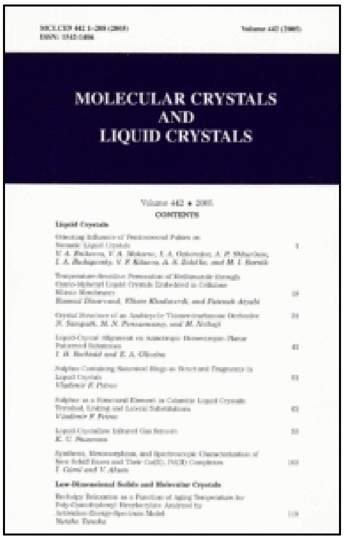

Molecular Crystals and Liquid Crystals

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Nanocomposites Consisting of Gold Nanorods and Nematic Liquid Crystals: Optical Properties

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Composites consisting of nematic liquid crystal and gold nanorods have been elaborated and investigated with a polarizing microscope. It was detected, that the nanorods form inside the oriented liquid crystal matrix their own self-assembling well-ordered structures. Nanorods ordered structures appear as a result of aligning layers action and provide defects corresponding to spatial distortion of the nematic liquid crystal director field. The defects have elongated stick-like shape with long axis perpendicular to liquid crystal director. Their size, orientation and ordering depend on the technology of the cell surface treatment, on the cell filling conditions and on the nature of liquid crystal matrix.

Keywords Gold nanorods; liquid crystals; nanocomposites; self-assembling structures

Introduction

Nanoscience is the exploration of materials on nanometer length scales. These new materials will lay the foundations for a whole set of technological developments which are commonly termed nanotechnology, and that have in common the use and manipulation of objects with at least one dimension in nanometer size range (typically 1–100 nm). The aim is generally preparation of various kinds of nanoparticles of controlled composition, shape and size, so that the influence of particle radius on the physical, chemical, optical and electro-optical properties of the material can be studied and used for the elaboration of composite materials with new features. To date the most widely studied nanoparticles have been those made of metals, semiconductors and magnetic materials. Once size control and monodispersity have been reasonably achieved, the next level of sophistication is shape control, i.e., synthesis of non-spherical nanoparticles where not only the size, but also other topological aspects can be controlled through judicious choice of experimental

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conditions and additives. For example, materials may be fashioned as rods, tubes or concentric core-shell structures [1].

A new direction in nanoparticles study gave their insertion in a liquid crystal matrix as a new non-synthetic method for modification of existing liquid crystals properties. Today it is a top of scientific interest and a huge amount of papers are dedicated to this subject. Here we mentioned just few of them, where nonoparticles constitute carbon nanotubes, metallic spheres and ferroelectric nanoparticles [2–8]. In the present paper the new results concerning the introduction of gold nanorods in nematic liquid crystal matrixes are reported.

Experiment

Hydrosols of gold nanorods were synthesized according to the methods presented in [9,10]. The nanorods had hemispherical ended cylinders shape. Average nanoparticle length was about 70–100 nm and thickness about 15–20 nm. The particles concentration in hydrosols was not less than 10^{11} particles/ml. There were used two types of nanorods suspension:

1. CTAB coated nanorods dispersed in water (Fig. 1a);
2. PEG functionalized nanorods dispersed in ethanol (Fig. 1b).

The substitution of the surfactant CTAB with mPEG-SH was done according to the following procedure [9]:

Gold Nanorod PEGylation. Thiol-terminated methoxypoly-(ethylene glycol) (mPEG-SH) was purchased from Nektar Therapeutics (2M4E0H01). The raw nanorod solution was centrifuged at 7000 g for 20 min to pellet the nanorods, decanted, and then re-suspended to 1 ml of DI water to reduce the CTAB concentration to 10 mM. 100 μl of 2 mM water solution of potassium carbonate and 10 μl of 1 mM mPEG-SH were added to nanorod solution. The mixture sat overnight at room

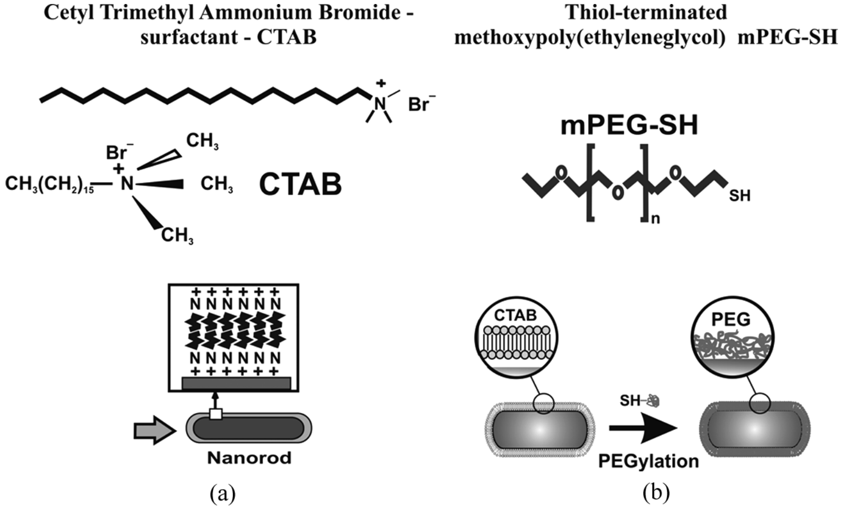


Figure 1. Gold nanorods are surrounded by: (a) CTAB as surfactant; and (b) mPEG-SH as ligand.

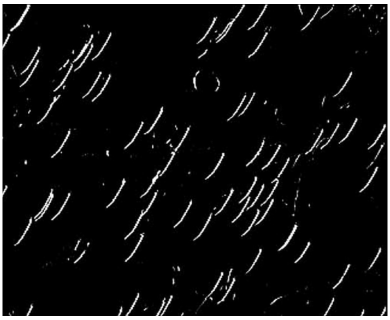


Figure 2. Microphoto of nano-composite layer (NC-1, LC matrix is 5-CB, surfactant CTAB) in the cell with the thickness 1.8 μm treated for planar alignment of the liquid crystal. The cell was filled by capillary method at the temperature higher than the clearing point. The photo was done between crossed polarizers at room temperature. The size is 500 μm × 400 μm.

temperature, then was centrifuged, decanted, re-suspended before in DI water several times to remove excess of CTAB and mPEG-SH, and finally re-suspended in ethanol.

The gold nanorods were inserted in liquid crystalline (LC) matrices in very small amount (0.02% v/v).

In order to obtain the composites based on gold nanorods and nematic LC, LC was dissolved in ethanol, after this, water (or alcohol) suspension of nanoparticles covered by appropriate surfactant (or ligand) was added, and then the solvents were removed in vacuum. The obtained nanocomposites (NC) were treated by ultrasound before the insertion in the cell. Three types of nanocomposites were elaborated with different LC matrices: NC-1 and NC-4 with 5-CB, NC-2 with ZhK-1289 (mixture, mainly contains different cyanobiphenyls) and NC-3 with ZhK-805 (mixture of alkyl-substituted cyclohexane carboxylic acids).

Two types of nanocomposites were done according to the surfactant (or ligand): NC-1, NC-2, NC-3 with CTAB and NC-4 with mPEG-SH.

The optical properties of **NC** were observed by a polarizing microscope. The results obtained are shown in the Figures 2–7.

Figure 3. Microphoto of NC-1 droplet squeezed between two glasses without any aligning layers, made with crossed polarizers at room temperature. The size is 500 μm × 400 μm.

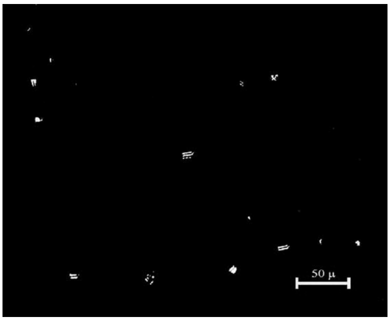


Figure 4. Microphoto of nano-composite layer (NC-1, LC matrix is 5-CB, surfactant CTAB) in the cell with the liquid crystal layer thickness 1.8 μm treated for homeotropic alignment by chromolane. The cell was filled by capillary method at the temperature higher than the clearing point. Photo was done between crossed polarizers at room temperature.

Figure 5. Microphoto of nano-composite layer (NC-2, LC matrix is ZhK1289, surfactant CTAB) in the cell with the liquid crystal layer thickness 1.8 μm treated for planar alignment. Cell was filled by capillary method at the temperature higher than the clearing point. Photo was done between crossed polarizers at room temperature. The size is 500 μm × 400 μm.

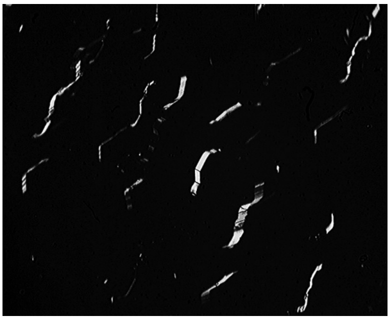


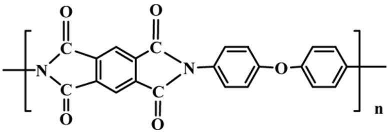
Figure 6. Microphoto of nano-composite layer (NC-3, LC matrix is ZhK805, surfactant CTAB) in the cell with the thickness 1.8 μm treated for planar orientation. The cell was filled by capillary method at the temperature higher than the clearing point. Photo was done between crossed polarizers at room temperature. The size is 500 μm × 400 μm.

Figure 7. Microphoto of nano-composite layer (NC-4, LC matrix is 5-CB, ligand – mPEG-SH). All other conditions are the same as in the Figure 2.

Results and Discussion

In the present work we investigated an influence of the insertion of very small amount of gold nanorods in LC matrix. We observed, that gold nanorods form inside the ordered structure of liquid crystal different self-assembling well-ordered structures (defects) corresponding to spatial distortion of the LC director field (see Figs. 2–7). The size of these defects is much bigger than the size of the particles themselves and varies from few to hundred micrometers. It is necessary to underline, that the size, the shape, the orientation and the ordering of the defects depend on many reasons, namely: on the technology of cell surface treatment, on the thickness of nanocomposite (NC) layer, on the cell filling conditions, on the nature of LC matrix and surfactant. It was shown, that the orientation of the LC principal optical axis (LC director) and the self-assembling ordered nanorod structures long axis are match together. On the other hand, the LC and defects principal optical axis never match together, what can be explained due to the difference in-between the surface tension of LC and of gold nanorods covered by surfactant: the surfactant surface tension is considerably less than the surface tension of liquid crystals. The appearance of some defects due to the insertion of nanoparticles in LC matrix under permanent electric field was mentioned in [7].

The most ordered defects were observed in the cells treated for planar alignment, where the liquid crystal layer thickness is 1.8 μm. Asymmetric boundary conditions were used for manufacturing of the cells. In this approach only one indium tin oxide (ITO) surface of LC cells was covered with the polyimide PMDA-ODA having a structure of repeating pyromellitic dianhydride (PMDA) and 4,4′-oxidianiline (ODA) units, shown below,



while another one was simply washed in *N,N*-dimethyl formamide (DMF) and covered by 1.8 μm calibrated spacers. The polyimide was deposited on ITO surface by spin-coating of a diluted solution of polyamide acid based on PMDA and ODA in dimethylformamide with subsequent drying and thermal imidization under conventional conditions and then the PMDA-ODA surface was rubbed with a piece of lawn to provide an anisotropy of the surface free energy that is necessary for the LC alignment.

The concentration of nanorods in NC (NC-1, where the LC matrix is 5-CB, the surfactant – CTAB) is 0.02% v/v, (see Fig. 1) and the insertion of NC in the cell was done at a temperature higher than transition of LC from nematic to isotropic phase. At these conditions the defects have elongated stick-like shape, forming well-ordered regular planar structures, which are perpendicular to the LC director (see Fig. 2).

It is possible to understand the importance of the boundary conditions influence on the defects formation and ordering comparing Figures 2, 3 and 4. There is no any preferable direction of the principal optical axis of planar defects in a cell without any aligning layers (Fig. 3), while the liquid crystal itself is aligned homeotropically.

The same NC-1 inserted in the homeotropically aligned cell at the same conditions shows completely different results – homeotropic alignment of both LC and defects (see Fig. 4).

It is known [11] that for nematic liquid crystals the type of the principle axes alignment in electro-optical cells (planar or homeotropic) is determined by the difference $\Delta\gamma$ in the surface free energy of the liquid crystal γ_{LC} and the aligning layer γ_S:

$$\Delta\gamma = \gamma_{LC} - \gamma_S \tag{1}$$

An energy criterion for the formation of a specified alignment type of the nematic LC principal axes is recorded in the form [11]:

$$\begin{aligned} &\Delta\gamma < 0 - \text{planar alignment} \\ &\Delta\gamma > 0 - \text{homeotropic alignment.} \end{aligned} \qquad (2).$$

In our experiments the type of the principle axes alignment both LC and defects generally satisfied condition (2). In fact, typically for liquid crystals $\gamma_{LC} = 35 - 45\,\mathrm{mJ/m^2}$ [12–14], PMDA-ODA aligning layers are characterized by $\gamma_S = 65\,\mathrm{mJ/m^2}$, ITO surface – $\gamma_S = 75\,\mathrm{mJ/m^2}$ [14], therefore planar alignment of LC and defects in Figure 2 evidently corresponds to the case $\Delta\gamma < 0$. On the other hand the surface free energy of chromolane aligning layer used for homeotropic alignment $\gamma_S = 33\,\mathrm{mJ/m^2}$; as a result, homeotropic alignment of the LC and defects occurs in this case (see Fig. 4) under condition $\Delta\gamma > 0$.

The influence of the LC matrix on the structure of the defects is evidently demonstrated by the comparison of Figure 1 with Figures 5 and 6.

The presence of the surfactant or ligand is important as well. Substituting the surfactant CTAB by ligand mPEG-SH we can see the difference in the defect formation (compare Figs. 2 and 7).

A possible explanation of the defects formation is the following: the filling of the cell by capillary method orients nanorods and main amount of NLC matrix in planar. The surfactant of the nanorod anchors with the aligning layer of the cell. The surfactant locally orients the NLC matrix perpendicular to the surface of nanorod during the transition from isotropic liquid to nematic phase. This local orientation is schematically shown on the Figure 8. This hypothesis is in a good agreement with the experimental data, i.e., dramatically change in the case of homeotropic orientation, the influence of the NLC matrixes nature and the substitution of the surfactant CTAB by ligand m-PEG-SH as well.

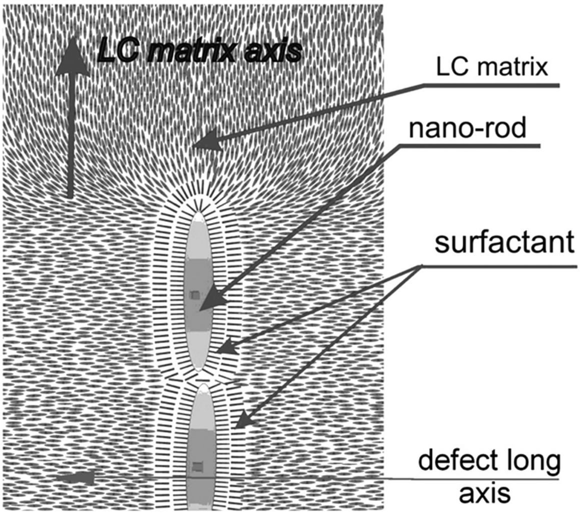


Figure 8. Schematical explanation of the defect formation.

Thus, we propose, that the origin of the defects appearance is the formations of nano-clusters. Such nano-clusters are the cores of the defects and consist of the surfactant surrounded nano-rods with the nearest NLC molecules oriented by surfactant. These nano-clusters anchored to the aligning layers and are considerably smaller than the defects themselves. The clearing point of the defects in NC-1 is at least 2–3 degree higher, than the clearing point of 5-CB itself (35°C). The position and the size of the defects in NC-1 do not change at the heating process till the clearing point (37–38°C). Moreover, the nano-clusters disappear only at the temperature, higher than 75°C. It demonstrates that the nano-clusters are sufficiently more thermally stable then the NLC matrix.

Conclusions

In the present work nanocomposites consisting of nematic liquid crystals (NLC) and gold nanorods were obtained. We observed, that gold nanorods form different self-assembling well-ordered structures (defects) inside the oriented liquid crystal matrix. These defects correspond to spatial distortions of the NLC director field.

The size, the shape, the alignment and the ordering of the defects depend on many reasons and are very sensitive to any change of the experimental conditions.

The NLC director alignment (coincident with the main optical axis) and the self-assembling well-ordered structures axis never match together (in the main cases they are perpendicular to each other), what can be explained due to the difference in-between the surface tension of LC and of the gold nanorods covered by surfactant, taking into account the long-range order interaction inside this system.

Acknowledgments

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References

[1] Xia, Y., & Halas, N. J. (2005). *MRS Bulletin.*, *30*, 338.

[2] Shiraishi, Y., Maeda, K., Yoshikawa, H., Xu, J., Toshima, N., & Kobayashi, S. (2002). *Appl. Phys. Lett.*, *81*(15), 2845.

[3] Reznikov, Y., Buchnev, O., Tereshchenko, O., Reshetnyak, V., Glushchenko, A., & West, J. (2003). *Appl. Phys. Lett.*, *82*(12), 1917.

[4] Kobayashi, S., Miyama, T., Nishida, N., Sakai, Y., Shiraki, H., Shiraishi, Y., & Toshima, N. (2006). *J. Disp. Technol.*, *2*, 121.

[5] Kundu, S., Akimoto, M., Hirayama, I., Jnoue, M., Kobayashi, S., & Takatoh, K. (2008). *Jpn. J. Appl. Phys.*, *47*, 4751.

[6] Scolari, L., Gauza, S., Xianyu, H., Zhai, L., Eskildsen, L., Alkeskjold, T. T., Wu, S. T., & Bjarklev, A. (2009). *Opt. Express*, *17*, 3754.

[7] Trashkeev, S. I., Grachev, G. N., & Posdnjakov, G. A. (2007). *J. Techn. Phys. (Russian)*, *77*(9), 85.

[8] Qi, H., Kinkead, B., & Hegmann, T. (2008). *Adv. Funct. Mater.*, *18*(2), NA.

[9] Liao, H., & Hafner, J. H. (2005). *Chem. Mater.*, *17*, 4636.

[10] Nikoobakht, B., & El-Sayed, M. A. (2003). *Chem. Mater.*, *15*, 1957.

[11] Kreagh, L. T., & Kmets, A. R. (1973). *Mol. Cryst. Liq. Cryst.*, *24*, 59.

[12] Shuring, H., Thieme, C., & Stannarius, R. (2001). *Liquid Crystals*, *28*(2), 241.

[13] Haller, I. (1974). *Appl. Phys. Lett.*, *24*, 349.

[14] Zhukov, A. A., Pozhidaev, E. P., Bakulin, A. A., & Babaevski, P. G. (2006). *Crystallography Reports*, *51*(4), 680.