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SHORT COMMUNICATION

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Electrically developed morphology of carbon nanoparticles in suspensions monitored by in situ optical observations under sinusoidal electric field

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Abstract In situ optical observations were performed for suspensions composed of carbon nanoparticles under the sinusoidal electric field with an amplitude around 20 kV/mm (volt per micrometer) and various frequencies. For extremely diluted suspensions of mixed fullerenes or multiwalled carbon nanotubes (MWNTs) in a silicone oil, the dark-field optical microscopy was effective for the in situ observation of the particle behavior under the electric field. The nanoparticles in a fullerene suspension under the sinusoidal electric field with a frequency of 100 Hz (in short, 100 Hz electric field) were aggregated to form a rigid spherical microstructure around the halfway between the electrodes. On the other hand, the nanoparticles in an MWNT suspension under 100 Hz electric field were also aggregated but aligned to form a chain-like microstructure which spans the electrodes. Both of the aggregated particles were stable even after the removal of the electric field, and they were redispersed by application of 10 Hz electric field.

Keywords In situ optical observations · Morphology · Carbon nanoparticles · Suspensions · Sinusoidal electric field

Introduction

Carbon nanoparticles, such as fullerenes or carbon nanotubes, have attracted intense interest because of their characteristic structures and physical properties of single particles [1–3]. At the same time, composite materials or suspensions of these nanoparticles, which are incorporated into appropriate media, such as polymers, are also of great interest for applications [4]. In view of material processing, however, most nanoparticles are supplied as powders, which are aggregates of the primary or secondary particles, and the processing of the powders as supplied is usually a hard problem. Therefore, studies on nanoparticles in diluted and concentrated suspensions are important to have desirable nanocomposite materials. Especially, it is attractive to manipulate and monitor dynamic behavior of nanoparticles under external fields such as shear field [5–9], magnetic field [10], and electric field [11–13]. For instance, a chain-like macrostructure of nanoparticles in suspension or polymer composite would be developed by external electric field as well as magnetic field. Up to now, the particle behavior is mostly investigated after processing using external fields. In situ monitoring of the particle behavior during manipulation is highly demanded for precise processing of nanoparticle materials. From the results of in situ monitoring, macroscopically developed morphology of nanoparticles in polymer composite would be controlled precisely by appropriate conditions of external fields.

In the present paper, in situ optical observations of dynamic behavior of carbon nanoparticles in suspensions are reported under the sinusoidal electric field with an amplitude around 20 kV/mm (volt per micrometer) and various frequencies using the dark-field as well as the bright-field optical microscopy. Preliminary results of the nanoparticle behavior under the electric field are also reported, which was effectively monitored using the dark-field microscopy. Further, electrically developed morphology of the carbon nanoparticles will be discussed in terms of the shape of the primary particles.

Experimental

Fullerenes and multiwalled carbon nanotubes (MWNTs) were purchased from MTR, Ltd. The fullerenes were supplied as a mixture of C_{60} and C_{70}. The MWNTs were made by arcing graphite, and the ends of each tube were capped. A small amount of the fullerene mixture was thoroughly suspended in chloroform with sufficient sonic agitation, and it was stored for several days to separate precipitates. A stable suspension obtained by removing the precipitates was then mixed with a 50 cSt silicone oil under vigorous stirring. Chloroform as a cosolvent was removed under reduced pressure. The suspension of MWNTs was also prepared with a cosolvent of xylene in a similar manner. After removing cosolvents sufficiently, the suspensions sometimes showed small fractions of precipitates, which were also removed prior to use. Eventually, the concentration of the fullerene suspension was less than 0.02 wt%, and that of the MWNT suspension was less than 0.05 wt%. The precise concentrations of these suspensions were unable to be determined, because the weight of the precipitates was too light for our electronic balance. The lower limit of the concentration of the fullerene suspension would be 0.009 wt%, which was estimated from the resolution of our electronic balance, while that of the MWNT suspension was still unclear in the present study.

Electrodes with a needle and plate-edge configuration were constructed on a glass slide using a fine copper wire and a copper ribbon with a thickness of 100 μm. The distance between the needle tip and the plate edge was approximately 50 μm. The sinusoidal electric field was applied between the electrodes using a signal generator and an amplifier. Characteristic amplitude of the electric field, which was simply calculated from the applied amplitude of the voltage output and the distance between the needle tip and the plate edge, was approximately 20 kV/mm (volt per micrometer). A small amount of the sample suspension was placed between the electrodes. Particle behavior was observed using an optical microscope (Eclipse E600W, Nikon) equipped with a charge-coupled device camera with dark-field as well as bright-field illuminations of white light. The image data were recorded with a video tape recorder, which took 30 frames/s. The data were transferred to a PC.

Results and discussion

Particle behavior in fullerene suspension

Figure 1 shows captured video images of a fullerene suspension under no electric field. The suspension was observed with bright-field (Fig. 1a) and dark-field (Fig. 1b) illuminations. The image observed with bright-field illumination of white light is normally bright when there is no detectable contrast in the sample suspension. On the contrary, the image observed with dark-field illumination is normally dark, and the bright features in the image can be observed when there is detectable contrast in the suspension. In the image shown in Fig. 1b, almost no characteristic bright features can be found except the electrodes with a needle and plate-edge configuration, because the concentration of the fullerene particles was extremely low. In the present paper, the images were observed with the dark-field illumination unless otherwise stated.

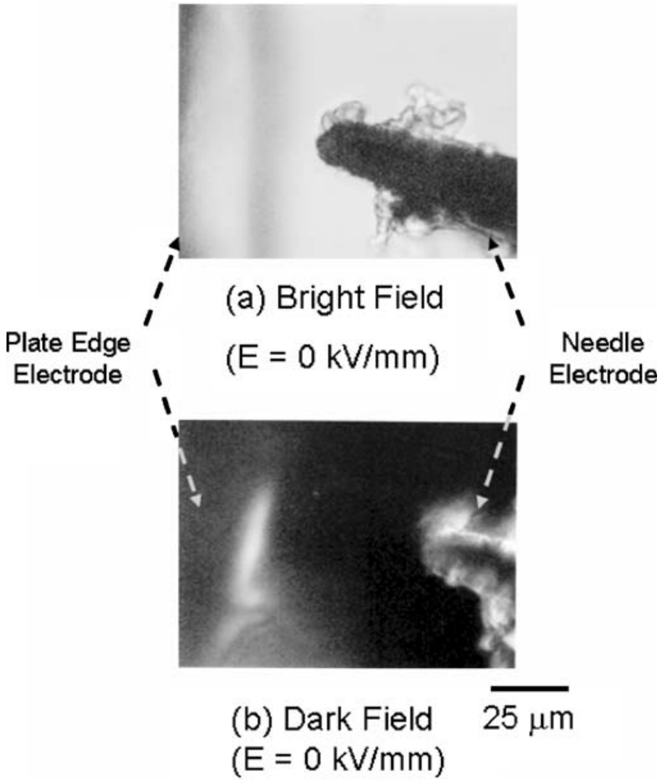

Fig. 1 Captured video images of fullerene suspension under no electric field with **a** bright-field and **b** dark-field illuminations

Figure 2 shows sequential images of the suspension before and after application of the sinusoidal electric field. The frequency was 100 Hz, in short 100 Hz electric field. As mentioned above, almost no characteristic bright features except the electrodes can be found in Fig. 2a before application of the electric field. On the other hand, bright aggregates of the fullerene particles between the electrodes are found in Fig. 2b,c after application of the electric field: When the sinusoidal electric field was applied, small secondary particles were found. The secondary particles first moved quite rapidly and back and forth between two electrodes. Some secondary particles also came from outside the frame. Then, a bright cloud appeared as shown in Fig. 2b, and it developed around the halfway

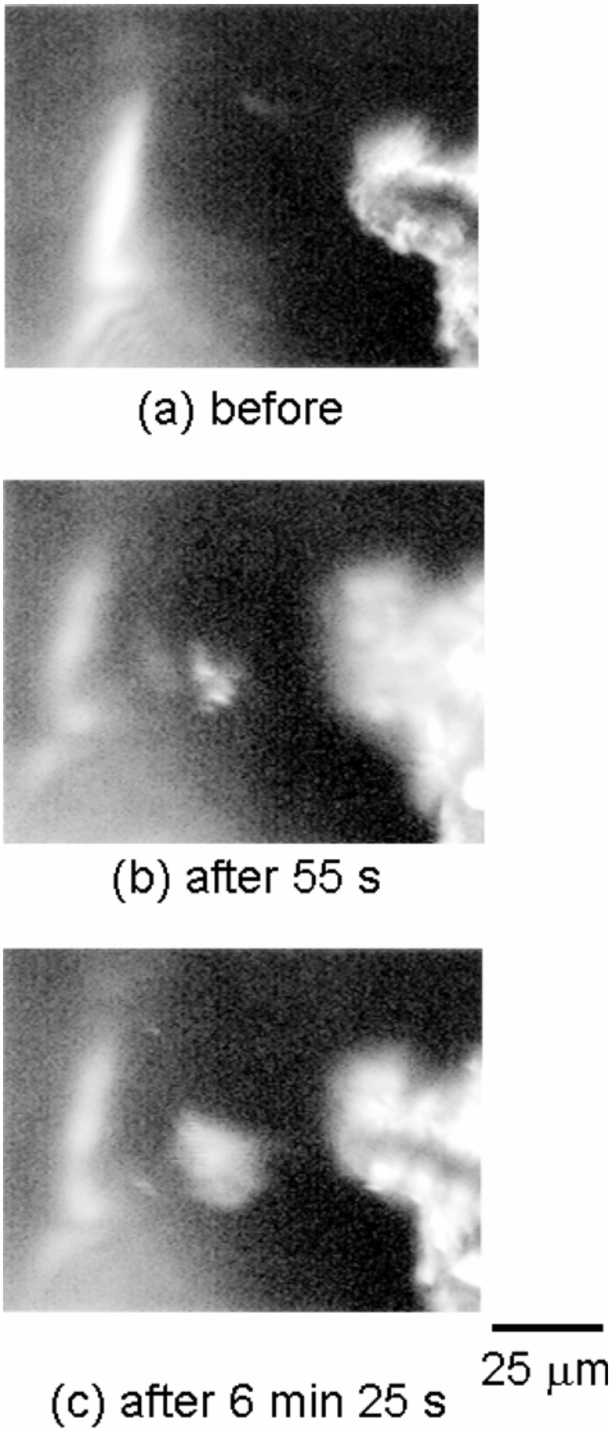

Fig. 2 Sequential dark-field images of fullerene suspension before and after application of 100 Hz electric field: **a** before application of the electric field, **b** after 55 s, and **c** after 6 min 25 s

between the electrodes. In the cloud, the density of the fullerene particles would be relatively high. From the cloud, macroscopic aggregates made of the secondary particles were finally developed between the electrodes. No detectable aggregates were macroscopically developed after application of 1 and 5 kHz electric fields. Further, no characteristic bright features were found when only the silicone oil used as continuous phase of the fullerene suspension was observed under similar conditions. It is notable that macroscopic morphology of the electrically developed aggregates is not chain-like with spanning the electrodes, but it is rather spherical as shown in Fig. 2c. Furthermore, the developed aggregates were stable even after removal of the electric field.

In the formation of electrically developed morphology of nanoparticles, there are competitions among particle–particle interactions with or without external electric fields and thermal randomization. In the particle–particle interaction without external electric fields, attractive forces would be larger than repulsive forces, because the developed aggregates were stable even after removal of the electric field. However, the particle–particle interaction without external electric fields would be smaller than thermal randomization before application of the external electric field, because the suspension was extremely diluted. When the external electric field was applied, the dipoles were induced. In the present experiment, the electrode with a needle and plate-edge configuration was used so that nonuniform electric field was applied. Under nonuniform electric field, translational forces acted on the nanoparticles with induced dipoles [14], and the nanoparticles would be moved from outside the frame of the image shown in Fig. 2. Then, the chance of collision among the nanoparticles would be increased remarkably, and the macroscopic aggregates were developed by the (induced) dipole–dipole interaction as well as the particle–particle interaction without external electric fields. After removal of the external electric field, the particle–particle interaction without external electric fields would now be much larger than thermal randomization, because the particles were sufficiently condensed by application of the external electric field. Further, the particle–particle interaction without external electric fields would be rather isotropic, because the primary particles of fullerenes are roughly assumed to be spherical.

Figure 3a shows an image of the electrically developed aggregates under no electric field. The image was taken after removal of the electric field shown in Fig. 2c. The developed aggregates were stable and around the halfway between the electrode. When 10 Hz electric field was applied, the aggregates moved back and forth between two electrodes. The aggregates collided with the electrodes and broke into smaller pieces as shown in Fig. 3b. There seems to be a specific frequency of the sinusoidal electric field, although the dominant factors of the specific frequency are still unclear at present. Application of 1 Hz electric field also induced a similar movement of the aggregates between the two electrodes. The dependence of the particle behavior on the electric field strength was still unclear: No significant responses of the fullerene particles were observed

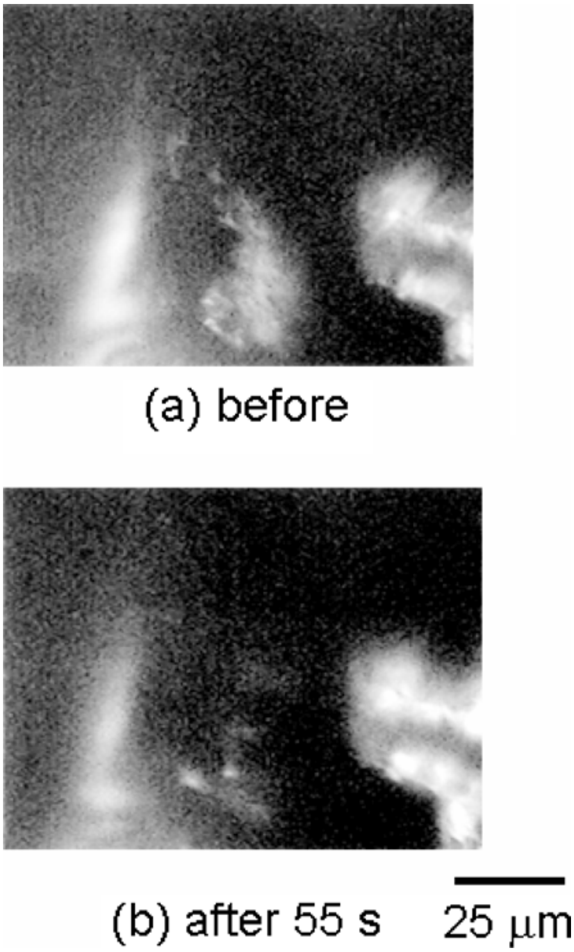

Fig. 3 Captured dark-field images of developed aggregates in fullerene suspension: **a** under no electric field and **b** 55 s after application of 10 Hz electric field

in the sinusoidal electric field with amplitudes on the order of 1 V/mm, while similar responses were observed in the sinusoidal electric field with amplitudes around 20 kV/mm.

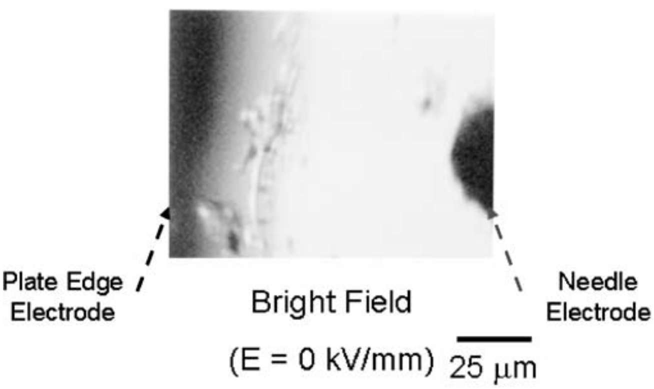

Fig. 4 A captured bright-field image of MWNT suspension under no electric field

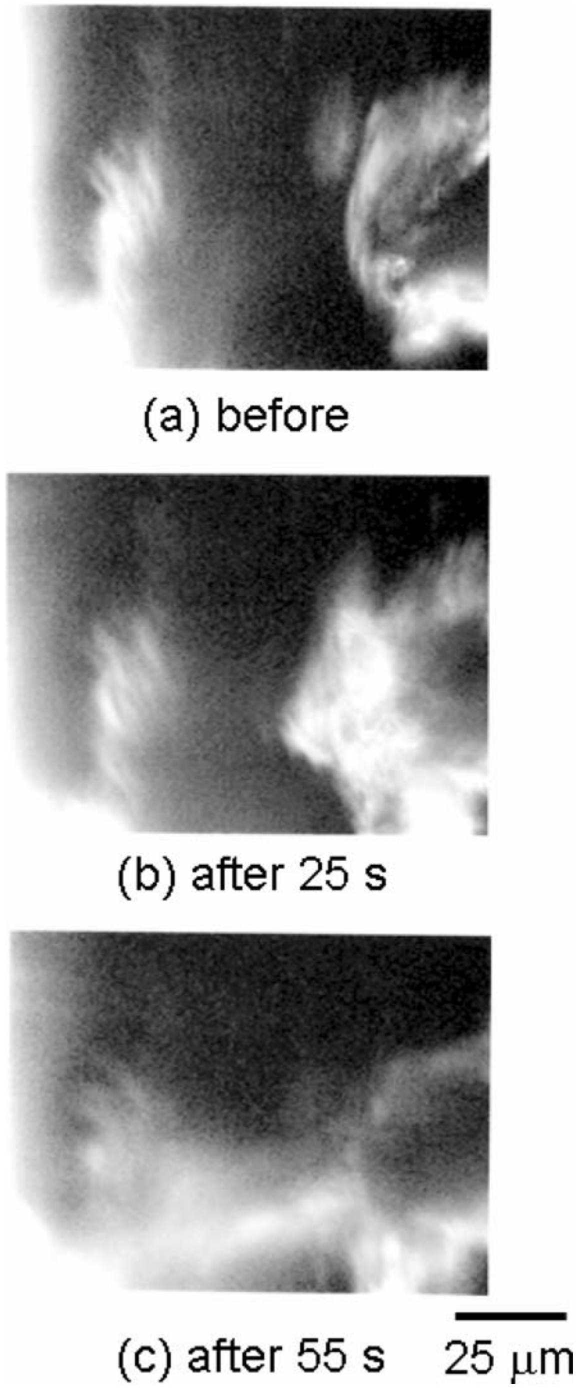

Fig. 5 Sequential dark-field images of MWNT suspension **a** under no electric field, **b** 25 s after, and **c** 55 s after application of 100 Hz electric field

The amplitude dependence of the particle behavior in the MWNT suspension was qualitatively similar. Further study is needed to make clear the dependence of the particle behavior on the electric field strength. It should be pointed out again that the fullerene particles are roughly spherical. The behavior of long and rod-like particles is slightly different from the behavior of the spherical particles, which is discussed in the next section.

Particle behavior in MWNT suspension

Figures 4 and 5a show captured bright-field and dark-field images of an MWNT suspension under no electric field, respectively. From the dark-field image shown in Fig. 5a, almost no characteristic bright features can be found except the electrodes with a needle and plate-edge configuration. In Fig. 5b, bright aggregates of the particles are found near the needle electrode after application of 100 Hz electric field. Further, a chain-like microstructure of the electrically developed aggregates, which spans the electrodes, is found in Fig. 5c. The chain-like microstructure found in the MWNT suspension is anisotropic and quite different from that found in the fullerene suspension. Therefore, the shape of the primary particles would affect the morphology of the electrically developed aggregates of the secondary particles.

The aggregates in the suspension shown in Fig. 5c further developed between the electrodes during the subsequent application of the electric field. After removal of the electric field, the observed field of view between the electrodes was almost completely covered with a stacked microstructure of the developed aggregates, and the stable microstructure is seen in Fig. 6a even after removal of the external electric field. In the case of MWNT particles, the particles were rod-like and much longer than the fullerene particles. Therefore, the particle–particle interactions with or without external electric fields would be much larger than the particle–particle interactions among fullerene particles. The rod-like particles easily responded to the external electric field, and the chain-like microstructure or stacked microstructure was easily developed and stable enough against thermal randomization after application and removal of the external electric field. When 10 Hz electric field was applied to the suspension, the stacked microstructure of the developed aggregates oscillated rapidly. The stacked microstructure eventually broke into smaller pieces of the aggregates as shown in Fig. 6b, the tendency of which is qualitatively similar as shown in Fig. 3b.

Figure 7 shows captured bright-field images of the MWNT suspension under 1 Hz electric field (Fig. 7a,b) and after removal of the subsequent application of 0.1 Hz electric field (Fig. 7c). During application of the electric field, various types of morphology were found. Among them, three types of significant features are summarized in the figure: fiber-like type (Fig. 7a), sheet-like type (Fig. 7b), and ribbon-like type, (Fig. 7c). However, no detectable

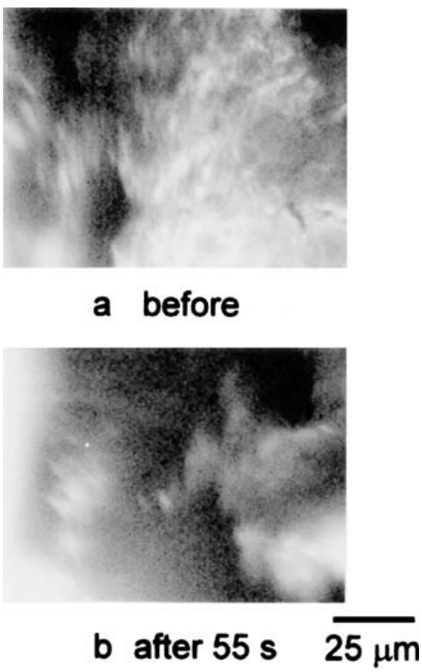

Fig. 6 Captured dark-field images of MWNT suspension **a** after removal of 100 Hz electric field and before application of 10 Hz electric field and **b** 55 s after application of 10 Hz electric field

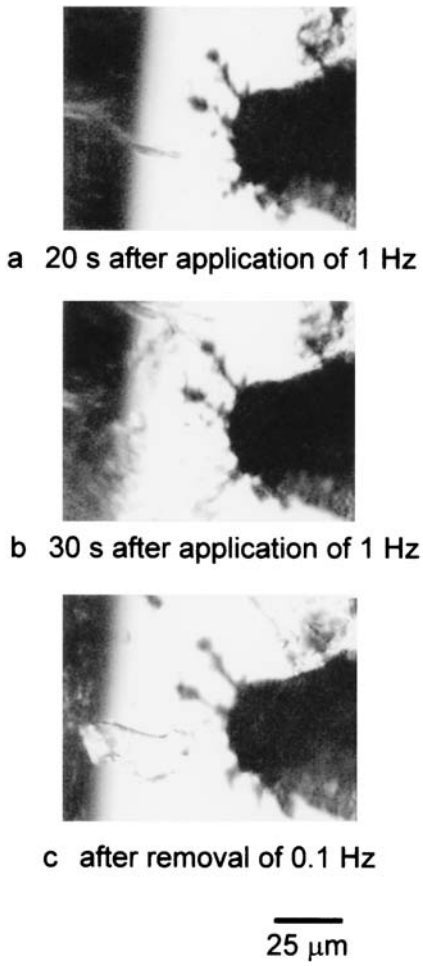

Fig. 7 Captured bright-field images of MWNT suspension **a** 20 s after, **b** 30 s after application of 1 Hz electric field, and **c** after removal of the subsequent application of 0.1 Hz electric field

aggregates were macroscopically developed after application of the sinusoidal electric field with frequencies of 1 and 5 kHz.

The morphology of aggregates shown in Fig. 7 is rather anisotropic. Therefore, long and rod-like shape of the primary particles would affect the morphology significantly. Although it is still unclear at present why the aggregates broke into smaller pieces of the aggregates remarkably by 10 Hz electric field, the configuration (or geometry) of the electrodes, the distribution of the electric field, and the size and shape of the primary particles would affect the redispersion behavior of the aggregates. Further study is needed to clarify the frequency dependence of the particle behavior.

Conclusions

In the present study, the dark-field optical microscopy was found to be effective for the in situ observation of the particle behavior of carbon nanoparticles in diluted suspensions under the electric field. The nanoparticles in fullerene and MWNT suspensions were aggregated to form developed microstructures under the sinusoidal electric field with a frequency of 100 Hz, and the electrically developed aggregates were stable even after removal of the electric field. Further, the electrically developed aggregates were redispersed by application of the sinusoidal electric field with a frequency of 10 Hz. However, the morphology of the electrically developed aggregates found in the fullerene suspension was different from that found in the MWNT suspension. It was pointed out that the shape of the primary particles would significantly affect the morphology of the electrically developed aggregates of the carbon nanoparticles.

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