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Supporting information

Preparation and optical properties of Fe3O4 nanoparticles doped blue phase liquid crystal composite

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1.Experimental Section

Preparation of Nanoparticles: Chemicals used in this work were commercially available from ACROS Company or from Beijing Chemical Product Factory, and used as supplied without further purification. In this paper, oleic acid (OA), 3-Methacryloxypropyltrimethoxysilane (KH570) and hexadecyl trimethoxy silane (HTS) modified Fe3O4 nanoparticles was prepared to research the effect of different modification methods on the dispersion in the LC matrixes. The surface modified route of the Fe3O4 nanoparticle were summarized as following.

Typical preparation process for oleic acid modified Fe3O4 nanoparticles through a chemical coprecipitation technique: FeCl3·6H2O (13 g, 48 mmol) and FeCl2·4H2O (4.8 g, 24 mmol) were dissolved in deionized water (200 mL) in the three necked flask with a magnetic stirrer under the protection of nitrogen. When heated to 80 °C, the solution was added by ammonia (25%–28%, 14 mL) and then slowly dropped with oleic acid (4 mL) under strong stirring conditions, followed by reaction for 2 h at 80 °C. The reaction mixture was cooled down to room temperature, and the resulting Fe3O4 nanoparticles were washed by deionized water three times under an external magnetic field. The magnetic nanoparticles were purified by dispersing in ethanol and centrifugation three times. Finally, the modified Fe3O4 nanoparticles were obtained by drying at 60 ^{o}C under vacuum conditions for 12 h.

Typical preparation process for silane coupling agent surface modified Fe3O4 nanoparticles: At first, Fe3O4 nanoparticles (0.5 g) and HTS (2.5 mL) were added in a mixture of ethanol (80 mL) and deionized water (20 mL). After subjecting the mixture to ultrasonic treatment for 30 min, acetic acid (about 20 mL) was dropped into the reaction mixture until the pH reached 4, and the solution was heated for 2 h at 80°C under strong stirring conditions. At the end, the modified Fe3O4 precipitant was separated with a magnet and was washed with ethanol three times in order to remove the excessive coupling agent. The resulting precipitant was dried at room temperature.

Preparation of the Fe3O4 doped LC composites: The BP-exhibiting LC material was a mixture comprising the following materials: R811 (10.0 wt%, Merck), ISO-C8OBA$_2$ (8.0 wt%, synthesized in our laboratory), SLC7011 (97.0 wt%, Yongsheng Huatsing Liquid Crystal Co., Ltd; birefringence: $\Delta n = 0.148$, dielectric anisotropy: $\Delta\varepsilon = 16.1$ at 298 K). The liquid-crystalline composites doped with different concentrations of Fe3O4 particle were prepared by dispersing it into the LC mixture.

Preparation of magnetic-driven LC display:

The 7~10 wt% modified nanoparticles (Fe3O4-OA or Fe3O4-HTS) was completely mixed with the BPLC maxtrix. The well-mixed BPLC mixture and nylon polymer network (grid distance about 200μm) were sandwiched and sealed between two glasses or flexible PET films by glue.

Measurements: The phase transition temperatures and the natural textures of BPI for the liquid-crystalline composites were achieved by using the thermal optical microscopy with a polarizing microscope (Olympus BX-51) equipped with a Linkam Scientific LTS 350 heating/freezing stage. The structure information of particle was characterized by Fourier transform (FTIR) spectra on Nicolet 510P FT-IR spectrometer and thermogravimetric analysis (TGA, Netzsch TG 209) conducted in a nitrogen atmosphere from ambient temperature to 700°C with a heating rate of 10°C/min. The particles were studied by scanning electron microscopy (SEM, Leicas 440I) and X-ray photoelectron spectroscopy (XPS) performed on vacuum-filtered films in a system equipped with a VG CLAMII electron analyser and PSP twinanode source. Optical transmittance was observed for a sample contained in the region between the comb-type interdigital electrodes under the crossed polarizers, as a function of applied AC rectangular voltage of 60 Hz. The voltage dependent transmittance (V-T) of doped BPLC composites was investigated in detail by incorporating in-plane electric field in the combtype interdigitated electrodes under the crossed polarizers. The LC samples were filled into the IPS cells with electrode width 5.0 μm, cell gap 10.0 μm and electrode gap 5.0 μm and placed at an inclination angle of 45° with respect to incident light. When the temperature of sample was controlled into BP temperature range with a hot stage calibrated to an accuracy of ± 0.1 ° C (Linkam LK-600PM), its E-O performance could be investigated using Tektronics AFG3011 C during the voltage-rising process and the decaying process. The response time for the rise process is defined as T-on, which is the time for the increase in the transmittance from the initial state to 90% of the saturated state. That for the decay process is defined as T-off, which is the time for the decrease in the transmittance from the initial state to 10% of the saturated state.

For the cell of polarizing microscope, when the Fe3O4 doped LC mixture was prepared and then sandwiched between two planar treated cells by capillary action, and the cell gap was maintained at 25 μm by spacer.

2. X-ray powder diffraction

From the X-ray powder diffraction patterns in **Figure S1**, the different peaks were found well indexed to the cubic structure of Fe3O4 (JCPDS card No. 19-0629), each peaks could be assigned to the (220), (311), (400), (422), (511) and (440) crystal planes. The results mean that these particles were Fe3O4 with spinel structure, and the crystal form of nanoparticles was not changed after surface modification. In addition, the diffraction peaks of the diffraction peak were sharp and no other obvious impurity crystal phase, which indicated that the modified Fe3O4 nanoparticles had pure crystal state.

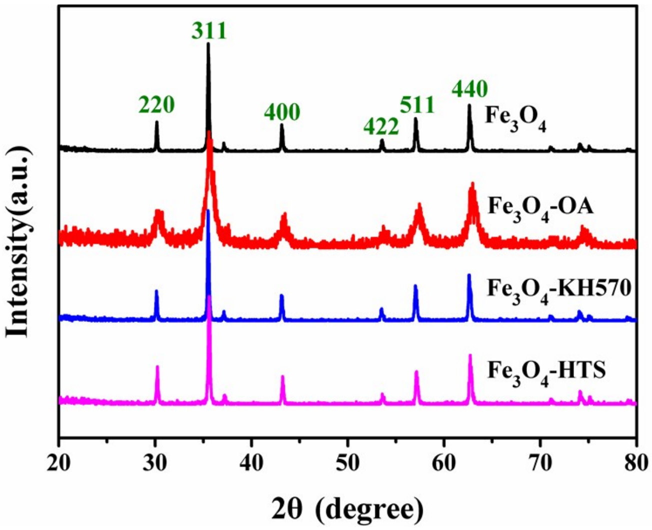

Figure S1. X-ray photoelectron spectroscopy spectra of Fe3O4 nanoparticles before and after modification

3. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was sensitive to the presence of contaminations such as water and hydrocarbons on the surface. Thus here XPS was used to investigate the change of the surface chemical bond and the information about the electronic structure on the surface of Fe3O4 nanoparticles before and after modification as shown in **Figure** S2 and **Figure** S3 with carbon (electron binding energy for 285.0 eV) for internal standard. It was found that the unmodified particle had only Fe and O peaks, while the OA modified had new obvious C peak. Additionally, not only the obvious C peak, but also weak Si peak (a characteristic element for coupling agent) appeared in the KH570 or HTS modified particles. Additionally, the electron binding energy of Fe2p3/2 of unmodified Fe3O4 increased from 710.9 eV to 712.0 eV after modified, which was because the electro-negativity of Si atom was stronger than that of H atom, which made the shielding effect of around Fe decrease and the binding energy of Fe2p3/2 thus increased. And this change can prove the deduction that Fe-O-Si chemical bond between Fe3O4 nanoparticles and KH570 or HTS were formed instead of the chemical bond Fe-O-H. On the other hand, the electron binding energy of Fe2p3/2 in OA modified particles increased from 710.9 eV to 711.9 eV, which may be due to the formation of hydrogen bond between the carboxylic acid and the hydroxyl groups on the particles. The binding energy of O1s unmodified was 530.0 eV of peak, but it increased to 531.0 eV after modified. This may be explained by the deduction that there is Fe-O-Si chemical bond between KH570 (or HTS) and Fe3O4 nanoparticles. The electro-negativity of Si was stronger than that of atom H, which made the shielding effect of around O atom decrease and thus the binding energy of O increased. From above analysis, oleic acid modified the nanoparticle by physical bond , while the silane coupling agent modified the nanoparticles by chemical bond.

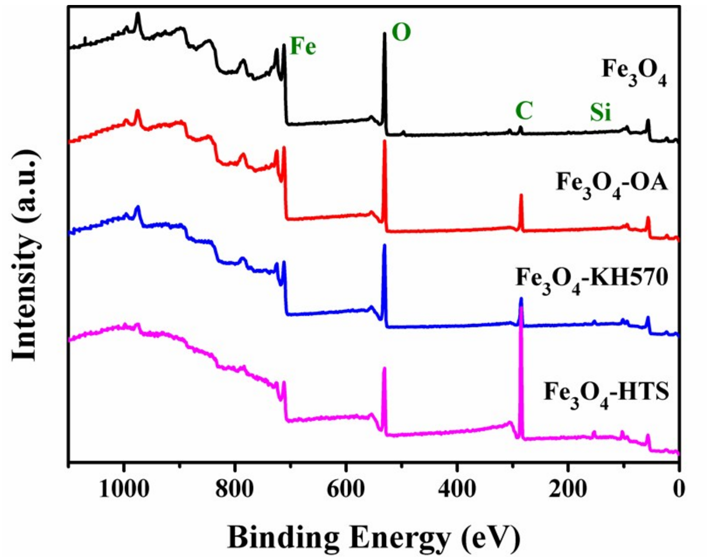

Figure S2. The X-ray powder diffraction curve of Fe3O4 nanoparticles before and after modification

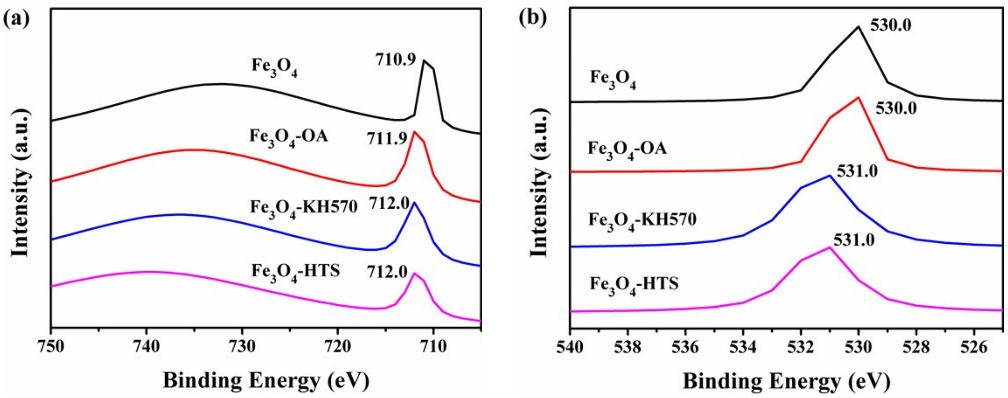

Figure S3. X-ray photoelectron spectroscopy spectra of Fe3O4 nanoparticles before and after modification: (a) electron binding energy of $Fe_{2p3/2}$; (b) electron binding energy of O_{1s}

Table S1. The BP range of the BPLCs doped with Fe3O4-HTS

BPLC (wt%)[a]	Fe3O4-HTS (wt%)	N*-BP (°C)	BP-I (°C)	ΔT(°C)
100	0	38.1	45.0	6.9
99.9	0.1	37.0	45.0	8.0
99.7	0.3	37.0	45.1	8.1
99.5	0.5	36.8	45.0	8.2
99.3	0.7	36.5	45.2	8.7
99.0	1.0	36.9	45.1	8.2
98.5	1.5	36.8	44.7	7.9
97.0	3.0	36.1	43.8	7.7

a) BPLC: 82.0 wt%SLC-7011, 10.0 wt% R81 and 8.0 wt% Iso-(8OBA)2.