Linear aggregation of spherical nanogolds in carbon nanotube suspension under influence of AC electric field

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Abstract. We reported a novel method to align spherical nanogolds into linear chains, mediated by induced-electric dipoles from carbon nanotubes in the suspension under AC field. Nanogolds were suspended along with carbon nanotube in water under an AC field of magnitude 100 volts/mm and frequency range of 25 - 1,000 KHz. Typically the electric polarization of nanoparticles are very small because of their small volume and we did not observe their dipole-dipole interaction forces under the presence of electric field. However, introducing carbon nanotubes into the suspension made the nanogolds interact with each other and form linear chains directed along the field line. We also found that linear chains can attract from the side and form fatter chains.

1. Introduction

Electric fields have been utilized, in both linear and rotating forms, to manipulate micro-objects for decades. Gunter Fuhr et al. applied rotating electric fields to mouse-fibroblast cells and measured cell rotation and dielectrophoresis [1]. Electric fields can be applied to electrorheological (ER) fluids, also known as “smart fluids”, whose viscosity and shear stress can change greatly in response to external electric fields. ER fluid, consisting of polarizable particles dispersed in a non-conducting liquid, is considered to be one of the most interesting and important smart fluids. Under applied electric fields, the colloidal particles get induced electric dipole moments and align in a chain-like structure, where the chain lengths are parallel to the direction of the field [2]. This causes the suspension to be solid-like in the direction perpendicular to the field direction, increasing its viscosity along that direction. The spherical microparticles in ER fluids can also be tuned to achieved a body-centered tetragonal (BCT), or hexagonally close-packed (HCP), or face centered cubic (FCC) lattice, or body-centered cubic (BCC), depending on the particle concentration and field [3].

Composite materials were used to improve electric polarizability of microparticles in ER fluids, the popular solution being carbon nanotubes (CNTs) adsorbed on polymer microspheres. Due to their highly anisotropic shapes, CNTs have high electric polarizability along the tube’s long axis, and help improve overall polarizability when adsorbed on the surface of micro-spheres. Several kinds of composites containing CNTs were further developed by different techniques for ER fluid application [4].

Even though most of electrorheological research has been focused around polymer-based colloidal suspensions, metallic particles, such as gold nanospheres, also exhibited chain-like structures under external fields [5]. Moreover, gold colloidal particles were found to spontaneously organize into linear aggregates in ethanol [6]. In this paper we used CNTs to improve alignment response of spherical nanogolds under AC electric fields. Unlike other well-prepared methods to disperse CNTs in liquids [7], we showed that simple hand-shaking of CNTs in colloidal suspensions was enough to enhance the linear aggregation of gold colloidal particles greatly. These metallic colloidal
Particles in an applied field have found application in making quick nanowires [5-6] and inkjet-printing of electric-conductive patterns [8].

2. Methods
Our sample cell composed of a cover slip, two parallel conducting wires coated with insulating material, and a plastic O-ring, glued together. The two conducting wires were placed on the cover slip surface and used as electrodes. The O-ring was glued on top of the wired, acting as the wall to contain sample solutions. An AC electric source (RIGOL Function/Arbitrary Waveform Generator DG 2021A) and an amplifier (TEGAM High-Voltage Amplifier Model 2350) were used to applied a peak voltage of $V_p = 125$ volts through the electrode gap of 2.0 mm, yielding an in-plane peak electric field of $E_p = 62.5$ V/mm. The frequency of the AC field used in the experiment ranged from 1 kHz to 1 MHz. The samples were observed under reflected light microscope (Nikon’s Eclipse polarizing microscopes) under transmission light using a 100X objective lens (Nikon LU Plan Fluor 100X/1.30 oil WD 0.20). The videos and images were record using a CCD camera (Canon EOS Kiss X5) as shown in figure 1.

CNTs with three different outer diameters (OD) were used in the experiments: OD 20-30 nm (S-MWNT, Purity > 90%, ID : 5-10 nm, Length : 1-2 μm), OD 30-50 nm (S-MWNT, Purity > 90%, ID : 5-12 nm, Length : 0.5-2 μm), and OD > 50 nm (S-MWNT, Purity > 95%, ID : 5-15 nm, Length : 1-2 μm). The CNTs were mixed with either distilled water or Dimethyl sulfoxide (DMSO) solution and shaken for 3 minutes. The CNTs were not well soluble in either water or DMSO. Most of the CNTs fell to the bottom of the containers, and the mixtures also looked pretty clear. Only the clear part of the CNT mixtures was used in the experiments. Spherical gold particles with 400-nm diameter, stabilized suspension in citrate buffer (Sigma Aldrich, part number 742090), were mixed with the CNT mixture at same volume ratio 25 μL : 25 μL. The solution was placed in the sample cell under the applied AC field as described above.

![Figure 1. The setup for the experiment.](image)

3. Results
Without CNTs in the solution, our applied field strength of $E_p = 62.5$ V/mm clearly did not induced linear aggregation throughout all frequency range (see figure 2). When CNT is introduce in the solution, the linear aggregation of gold particles start after some threshold frequency ($f_{th}$) which depend on the OD of CNTs, as presented in Table 1. CNTs with OD 20-30 nm and OD 30-50 nm in water solution induced linear aggregation of gold particles at frequency around 80-100 kHz or higher. However, CNTs with OD > 50 nm respond quicker at frequency above 25 kHz.

Figures 3-5 compare aggregations of gold particles in water mixed with CNTs with various ODs, under an applied field of $E_p = 62.5$ V/mm and frequency $f = 1$ MHz, observed at 20 min (a and b) and 90 min (c and d). The gold particles started to fall down to the bottom of the cell, just above the cover slip, after 10 min, where they experienced the induced dipole-dipole interaction due to the applied field. The chain formation started after 10 min and can be clearly observed after 20 min (figures 3-5 a and b). After 90 min, the aggregates were very slow moving due to their large sizes. Some aggregates were stuck on the cover slip, and we did not observed significant changes in chain lengths or aggregate sizes after this time.
CNTs with OD > 50 nm were the best of the three sizes used in enhancing linear aggregation of gold nanoparticles under the AC field. CNTs in water solution align such that their long axes are parallel to the field direction. Due to their large electric polarization, CNTs create greater induced charges near the surface of the nanoparticles, where the polarization mismatch occurs, thus enhancing the dipole-dipole interaction forces. Since the polarization scale with the volume of the dielectric material, the larger-diameter CNTs process larger polarization and greater enhance the linear aggregation of nanoparticles. However, comparing CNTs with OD 20-30 nm and OD 30-50 nm (figures 3-4), we did not see significant difference at time 20 min, and in contrast we saw better linear aggregation for OD 20-30 nm at time 90 min.

Table 1. Frequency threshold for linear aggregation of gold particles in CNT-water solution under AC field.

| OD of CNTs (nm) | threshold frequency (kHz) |
|-----------------|---------------------------|
| 20-30           | 100                       |
| 30-50           | 80                        |
| > 50            | 25                        |

Figure 2. Spherical gold particles with 400-nm diameter dispersed in water (no CNT), under an applied field of $E_p = 62.5 \text{ V/mm}$ and frequency $f = 1 \text{ MHz}$.

Figure 3. Spherical gold particles with 400-nm diameter aggregated in water with CNTs (OD 20-30 nm), under an applied field of $E_p = 62.5 \text{ V/mm}$ and frequency $f = 1 \text{ MHz}$. a) and b) show different locations on the cell at time 20 min. c) and d) show different locations on the cell at time 90 min.

Figure 4. Spherical gold particles with 400-nm diameter aggregated in water with CNTs (OD 30-50 nm), under an applied field of $E_p = 62.5 \text{ V/mm}$ and frequency $f = 1 \text{ MHz}$. a) and b) show different locations on the cell at time 20 min. c) and d) show different locations on the cell at time 90 min.

Figure 5. Spherical gold particles with 400-nm diameter aggregated in water with CNTs (OD > 50 nm), under an applied field of $E_p = 62.5 \text{ V/mm}$ and frequency $f = 1 \text{ MHz}$. a) and b) show different locations on the cell at time 20 min. c) and d) show different locations on the cell at time 90 min.
Figures 6-8 compare aggregations of gold particles in DMSO mixed with CNTs with various ODs, under an applied field of $E_p = 62.5 \text{ V/mm}$ and frequency $f = 1 \text{ MHz}$, observed at 20 min (a and b) and 90 min (c and d). The results were similar to those linear aggregation in water mixed with CNTs. We also observed the best linear aggregation in DMSO when mixed with CNTs with OD $> 50 \text{ nm}$. There were no significant difference between CNTs with OD 20-30 nm and OD 30-50 nm (figures 6-7). The main difference between experiments in DMSO and water is that the aggregation in DMSO is reversible. When the AC field is off the nonogold aggregates slowly move apart and become isotropic after 10 minutes, while in water the nonogold aggregates remain stick together.

**Figure 6.** Spherical gold particles with 400-nm diameter aggregated in DMSO with CNTs (OD 20-30 nm), under an applied field of $E_p = 62.5 \text{ V/mm}$ and frequency $f = 1 \text{ MHz}$. a) and b) show different locations on the cell at time 20 min. c) and d) show different locations on the cell at time 90 min.

**Figure 7.** Spherical gold particles with 400-nm diameter aggregated in DMSO with CNTs (OD 30-50 nm), under an applied field of $E_p = 62.5 \text{ V/mm}$ and frequency $f = 1 \text{ MHz}$. a) and b) show different locations on the cell at time 20 min. c) and d) show different locations on the cell at time 90 min.

**Figure 8.** Spherical gold particles with 400-nm diameter aggregated in DMSO with CNTs (OD $> 50 \text{ nm}$), under an applied field of $E_p = 62.5 \text{ V/mm}$ and frequency $f = 1 \text{ MHz}$. a) and b) show different locations on the cell at time 20 min. c) and d) show different locations on the cell at time 90 min.

**Figure 9.** Dynamic linear aggregation of spherical gold particles. a) gold particles aggregated into small linear chains and further merged to form a single long chain. b) long chains merged from the side to form a fatter chain. The drawing on the top right shows a single chain formation and the drawing on the bottom right shows merging of two linear chains.

Dynamic linear aggregation of spherical gold particles is shown in figure 9. First, the gold particles aggregated into small linear chains and further merged to form a single long chain. Then, long chains merged from the side to form a fatter chain. When two linear chains combined from the side, the positions of the gold particles were slightly shifted with respect to the particle positions in the other chain. This is to minimize the dipole-dipole interaction energy of the system.
4. Conclusions

We have shown that CNTs greatly enhanced the linear aggregation of spherical nanogolds in water and DMSO solutions, under applied AC field. The CNTs in the solution do not have to be well dispersed: simply hand shaking to mix the CNTs with the solution is enough and yield satisfactory result. CNTs with greater OD tend to better enhance the linear aggregation. The working frequency of the AC field ranges from 100-1,000 kHz, with the peak electric field about $E_p = 62.5$ V/mm. These metallic colloidal particles in an applied field have found applications in nanowire and electric-conductive inkjet-printing technologies. Improving the field response of the metallic colloids can reduced the field amplitude used in those technologies and thus reducing production costs.

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