Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Orientation Control of Liquid Crystals using Carbon-Nanotube-Magnetic Particle Hybrid Materials

Hyeon Su Jeong[a], Sang Cheon Youn[b], Yun Ho Kim[c], and Hee-Tae Jung[d,*]
[a] *Material R&D center, SK Innovation Global Technology, Daejeon 305-712, Korea*
[b] *R&D center, LG display, Paju 413-779, Korea*
[c] *Advanced Functional Materials Research Group, Korea Research Institute of Chemical Technology, Daejeon, Korea*
[d] *Department of Chemical and Biomolecular Eng. Korea Advanced Institute of Science and Technology, Daejeon 305-701 Korea*

Supplementary Information

Experimental methods

Preparation of materials and cell. The as-prepared SWNTs were heated at 365 °C for 90 min under an air atmosphere to remove any amorphous carbon and sonicated in hydrochloric acid for 60 min to remove the metal catalyst. After these purification steps, the clean nanotubes were cut by immersing them in a piranha solution (H_2SO_4/H_2O_2) 4:1 vol/vol %) for five hours at room temperature. A small amount of magnetic nanoparticles, such as iron or iron oxide, was then attached to the SWNT surfaces by means of thermal decomposition. The resulting Fe-oxide/SWNT samples were dispersed in N,N-dimethylformamide (DMF) (<100 mg/L) using ultrasonication for several hours. The solution was centrifuged for an hour at 12000 g to obtain well dispersed and separated SWNT solutions without flocculated SWNT particles, and the supernatant solution was collected. The concentration of the supernatant solution was determined to be ~6.37 mg/L by UV-Vis spectroscopy using the specific absorbance at 500 nm. The composites with various mass ratios up to 0.5 wt% of Fe-oxide/SWNT in 5CB were prepared by simply adding 5CB to the suspended Fe-Oxide/SWNT in DMF, followed by sonication for 60 min. After evaporating DMF in a vacuum oven at 80 °C for 12h, the composite was sonicated again for 60 min, above the Tiso of 5CB (40 °C) to further disperse Fe-oxide/SWNT in 5CB. The sandwich cell was prepared by assembling two clean pieces of glass. The cell thickness was controlled with a 10 μm microbead and a 100 μm PTFE gasket for planar and homeotropic alignment, respectively, followed by fixing them with a UV-curable prepolymer (NOA63, Norland Optical Adhesive 63). The cell was placed on a temperature-controlled hot stage (Mettler FP82HT) and subsequently heated to above the clearing temperature of 5CB to introduce the mixture of 5CB and Fe-oxide/SWNT s by capillary action.

Characterization. Transmission electron microscopy (TEM, JEOL Ltd, JEM-2100F) and Scanning electron microscopy (SEM, Sirion FE-SEM, NNFC in KAIST) was employed to characterize SWNTs modified with Fe-oxide and its alignment behavior under magnetic field. Polarized optical microscopy (POM, Nikon, LV-100POL) equipped with Bertrand lens was used to examine the alignment of 5CB by Fe-SWNT-assisted hybrid materials. Raman microscope (Horiba Jobin, LabRAM HR/UV/Nir) was used to detect the non-covalent interaction between SWNTs and LCs. In the case of detecting Fe-oxide/SWNTs alone, the Fe-oxide/SWNTs in DMF suspension was placed on a glass substrate and the DMF was evaporated. A droplet of 5CB was placed on a glass substrate and directly analyzed with no further treatment in the case of LC alone. For the mixture of 5CB and Fe-Oxide/SWNTs, the cell used for the POM experiment was directely used to detect the hybrid peak. Due to the distinctive overlapping of 5CB in the radial breathing mode (RBM) region, it is difficult to compare the Raman shift of RBM between SWNTs and SWNTs in the hybrid materials. To isolate the detection of the RBM in Fe-Oxide/SWNTs, a droplet of the mixture was applied to a 200 nm pore filter membrane (Anodisc 25, Whatman) and drawn slowly through the pores with a mild vacuum to remove excess LCsAll samples were mounted on an optical microscope (OM) stage, and positioned in the focus of an Ar ion laser operating at 514.5 nm.

Preparation of the samples for SEM experiments. The DMF solution containing Fe-oxide/SWNTs was deposited on an ITO glass substrate using the spraying method. We positioned a magnet behind the ITO substrate to apply a magnetic field to the samples. After evaporation of the SWNT solution in the presence of a magnetic field, we transferred the nanotubes to the vacuum evaporator chamber, which operates at a pressure of around 10^{-6} torr. The SWNT films were positioned between the evaporation source (holding material) and the poles of the magnets, such that the magnetic field vector and the electron-beam irradiation were mutually. We used titanium as an evaporating molecules required to hold the alignment of the SWNTs. When the magnetic field was applied from a magnet placed behind the ITO substrate, the SWNTs were observed to align perpendicularly to that substrate. Accordingly, the magnetic field was removed for the SEM measurements. Further SEM specimens for in-plane alignment of SWNTs were just prepared by spraying the Fe-oxide/SWNTs suspension on a silicon wafer with a magnetic field parallel, followed by evaporation of the solution in the presence of a magnetic field.

Supplementary Information

Figures

S1. Purification and cutting SWNTs

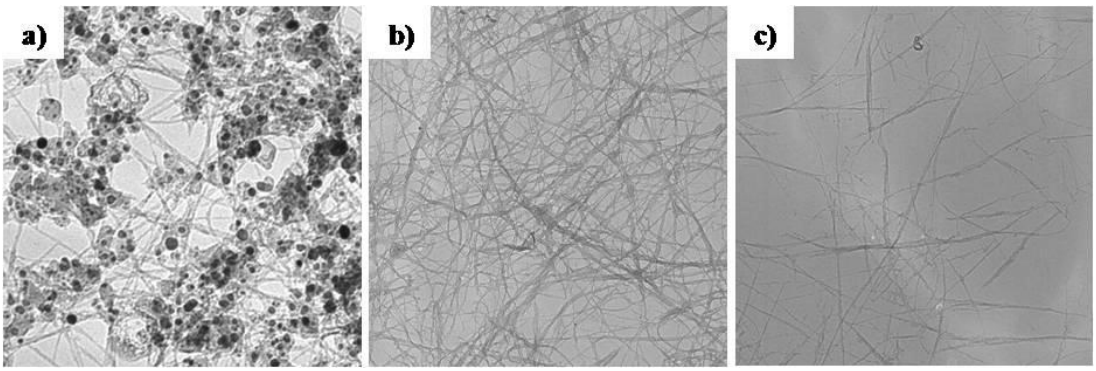

Figure S1. TEM images of (a) As prepared SWNTs, (b) purified SWCNTs, (c) cut SWCNTs.

These images clearly show SWCNTs were successfully purified and cut.

S2. Vertical alignment of 5CB with 0.001wt% of SWNTs under low magnetic filed (230 gauss

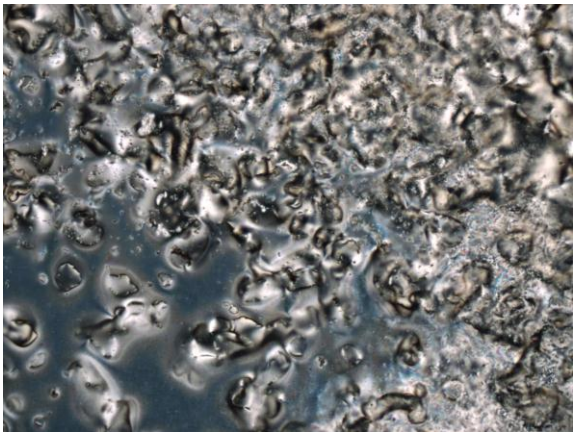

Figure S2. POM image of co-existence of homeotropic and planar texture of 5CB when a 100μm thickness cell was exposed to a 230 gauss magnetic field normal to the substrate

S3. Alignments of 5CB containing relatively large amount of SWNTs (0.05 wt%)

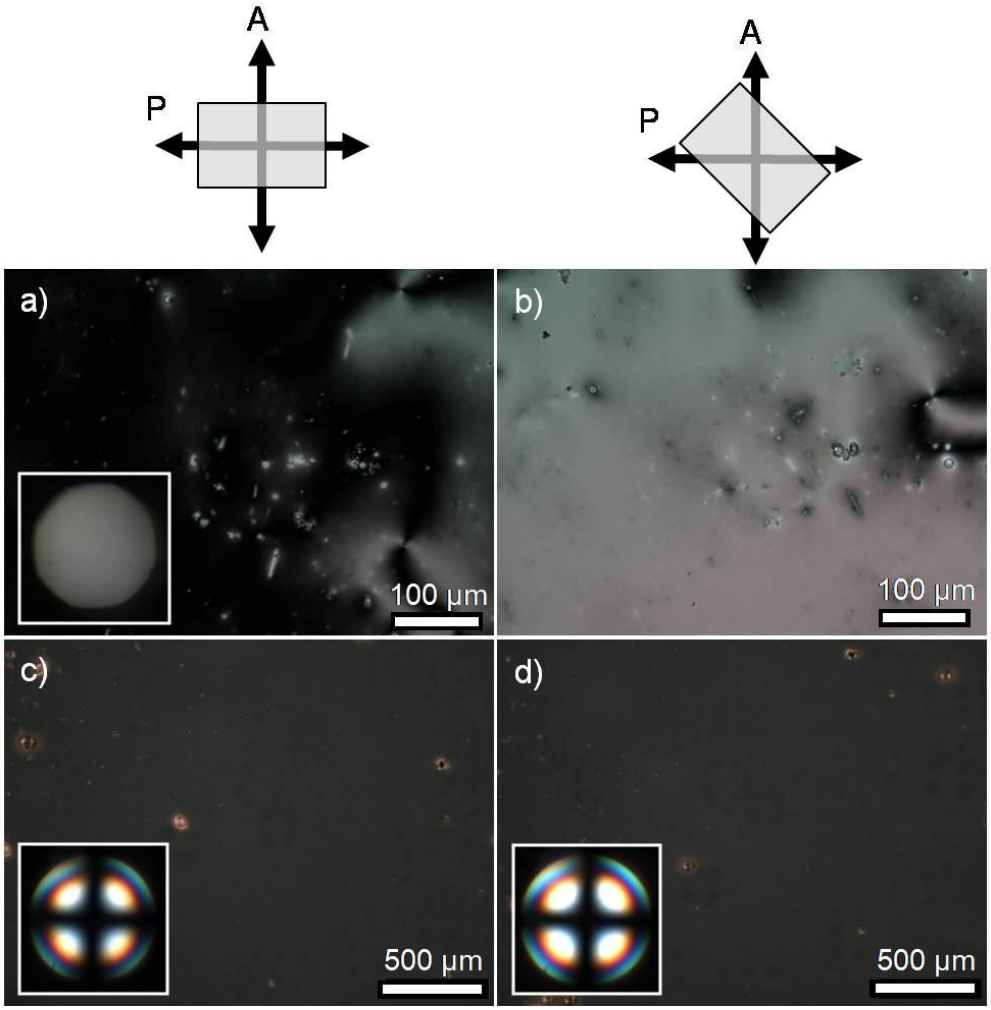

Figure S3. POM images of planar- (a, b) and homeotropic (c, d) alignment of 5CB by field-oriented SWNTs (0.05 wt%). The sample was rotated by 45° between crossed polarizers (b, d). Insets show Bertrand interference pattern for each corresponding alignments.

S4. Stability test upon repeated heating and cooling process without a magnetic field

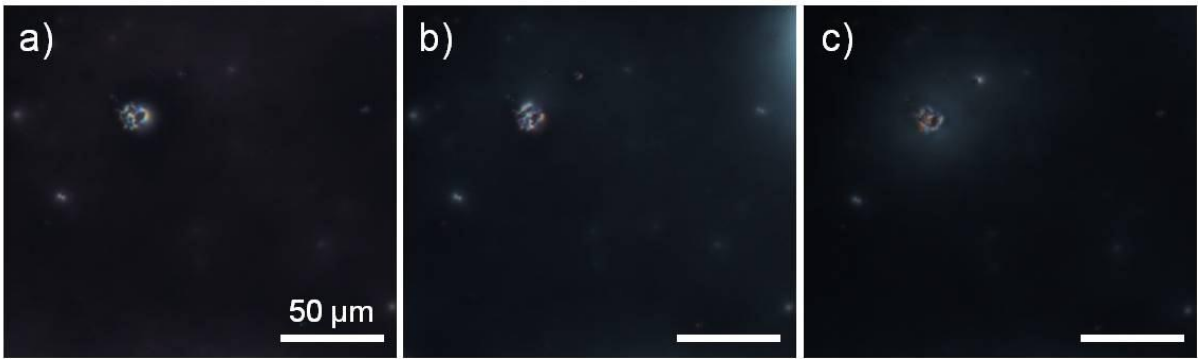

Figure S4. POM images of identical planar region (a-c) of 5CB. The sample was arrested above Tiso for 5 min and subsequently cooled to N phase: (a) 1st, (b) 2nd and (c) 3rd round of heating and cooling. All Images were taken under crossed polarizers. (All scale bar: 50µm)

S5. Stability test of homeotripcially aligned 5CB in the N phase without a magnetic field.

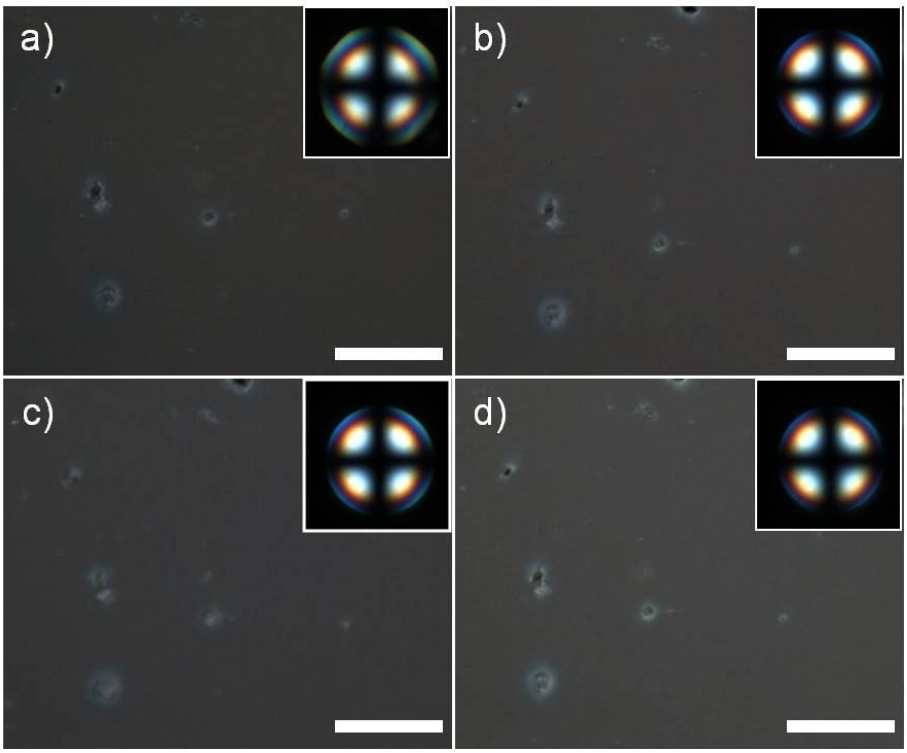

Figure S5. POM images of identical homeotropic region of 5CB containing 0.001 wt% SWNT upon arresting temperature in N phase for (a) 24 hours, (b) 48 hours, (c) 72 hours and (d) 96 hours. Insets show corresponding Bertrand interference pattern from identical region for 96 hours. Images were taken under crossed polarizers. (All scale bar: 200 μm)

S6. Collective behavior of 5CB cell driven by 0.05 wt% SWNTs

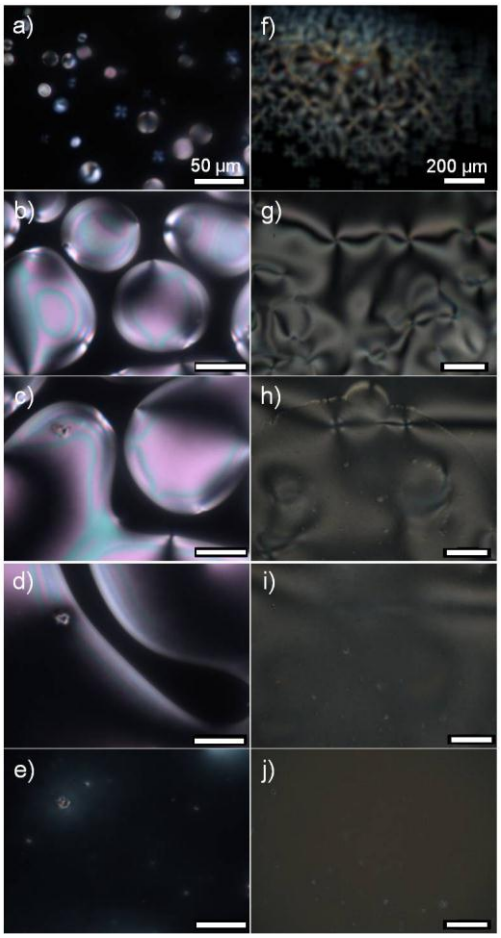

Figure S6. Close inspection on POM images of planar- (a-e) and homeotropically- (f-j) aligned 5CB cooled from T_{iso} to N phase at a rate of 0.01 °C/min. Images were taken under crossed polarizers right after initial domain formation was observed. No preferential orientation initially occurred (random orientation) in both planar (Figure S6a-e) and homeotropic (Figure S6f-j) cells. Over time, the LC molecules in the mesophase (N phase) start to align and appear dark in both planar and hoemeotropic cells, indicating macroscopic orientation.