition, it is evident that the CNTs are negatively charged in aqueous solution. The addition of dispersants contribute to increase of the magnitude of zeta potential and to make the alkaline solution by increasing the pH values from 8.5 to 11.8.

The effect of the PEI for stable suspension is follows. The PEI can be wet to surfaces of CNTs and create the repulsive potential. Electrostatic repulsion between the relatively charged CNT surfaces plays useful role in the stabilization of the CNT clusters by van der Waals attraction in aqueous solution. It was reported that the PEI in ceramic colloidal dispersion attributed to stabilize the ceramic aqueous suspension such as Al₂O₃, SiO₂ by the electrostatic repulsion [26].

Fig. 5 shows typical SEM micrographs of dispersed CNTs. The CNT morphology of Fig. 5 (a) consists of huge agglomerates of CNTs because of the mutual attraction between nanotubes. In contrast, the CNTs in Fig. 5 (b) are well dispersed and individually distinguishable. Fig. 5 (b) does not show any huge agglomerates, although there are still small agglomerates visible (indicated by arrows). The well-dispersed CNTs are randomly distributed like individual strands of hair. This result clearly demonstrates that PEI is a suitable dispersant for separating CNTs in suspension.

### Table 2. Zeta potential and pH of CNT dispersed samples in aqueous solution.

| Sample  | Zeta potential (mV) | pH  |
|---------|---------------------|-----|
| Sample A | -13.7               | 8.5 |
| Sample B | -14.6               | 9.6 |
| Sample C | -18.5               | 11.8|
| Sample D | 20.3                | 9.2 |

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![Figure 5](image_url)
3.2. Alignment of CNTs

Fig. 6 shows SEM micrograph at high magnification after applying a magnetic field to obtain the aligned CNTs. In Fig. 6, small curved CNTs show a tendency to align. However, the larger curved CNTs are not as well aligned. It might reasonably be expected that straight CNTs will align more easily than curved CNTs.

The aligning mechanism of ceramic particles by a strong magnetic field can be explained as follows [19,20]. Two conditions are necessary for the particles to align, namely, good dispersion and an anisotropic structure of the particles. Particles with an anisotropic magnetic susceptibility can rotate to an angle that minimizes the system energy when a magnetic field is applied. The energy induced by anisotropic magnetic susceptibility is expressed as follows [20]:

\[ \Delta E = - \Delta \chi VB^2/2 \mu_0 \]  

where \( \Delta \chi = \chi_{ab} - \chi_c \) is the anisotropy of the magnetic susceptibility, \( \mu_0 \) is the permeability in vacuum, \( B \) is the applied magnetic field and \( V \) is the volume of each particle. Alignment of anisotropic particles occurs when \( \Delta E \) is higher than the thermal energy, \( k_B T \).

The present result suggests that application of a magnetic field is very effective for aligning CNT particles. Further development of this method is expected to lead to the development of nanocomposites with superior structural and functional properties.

4. Conclusions

Alignment of multi-walled CNTs using a strong magnetic field on a dispersion of CNTs in aqueous solution was successfully achieved. Polyethyleneimine was shown to be an effective dispersant for preparing the dispersion. Well-dispersed suspensions of CNTs have higher zeta potentials than poorly-dispersed suspensions. The aligned CNTs according to direction of magnetic field were successfully obtained. The degree of alignment of the CNTs depended on the shape of the CNTs.

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