

Comparative study of carbon nanotubes- and fullerenes-doped liquid crystal for different electrophoretic parameters

Anoop Kumar Srivastava · Avinash C. Pandey ·
Ram Kripal · Seung Hee Lee

Received: 6 July 2013 / Accepted: 31 October 2013 / Published online: 20 November 2013
© Springer Science+Business Media New York 2013

Abstract This research focuses on the study of different electrokinetic parameters of carbon nanotubes (CNTs) and fullerene aggregates in liquid crystal (LC) host medium, which are investigated in the homogeneously aligned nematic LC cells driven by in-plane field. The colloidal CNTs in LC medium are observed to move towards the negative electrodes whereas the fullerenes in LC medium are observed to move towards positive electrode at low frequencies. We propose a model to estimate the charge and zeta potential of colloidal particles by incorporating both the dielectrophoresis and electrophoresis forces in order to probe the reason of moving the colloidal particles in opposite direction. Interestingly, charge and zeta potential values on CNTs and fullerenes estimated from given model were positive and negative, respectively. The CNTs and fullerenes at high frequency and field are found to stretch along the direction of electric field. The CNTs dispersed whereas fullerenes start to move in perpendicular direction to the applied electric field with increasing electric field at high frequency.

Introduction

Electric field-induced particle motion refers to the migration of particles suspended in dielectric host solutions subjected to externally applied electric fields. It is derived from the interplay either between the applied electric field and the net charges on the particle surface and within the electrical double layer (EDL) formed adjacent to the charged surface [electrophoresis (EP) force] or due to dipole moment formed on the particles placed in non-uniform electric field [dielectrophoresis (DEP) force]. Electric field-induced force on the colloidal particle can cause fractal formation, chaining, net- or matrix-like structure or translation motion in the dielectric host medium and has been widely used in biotechnology and genetic engineering [1], nanotechnology [2–4], and display devices [5, 6].

Recently, there has been a growing interest in studying of colloidal particles in liquid crystal (LC) medium [7–19]. This feature can be used in electronic paper like display technologies, colloidal assembly and separation, microfluidic and micromotor application. Fukuda et al. [7, 8] theoretically investigated the interactions of colloidal particles in nematic LC medium. Liao et al. [9] reported electrorotation (Quincke rotation) and electro translation of microscopic cylindrical and spherical inclusions dispersed in LC. The Ryzhkova et al. [10] reported that average velocity of the microparticles in LC medium depends on the third power of the electric field strength. Bert and Smet [11, 12] noted the high value of zeta potential, which was due to contribution of DEP force. Lavrentovich et al. [13] reported that when EP is performed in liquid crystalline nematic fluid, the effect becomes strongly non-linear with velocity component. The translation motion of carbon nanotubes (CNTs) [14–16] and fullerenes (C₆₀S) [17] in LC medium and CNTs'

A. K. Srivastava (✉) · A. C. Pandey
Nanotechnology Application Centre, University of Allahabad,
Allahabad 211002, India
e-mail: srivastava_anoop@rediffmail.com

R. Kripal
Physics Department, University of Allahabad,
Allahabad 211002, India

S. H. Lee (✉)
Department of BIN Fusion Technology, Chonbuk National
University, Jeonju, Jeonbuk 561-756, Korea
e-mail: lsh1@chonbuk.ac.kr

elongation and dispersion [18, 19] under electric field have been recently reported by our group.

In spite of our extreme efforts to completely disperse the CNTs in LC to study the electro-optic properties of CNT-doped LC cell, a few agglomerates of CNTs were seen in the LC especially when the doping amount of CNTs exceeds the critical weight percent [20, 21]. Up till now, very little attention has been paid to calculate the zeta potential of nanoparticles by considering both the DEP and EP forces. In this paper, we modelled the EP equation [22] for zeta potential and charge on the colloidal particles by incorporating the DEP force. The charge and zeta potential on CNT and C₆₀ aggregates in LC medium have been evaluated and compared. The electric field-induced motion of CNT and C₆₀ cluster at high frequency has also been elucidated.

Experimental technique

The superfluorinated nematic LC mixture employed in this study was purchased from Merck and used as-received. Its physical properties are listed as follows: dielectric anisotropy $\Delta\epsilon = +7.4$ at 1 kHz, flow viscosity $\eta = 18 \text{ mm}^2/\text{s}$, at 20 °C, and nematic phase between -40 and 87 °C.

For a homogeneous alignment, driven by in-plane field, the interdigitated opaque electrodes made from aluminium were placed on the bottom substrate only. The electrodes have been separated at a distance of $40 \text{ }\mu\text{m}$ with an electrode width of $10 \text{ }\mu\text{m}$. For a cell fabrication, a homogenous alignment layer (AL-16139 from Japan Synthetic Rubber Co.) was first spin-coated to a thickness of 800 \AA on an electrode-patterned glass substrate. A rubbing process to the in-plane field direction was then performed on the substrate to align the nematic LC. The same alignment layer was coated on another glass substrate without electrode, and the similar rubbing process was then performed in antiparallel direction to the first one. The cell was assembled to give a cell gap (d) of $9 \text{ }\mu\text{m}$, where the plastic balls were used to maintain the cell gap.

The HiPco Single-walled Carbon nanotubes (SWCNTs) (Carbon Nanotechnology Inc.) were used after nitric acid treatment to remove catalysts. The diameter ranged from 4 to 10 nm with a wide distribution of CNTs length from 0.1 to $0.5 \text{ }\mu\text{m}$ (the most probable SWCNT length was 250 nm), which was observed from atomic force microscopy (AFM: Seiko SPA-400).

The SWCNTs in a powder type were not dispersed instantly in LC medium. In order to disperse SWCNTs in LC medium, 10^{-2} wt% of SWCNTs was dissolved into dichloroethane (DCE) solvent, followed by mixing with nematic LC. The amount of weight percentage of SWCNTs was determined by measuring the remaining CNTs on the filter and very nominal amount of CNTs was found to be altered after

centrifugation. If proper conditions such as sonicating time and power were not satisfied, SWCNTs would aggregate themselves during the dispersion process. After the solvent evaporation, we measured the clearing point of LC mixture to confirm the solvent evaporated perfectly. This gave rise to the same clearing temperature as the pure LC. The SWCNTs-dispersed LC mixture was thoroughly sonicated for an hour. Without further treatments, the mixtures were filled in the cell at room temperature by the capillary action. The fullerenes of 1.0 wt% were mixed into the LC medium then filled into the cell by capillary action followed by sonication process. The fabricated test cells were observed under optical polarizing microscopy (Nikon DXM1200) by applying an electric field of different magnitudes. The velocity (v) of the CNTs and C₆₀s was determined by monitoring their motion and textures at the rate of 30 frames per second.

Theoretical approach

When the effect of quadrupole and higher order multipoles are ignored, electric force acting on the particle in an external electric field can be expressed as [17, 19]

$$F_E = -qE + p(\nabla E), \quad (1)$$

where p is the dipole moment on the suspended particles and ∇E is the gradient of electric field (E). The first term describes the Coulomb interaction between the net charge q of the particle and an electrical field E and embodies all electrophoretic phenomena. This vanishes in the absence of net charge on the particle. The additional force terms arise from the interaction of dielectric polarization components induced in the particle by an electric field with spatial inhomogeneities in that field. This dielectric force term only vanishes if the field is spatially homogeneous ($\nabla E = 0$). Hence, in order to apply DEP force, the applied electric field must be inhomogeneous. The dipole moment on the particles can be expressed as [23]

$$p = 4\pi\epsilon_1 r^3 E \text{Re}\{K(\epsilon_2^*, \epsilon_1^*)\} \quad (2)$$

where ϵ_2^* and ϵ_1^* are complex dielectric permittivities of the colloidal particles and the host dielectric medium, respectively, r is the radius of the particles. $K(\epsilon_2^*, \epsilon_1^*)$ represents the complex polarization factor (for spherical objects this is known as Clausius–Mossotti function). The complex polarization factor is given by

$$K(\epsilon_2^*, \epsilon_1^*) = \frac{\epsilon_2^* - \epsilon_1^*}{\epsilon_2^* + 2\epsilon_1^*} \quad (3)$$

where $\epsilon^* = \epsilon - \frac{\sigma}{\omega}j$, and σ and ω stand for the conductivity and electric field frequency, respectively. Therefore, $\text{Re}\{K(\epsilon_2^*, \epsilon_1^*)\}$ can be expressed as

$$\text{Re}\{K(\epsilon_2^*, \epsilon_1^*)\} = \frac{\omega^2(\epsilon_2 - \epsilon_1)(\epsilon_2 + 2\epsilon_1) + (\sigma_2 - \sigma_1)(\sigma_2 + 2\sigma_1)}{\omega^2(\epsilon_2 + 2\epsilon_1)^2 + (\sigma_2 + 2\sigma_1)^2} \tag{4}$$

Substituting the value of p from Eq. 2 to Eq. 1, the net electric force acting on the particle would be

$$F_E = -qE + 4\pi\epsilon_1 r^3 E \text{Re}\{K(\epsilon_2^*, \epsilon_1^*)\} \nabla E \tag{5}$$

Since the Reynolds number ($\text{Re} = \rho v r \eta^{-1}$, where $\rho = 1.07 \times 10^3 \text{ kg/m}^3$ is the internal fluid density, $r = 1.25 \times 10^{-6} \text{ m}$ is the radius of CNTs, $v = 26.1 \text{ }\mu\text{m/s}$ is the velocity of the CNTs at the applied electric field of $0.5 \text{ V}/\mu\text{m}$, and $\eta = 19.3 \times 10^{-3} \text{ kg/m/s}$ is the shear viscosity of the LC) of the CNTs-doped LC is much less than unity and is found to be of order of 10^{-5} , one can neglect the inertial force [10] and take into account only the Stokes drag force $F_{ST} = 6\pi\eta r v$ and electric force $F_E = -qE + 4\pi\epsilon_1 \text{Re}\{K(\epsilon_2^*, \epsilon_1^*)\} r^3 E \nabla E$. The balancing of these forces leads to the equation

$$q = \frac{1}{E} [4\pi\epsilon_1 r^3 E \text{Re}\{K(\epsilon_2^*, \epsilon_1^*)\} \nabla E - 6\pi\eta r v] \tag{6}$$

Taking the zeta potential to be equal to the surface potential, Coulomb's law gives

$$\zeta = \frac{q}{4\pi\epsilon_1 r} \tag{7}$$

where q is the charge on the particles. From Eqs. 6 and 7, the expression of zeta potential in terms of EP and DEP terms can be written as

$$\zeta = r^2 \text{Re}\{K(\epsilon_2^*, \epsilon_1^*)\} \nabla E - \frac{3\eta v}{2\epsilon_1 E} \tag{8}$$

Results and discussion

Figure 1 shows optical micrographs of the dispersed CNTs in the LC medium. In the absence of an external electric field, the CNT cluster inside the LC medium appears in the form of black spots. When we apply ac electric field, CNTs in LC medium move back and forth between the electrodes whereas in case of dc electric field, CNTs move towards the negative electrode and remain over there and if we change the polarity of the applied voltage, CNTs come back to their original position. For present CNTs-doped LC system, we have $r = 1.25 \times 10^{-6} \text{ m}$, $\eta = 19.3 \times 10^{-3} \text{ kg/m/s}$, $\epsilon_1 = 5.4 \times 10^{-11} \text{ F/m}$ at room temperature ($20 \text{ }^\circ\text{C}$). The experimentally observed velocity of the CNTs at the applied electric field of $0.5 \text{ V}/\mu\text{m}$ was found to be $26.1 \text{ }\mu\text{m/s}$. Since the dielectric permittivity of CNTs is far greater than the dielectric permittivity of LC [19], the value of $\text{Re}\{K(\epsilon_2^*, \epsilon_1^*)\}$ would be equal to one. To evaluate the gradient of applied electric field (∇E) in Eq. 8, the

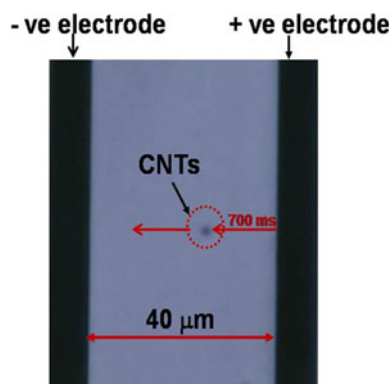


Fig. 1 Displacement of carbon nanotubes in liquid crystal medium after 700 ms of applied dc electric field of $0.5 \text{ V}/\mu\text{m}$

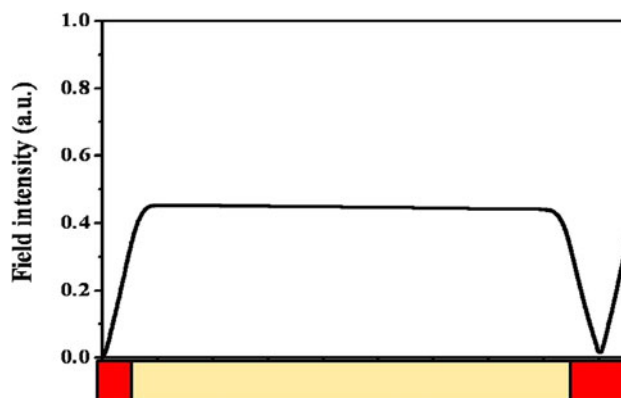


Fig. 2 Electric field pattern between electrodes in the in-plane switching cell

computer simulation of the electric field of $0.5 \text{ V}/\mu\text{m}$ has been performed and its spatial electric field distribution is shown in Fig. 2. As indicated in Fig. 2, the strong non-uniform electric field appears at the edge of the electrode. However, the electric field between the electrodes is almost constant. Therefore, the DEP force between the electrodes of the in-plane switching (IPS) cell is almost zero. However, at the edge of the electrodes, there is strong DEP force effect. As the motion of particle starts from the edge of the electrode itself, the strong DEP force impulse acting on the particle causes it to move to another electrode. The calculated gradient of the electric field (∇E) value at the edge of the electrode was $3.27 \times 10^{10} \text{ V/m}^2$. The value of zeta potential from Eq. 8 comes out to be 23.0 mV , whereas the charge on the CNTs using Eq. 6 comes out to be $+1.9 \times 10^{-17} \text{ C}$. There are positive charges present in the colloidal CNTs, as calculated above, this may be the reason for CNTs to move towards the negative electrode. According to the previous reports [24] on density functional calculations within local density approximation, the binding nature between the LC and CNTs is a hydrogen bonding rather than a simple van der Waals interaction due

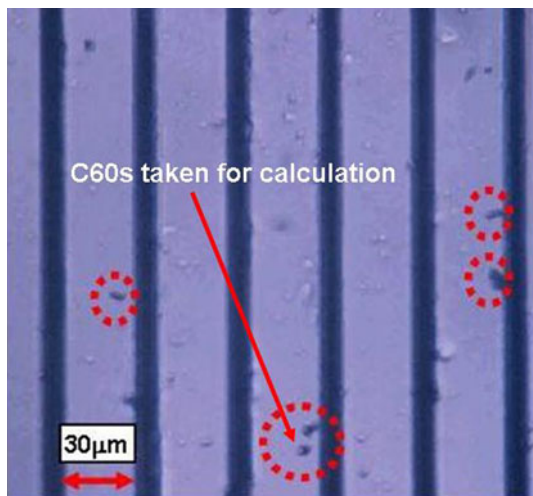


Fig. 3 Translations of C_{60} s between electrodes at a frequency of 1 Hz and electric field strength of $0.5 \text{ V}/\mu\text{m}$. Dislocation of C_{60} s after 250 ms of applied voltage

to the charge transfer from LC molecule to the CNT. As a result, the CNT has a net charge, which comes out to be positive from above calculation and the presence of net charge in the CNTs can also trap ions that are present in LC cells. This generates a permanent dipole moment in the CNTs, which originates from the asymmetric LC molecular anchoring on the CNTs surface causing the DEP force induced in the colloidal suspension.

Figure 3 shows optical micrograph of the fullerenes in the LC medium. In the absence of an external electric field, the C_{60} cluster inside the LC medium appears in a form of black domains. At low frequencies (1–5 Hz), C_{60} s translate between electrodes and migrate towards the positive electrode during the positive half cycle of the applied sine wave and bounce back in the next half cycle.

The experimentally observed velocity of the C_{60} s in LC medium at the applied electric field of $0.5 \text{ V}/\mu\text{m}$ was found to be $300.0 \mu\text{m}/\text{s}$ and its radius (r) was $2.23 \times 10^{-6} \text{ m}$ and the other parameters such as dielectric permittivity and flow viscosity of LC were the same as for CNTs-doped LCs. The value of $\text{Re}\{K(\epsilon_2^*, \epsilon_1^*)\}$ was equal to one [17]. We calculated the charge and zeta potential on the C_{60} s using Eqs. 6 and 8, respectively. The values of different parameters of CNTs- and C_{60} s-doped LC are given in Table 1 for comparison. Interestingly, the charge on the C_{60} s using Eq. 6 comes out to be $-2.4 \times 10^{-16} \text{ C}$, which is negative and the zeta potential on C_{60} s was found to be -160.9 mV . Because of negative charge on the C_{60} s, it moves to the positive electrode. Also, it is clear from Table 1 that there are 65 % of DEP and 35 % of EP forces acting in CNTs-doped LC colloidal suspension whereas in case of C_{60} s-doped LC, the DEP and EP forces were 33 and

Table 1 The values of different parameters of CNTs and C_{60} s-doped LC

Materials	DEP force (pN)	EP force (pN)	Zeta potential (mV)	Charge on the particles (C)
CNTs-doped LC	21.5	11.6	+23.0	$+1.9 \times 10^{-17}$
C_{60} s-doped LC	122.3	243.3	-160.9	-2.4×10^{-16}

67 %, respectively. It is noteworthy here that in our previously published paper [17], the zeta potential of C_{60} s was found to be very high perhaps due to DEP force acting on the colloidal particles. However, we could not estimate the exact contribution of DEP force. But, in this paper, we could estimate the zeta potential value by incorporating the DEP force, which comes out to be in reasonable range. Hence our suggestion regarding high value of zeta potential in earlier paper [17] seems quite reasonable.

Lazo and Lavrentovich [25] and Ryzhkova et al. [10, 26] have reported that the velocity of nano/micro-particles increases non-linearly with increasing electric field. The perpendicular component of the velocity has also been noted by Lazo and Lavrentovich [25]. At low frequency (1 Hz), the velocity of C_{60} s increases linearly with the third power of electric field strength as predicted by Ryzhkova et al. [10] (Fig. 4). At higher frequency (60 Hz), the C_{60} s stretch along the direction of electric field between the electrodes with increase in electric field. With further increase in electric field; they move perpendicular to the direction of the electric field. The stretching of C_{60} s at higher electric field is shown in Fig. 5 and the velocity of C_{60} s in perpendicular direction of applied electric field with increasing electric field is shown in Fig. 6. Initially, from 3.00 to $3.83 \text{ V}/\mu\text{m}$ of applied electric field, the velocity of C_{60} s was found in the range of $0.72\text{--}1.68 \mu\text{m}/\text{s}$. With further increase in the electric field, the velocity of C_{60} s increases gradually with increasing electric field. The velocity of C_{60} s was maximum at the applied electric field

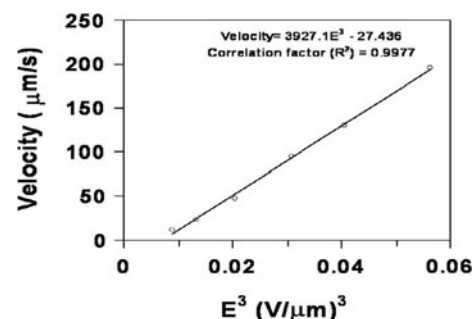


Fig. 4 Variation of velocity of C_{60} s in the LC medium at 1 Hz with the third power of the applied electric field

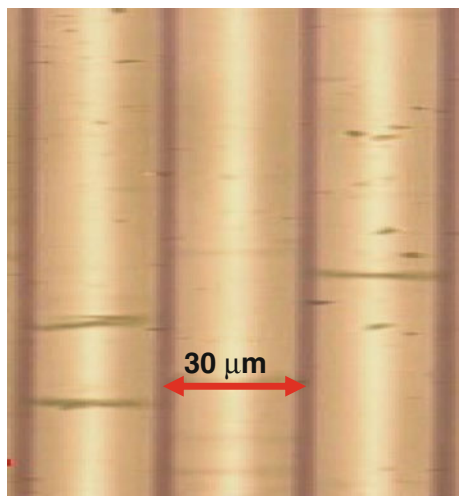


Fig. 5 The stretching of C_{60} s at the applied electric field of $3.33 \text{ V}/\mu\text{m}$. The horizontal black lines between the electrodes represent the stretching of C_{60} s in LC medium

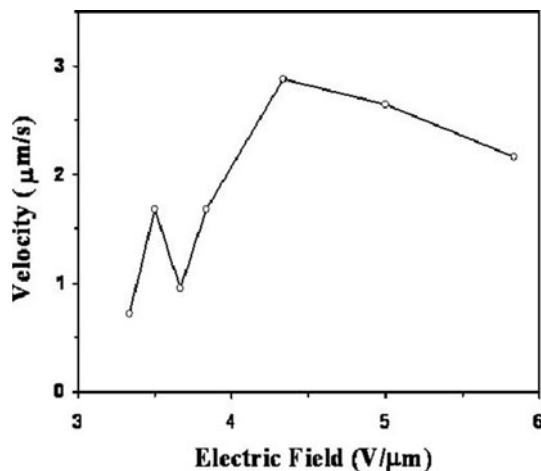


Fig. 6 Variation of velocity of C_{60} s in LC medium with varying electric fields at the applied frequency of 60 Hz. C_{60} s move perpendicular to the direction of applied electric field

of $4.33 \text{ V}/\mu\text{m}$ and afterwards it decreases gradually with increasing electric field. Above the electric field of $5.83 \text{ V}/\mu\text{m}$, no appreciable movement of C_{60} s was observed. According to Lazo and Lavrentovich [25], the velocity of the particle in the perpendicular direction of the applied electric field would be linearly proportional to the square of the applied electric field. However, in the present case it was not the same. The CNTs at higher electric fields are also observed to stretch along the direction of electric field. However with further increase in the electric field, the CNTs get dispersed into the LC host medium. The data for the stretching and subsequent dispersion of CNTs in LC medium have already been published by us in [18, 19].

Conclusions

The CNTs suspended in the LC medium moved towards the negative electrode whereas the fullerenes move towards positive electrode. Our theoretical model supports that there is positive charge induced in CNTs causing it to move towards the negative electrode whereas negative charges in fullerenes cause to move towards the positive electrodes. The contribution of DEP and EP forces was 65 and 35 %, respectively, for CNTs-doped LC, whereas in case of C_{60} s-doped LC, the DEP and EP forces were 33 and 67 %, respectively. At high frequency and field, both CNTs and C_{60} s stretch along the direction of the electric field. The CNTs at higher frequency and field get dispersed into the LC medium whereas C_{60} s start to move along the perpendicular direction of the applied electric field.

Acknowledgements This research was financially supported by the Department of Science and Technology, New Delhi, India under the scheme SERC Fast Track Young Scientist Project SR/FTP/PS-037/2011 entitled “Electrical and electrodynamic studies of carbon nanotubes dispersed in liquid crystal” at the Nanotechnology Application Centre, University of Allahabad, India. One of authors (SHL) would like to thank financial support funded by the Brain Korea 21 PLUS project.

References

- Mayer H (1997) Electrorotation of colloidal particles and cells depends on surface charge. *Biophys J* 73:1617–1626
- Baughman RH, Zakhidov AA, Heer WA (2002) Carbon nanotubes: the route toward applications. *Science* 297:787–792
- Kong J, Franklin NR, Zhou C, Chapline MG, Peng S, Cho K, Dai H (2000) Nanotube molecular wires as chemical sensors. *Science* 287:622–625
- Yu MF, Lourie O, Dyer MJ, Moloni K, Kelly TF, Ruoff RS (2000) Science strength and breaking mechanism of multiwalled carbon nanotubes under tensile load. *Science* 287:637–640
- Bert T, Smet HD, Beunis F, Neyts K (2006) Complete electrical and optical simulation of electronic paper. *Displays* 27:50–55
- Comiskey B, Albert JD, Yoshizawa H (1998) An electrophoretic ink for all-printed reflective electronic displays. *Nature* 394:253–255
- Fukuda J, Žumer S (2009) Confinement effect on the interaction between colloidal particles in a nematic liquid crystal: an analytical study. *Phys Rev E* 79:041703
- Fukuda J, Stark H, Yoneya M, Yokoyama H (2004) Interaction between two spherical particles in a nematic liquid crystal. *Phys Rev E* 69:041706
- Liao G, Smalyukh II, Kelly JR, Lavrentovich OD, Jakli A (2005) Electrorotation of colloidal particles in liquid crystals. *Phys Rev E* 72:031704
- Ryzhkova AV, Podgornov FV, Haase W (2010) Nonlinear electrophoretic motion of dielectric microparticles in nematic liquid crystals. *Appl Phys Lett* 96:151901
- Bert T, Smet HD (2003) The microscopic physics of electronic paper revealed. *Displays* 24:103–123
- Bert T, Smet HD (2003) Dielectrophoresis in electronic paper. *Displays* 24:223–250
- Lavrentovich OD, Lazo I, Pishnyak OP (2010) Nonlinear electrophoresis of dielectric and metal spheres in a nematic liquid crystal. *Nature* 467:947–950

14. Baik IS, Jeon SY, Jeong SJ, Lee SH, An KH, Jeong SH, Lee YH (2006) Local deformation of liquid crystal director induced by translational motion of carbon nanotubes under in-plane field. *J Appl Phys* 100:074306
15. Srivastava AK, Jeong SJ, Lee MH, Lee SH, Jeong SH, Lee YH (2007) Dielectrophoresis force driven dynamics of carbon nanotubes in liquid crystal medium. *J Appl Phys* 102:043503
16. Jeong SJ, Sureshkumar P, Jeong KU, Srivastava AK, Lee SH, Jeong SH, Lee YH, Lu R, Wu ST (2007) Unusual double four-lobe textures generated by the motion of carbon nanotubes in a nematic liquid crystal. *Opt Express* 15:11698–11705
17. Srivastava AK, Kim M, Kim SH, Kim MK, Lee K, Lee YH, Lee MH, Lee SH, Lee YH (2009) Dielectrophoretic and electrophoretic force analysis of colloidal fullerenes in a nematic liquid-crystal medium. *Phys Rev E* 80:051702
18. Jeong SJ, Park KA, Jeong SH, Jeong HJ, An KH, Nah CW, Pribat D, Lee SH, Lee YH (2007) Electroactive superelongation of carbon nanotube aggregates in liquid crystal medium. *Nano Lett* 7:2178–2182
19. Sureshkumar P, Srivastava AK, Jeong SJ, Kim M, Jo EM, Lee SH, Lee YH (2009) Anomalous electrokinetic dispersion of carbon nanotube clusters in liquid crystal under electric field. *J NanoSci Nanotechnol* 9:4741–4746
20. Baik IS, Lee JY, Jeon SY, An KH, Choi JW, Lee SH, Lee YH (2005) Electrical-field effect on carbon nanotubes in a twisted nematic liquid crystal cell. *Appl Phys Lett* 87:263110
21. Jeon SY, Park KA, Baik IS, Jeong SJ, Jeong SH, An KH, Lee SH, Lee YH (2007) Dynamic response of carbon nanotubes dispersed in nematic liquid crystal. *NANO* 2:41–49
22. Attard P, Antelmi D, Larson L (2000) Comparison of the zeta potential with the diffuse layer potential from charge titration. *Langmuir* 16:1542–1552
23. Jones TB (1984) Basic theory of dielectrophoresis and electro-rotation. *IEEE Eng Med Biol Mag* 22(6):33–42
24. Liu J, Rinzler AG, Dai H, Hafner JH, Bradley RK, Boul PJ, Lu A, Iverson T, Shelimov K, Huffman CB, Rodriguez-Macias F, Shon YS, Lee TR, Colbert DT, Smalley RE (1998) Fullerene pipes. *Science* 280:1253–1256
25. Lazo I, Lavrentovich OD (2013) Liquid-Crystal-enabled electrophoresis of spheres in a nematic medium with negative dielectric anisotropy. *Philos Trans R Soc A* 371:20120255
26. Ryzhkova AV, Podgornov FV, Gaebler A, Jakoby R, Haase W (2013) Measurements of the electrokinetic forces on dielectric microparticles in nematic liquid crystals using optical trapping. *J Appl Phys* 113:244902