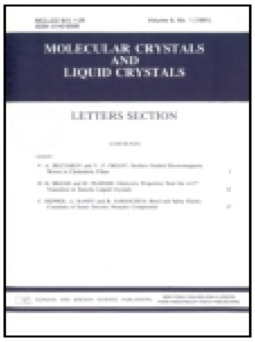

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Self-organisation processes and phase-structural states in hybrid metal-mesogenic nanosystems

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ABSTRACT

Hybrid nanosystems including silver and copper and long-chain mesogenic derivatives of alkylcyanobiphenyls have been obtained by low temperature vacuum co-condensation of reagent vapors on cooled surfaces of quartz, KBr, CaF_2 or polished copper under molecular beam conditions. Controlled thermal treatment of the samples allowed the directed formation of metal nanoparticles of definite size from 2 up to 100 nm. It was shown that manner of temperature treatment and molecular self-organisation of different liquid crystalline phases controlling of the size and morphology of nanoparticles and their aggregates formed in the system. Transmission electron microscopy (TEM) and atomic force microscopy (AFM) data of the samples show the formation of orientationally ordered structures in nematic mesophases. Formation of flat 2D-aggregates has been found in layered smectic mesophases Optical absorbance spectra of silver/4-pentyl-4-cyanobiphenyl (Ag/5CB) and copper/4-pentyl-4-cyanobiphenyl (Cu/5CB) samples encapsulated in polymer poly-para-xylylene at 300 K contain characteristic bands of plasmonic absorbance of metal nanoparticles at 420–440 nm and 560–600 nm. Rising of metal concentration in the sample led to the performable growth of rod-like metal particles with anisometric ratio $l/d>20$ and intensive absorbance at higher wavelengths ($\lambda \geq 650$ nm)

KEYWORDS
hybrid metal-mesogenic nanosystems; metal nanoparticles; low temperature deposition; optical properties

1. Introduction

Hybrid nanosystems, including nanosized metal particles stabilised in functionalized organic matrices possess rising interest of the researchers of different areas due to their highly promising applications in nanoelectronics, photonics and sensor systems [1–5]. The use of mesogenic compounds in different liquid crystalline states as soft ordered template matrices opens new possibilities for synthesis of anisotropic metal particles and their highly ordered assemblies. Introducing of metal atoms and ions in liquid crystalline systems significantly extended the possible areas of their exploitation. The most prospective are hybrid metal-mesogenic nanosystems, combining molecular ordering of mesogenic matrix compounds and quantum-size properties of nanometals, which are differed both from the characteristics of the single atoms and from the properties of bulk materials. The properties of such systems are dependent not only of the size and shape of individual nanoparticles formed the system, but also of the character of their joint organization and formation of the hybrid ordered structure. [6,7].

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Among different methods of metal particles incorporation into the organic systems and formation of hybrid nanosystems the most original and useful are methods of low temperature condensation of metal atoms with the molecular beam of organic component's vapors under high vacuum conditions [8,9]. The use of low temperatures and technique of vacuum condensation of metal atoms and organic molecular beams on the cooled support surfaces allowed researchers to stabilize and study such highly active species as metal clusters and nanoparticles, and their labile complexes. This approach allowed us to realize the formation of hybrid nanosystems by bottom up method and to carry out the directed metal atom and small clusters aggregation, controlled by structural and dynamic properties of molecular organized matrices, and also to create new ordered assemblies of nanoparticles.

In this work the formation of new hybrid metal-mesogenic nanosystems has been made on the example of two d-metals of the 11 group – silver and copper with mesogenic derivatives of alkyl cyanobiphenyls. Nanoparticles of silver and copper possess the intensive plasmonic bands in visible region of spectrum and can be used for visualization and marking of different biological objects. Mesogenic compounds of alkylcyanobiphenyl row are widely used nowadays as components of active layers for liquid crystalline displays and indicators. These compounds form ordered liquid crystalline phases of two types – nematic, characterized by the existence of molecular orientations long range order and smectic – with layered molecular ordering. The existence of molecular associates and formation of dimeric structures in solid and liquid crystalline phases is known for these compounds at low temperatures. They form several methastable and stable solid phases with local structure similar to the liquid crystalline mesophases with different molecular organization [10–11]. Terminal cyanogroup and aromatic core of the molecules can be considered as ligands suitable to formation of complexes of π- and σ-types with atoms and clusters of the metals under consideration [12].

Controlled formation of anisometric nanoparticles and ordered hybrid nanostructures is one of the main objectives of this work. The role and mutual influence of self-organization processes of metal species and organic component's molecules is considered. The phase-structural transitions and physico-chemical properties that appear for new hybrid metal-mesogenic nanosystems were demonstrated on the example of combination of silver and copper metal nanoparticles formed in mesogenic matrices of long chain ($n \geq 5$) alkyl-cyanobiphenyls 4-pentyl-4-cyanobiphenyl (5CB) and 4-octyl-4-cyanobiphenyl (8CB).

2. Experimental methods

Metal-containing film samples of $l = 20–50\ \mu m$ in thick were obtained by reagent's vapor co-condensation on the cooled surfaces of special spectral cryostats under molecular beam conditions. Cryochemical methods, i.e. low temperature joint and layer-by-layer vapor deposition and co-deposition [13–14], allow researchers to introduce metal atoms and clusters directly in the interaction with organic or inorganic compounds by low temperature co-condensation of component's vapors. In this case we can introduce metal atoms and small clusters directly into the mesogenic matrix and obtain hybrid metal-mesogenic nanosystem at atomic-molecular level. The metal/ligand ratio was controlled with the aim of special calibration procedure of the evaporation cells and varied from 1:1 to 1:100, metal contents in the sample was determined by photometric analysis and via ICP – mass-spectrometry technique. The atomic/molecular beams were obtained by the resistive heating of the individual components evaporators at 10^{-5} Torr vacuum conditions. The rates of reagent's flow were varied in the range $10^{14} - 10^{16}$ molecules/s.cm^2, the width of film samples were varies from 2 up to 100 μm Formation of metal nanoparticles were recorded by UV-Vis spectroscopy (Specord

M-40, Germany, and Mini2000, Ocean Optics, USA) and ESR technique (ESR-spectrometer Bruker EMX 500 with standard cryogenic cells and ESR-spectrometer Rubin with modified electronic scheme and cryogenic module available for the experiments under vacuum conditions under steady state and flow conditions).

The compopsition, structure and morphology of nanopaticles and nanostructured films obtained were studied by transmission electron microscopy (TEM), X-ray diffraction (Rigaku D/MAX-2600) and atomic force microscopy (AFM). Electronic micropictures and electronic difractogrammes of the samples were recorded by electron microscope LEO 912 AB (Zeiss). AFM studies of film samples were made at Nanoscope III (University of Potsdam) and experimental set up Solver Nano (NT MDT). Phase behaviour of the hybrid systems was studied by method of polythermal polarisation microscopy (Olympus BX41) with heating unit THM S600 and by method of thermal analysis at laboratory DTA set up and scanning thermpanalysator Netzch STA 449C.

3. Results and discussion

Possibilities of formation and stabilisation of anisometric nanoparticles of different size and shape and stable or metastable ordered stuctures including nanoparticles using mesogenic alkylcyanobiphenyl matrices with different molecular organisation can be realized during cryoformation of hybrid metal mesogenic nanosystems. The composition, morphology and stuctural characteristics were studied for nanoparticles and nanostructures formed in hybrid metal-mesogenic nanosystems including nanometals (silver and copper) and mesogenic alkylcyanobiphenyl compounds (5CB, 8CB), which possess several solid and liquid crystalline phases with different molecular organisation. The samples were obtained by joint and layer-by layer condensation of the components vapors under molecualr beam conditions followed by the controlled annealing of the samples with different heating and cooling rates [15 – 16]. The samples with different thermal prehistory and formed in different phase states of the system were studied and the process4es of self-organisation of the hybrid system as a whole were analysed in details.

3.1. Morphology of silver and copper nanoparticles, formed in cyanobiphenyl mesogenic matrices at low temperatures

Transmission electron microscopy (TEM) study of the film samples of hybrid nanosystems «silver-4-pentyl-4-cyanobiphenyl» (Ag/5CB) and «copper-4-pentyl-4-cyanobiphenyl» (Cu/5CB), obtained by low temperature co-deposition of components and annealing at 150–200 K during 1–2 hours, show the possibility of formation and stabilisation of mesogenic matrix of 5CB practically monodispersed sperical metal nanoparticles of 1 – 2 nm in size (Figure 1). These metal species were formed in the solid nanostructured matrix of 5CB as the result of thermal decomposition of unstable dimeric biligand π-complexes of metal atoms $M(5CB)_2$ [15]. The metal atoms liberated by degradation of the complexes localise and can agregate in the small areas formed by mobile alkyl chains of terminal subsituent in 5CB dimeric structures existing at such low temperatures. Results of the study of different small areas of the film sample by electron difraction method (SAED) show the formation of metal nanoparticles with fcc-cubic lattice. The size of metal nanoparticles formed in mesogenic matrices at these temperatures was close the the size of critical germ of the metal crystals.

These small metal particles are stable under the conditions of low molecular mobility of mesogenic matrix particles at low temperatures and can play a role of initial crystals (the

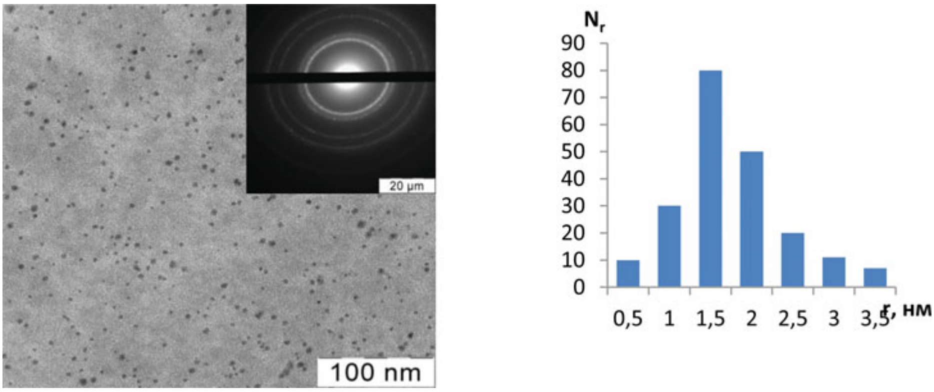

Figure 1. TEM pictures and electronic difraction of the samples, including silver nanoparticles stabilised in mesogenic 5CB matrix at 200 K and histogram of their size distribution.

embryo of a new phase) by rising the temperature. These small metal crystals appear in ESR spectra of the samples as a broadend singlet with g-factor close to the value for free electron $g_e = 2{,}003$, which could be reffered to conducting electrons spin resonance (CESR) in silver and copper nanosize clusters. By heating of co-condensate samples from 90 K up to 150 K the relative f the central component increases, that reveals the thermal decomposition of the metastable complexes and the simultaneous growth of metal nanoclusters. VIS- UV spectroscopic study of silver/CB and copper/CB systems the appearance of new plasmonic absorbance bands in visible region with maximum at 400 nm and 560nm, correspondingly.

Further heating of the samples ($T > 200$K) up to the temperatures of matrix crystallization led to sharp rising of molecular mobility and rapid coalescence of nanoclusters forming higher aggregates, which don't recorded by ESR-technique. Such thermal behavior of the system can be deduced from the specifics of self-assembling processes and supramolecular organization of mesogenic cyanobiphenyl matrix at different temperatures. The combination of rigid aromatic core and flexible hydrocarbon chains of terminal substituents in ligand molecules leads to the formation of dimeric cyanophenyl structures at low temperatures, which stabilised metal atoms due to formation of metastable complexes. Thermal degradation of the complexes by rising the temperature of the co-condensate samples followed by metal atoms escape into more soft domains formed by hydrocarbon chains and their rapid aggregation. Stabilization of nanosize metal clusters of 1–2 nm formed at this stage is possible due to their low diffusion mobility in the solid cyanophenyl matrix. Warming of co-condensate systems up to the temperatures more than 200 K ($T > 200$ K), corresponding to CB crystallisation, causes matrix softening and rising the translational mobility of matrix molecules. This process followed by metal nanoclusters coalescence and formation of higher nanoparticles. Rapid heating up of the co-condensate up to the room temperature followed by the phase transition of the system in nematic (orientationally ordered) and smectic phases (layered structure) led to the preformable formation of the anisometric particles. At 273–293 K in metastable crystal phase 5CB close to the temperature of crystal to nematic phase transition of hybrid metal-mesogenic Ag-5CB nanosystem under the conditions of maximal orientatonal ordering of liquid crystalline matrix the directed growth of highly anisotropic metal nanorods took place with length (l, nm) more than 200 nm and width (d, nm) about 15 nm, so l/d ratio is more than 10 (Fig. 2). Mechanism of such almost one dimentional growth of metal nanorods in this case is connected with the rapid growth of the molecular matrix mobility and maintaining of high orientational order of the system.

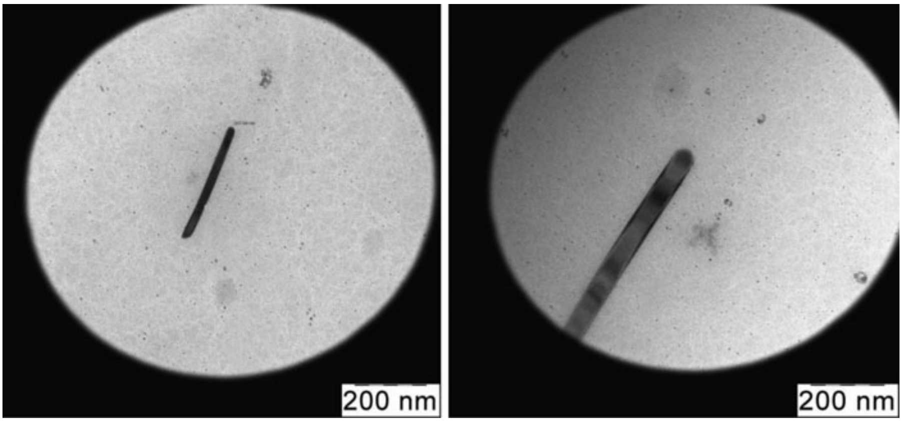

Figure 2. TEM pictures of silver nanorods, growing in 5CB matrix at 273-290 K.

Study of the samples by X-ray difraction technique show the exact crystal character of metal nanoparticles formed at these conditions. The samples possess texture appeared due to the directed growth of rods along crystallographic plane (100) and perpendicular to crystalographic plane (111). Observed mechanism of nanoparticles growth can be explained due to concurrent interaction of terminal functional CN-group of ligand molecules with metal atoms belonged to different crystallographic planes of forming nanoparticles. The interaction with metal centers of highly packed bulky Ag (111) is slower in comparision with more loose Ag(100), so the preferential growth of nanorods can realize just in this direction due to the effective acession of small metal clusters and atom by atom addition formin new add-layers and formation of highly anisometric metal nanoparticles.

3.2. *Morphology, supramolecular organization of metal nanoparticles and nanostructures formed in nematic and smectic phases of alkylcyanobiphenyls*

It was shown by combination of transmssion electron microscopy (TEM) data with the results of small area electron difraction (SAED) and X-ray difraction that hybrid metal-mesogenic nanosystems formed by low temperature co-condensation of silver and copper with mesogenic cyanobiphenyls and followed by controlled anneling of the samples constitute of nanohybrid materials includiong metal nanoparticles stabilised and organised by matrix of mesogenic ligands. Depending of the phase state of hybrid nanosystems Ag/5CB и Ag/8CB were formed nanoparticles of different size and morphology – globular with main diameter 15 nm, anisometric rods and flat 2-D aggregates. Rapid heating of metal-mesogenic co-condensate samples up to 313 K followed by phase transition of the hybrid system to the isotropic state and formation of globular metal particles of 15 nm in average diameter. The data of FTIR study of the system show the formation of monomeric alkylcyanobiphenyl molecules stabilising layer on the surface of nanoparticles due to donor-acceptor interactions of terminal CN-group of ligand with surface metal atoms. Rising metal concentration and carring out the nanoparticles self aggregation process in orientationally ordered nematic mesophase led to the formation of anisometric metal nanoparticles and their assemblies. The results of AFM study of the samples show the formation of linear aggregates and regular orientationally ordered structures of anisometric nanoparticles in nematic phase 5CB at 300 K (Fig. 3). Hystogram of size distribution for metal nanoparticles in this case is presented in Fig. 4.

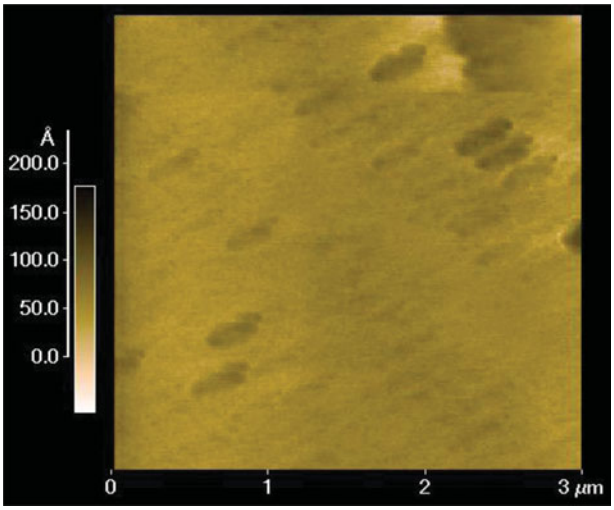

Figure 3. AFM image (tapping mode) of the sample of hybrid metal-mesogenic nanosystem Ag/5CB (1/10) in nematic phase.

Using higher homology 4-octyl-4-cyanobiphenyl (8CB) molecules as stabilising ligand gives us the possibility to carry out metal nanoparticles formation also in layered molecular structured smectic mesophase. In this case we saw the formation of quasi-fractal flat metal aggregates intercalated between smectic layeres of 8CB due to higher interacting energy into the smectic layers and microphase segregation (Fig. 5).

Thus, fullfilling of the self-organisation and self-assembly processes during formation of hybrid nanosystems in liquid mesophases of different types led to the production of metal nanoparticles of different size and morphology and their supramolecular organisation in hyghly ordered nanostructures, including anisometric nanoparticles and rod like aggregates stabilised in nematic mesophases, flat 2D metal aggregates in layered structured smectic phases of long chain alkylcyanobiphenyls. Increasing the ligand molecules concentration led to the stabilisation of metal nanoparticles of smaller size. Rising metal concentration in the orientationally ordered nematic system supporting the formation of anisometric rod like metal nanoparticles and their aggregates. The scheme of phase-structural states for Ag/5CB hybrid nanosystem indicating the conditions for the formation of metal nanoparticles with definite morphology is presented in Fig. 6. This scheme is considered the combination of the

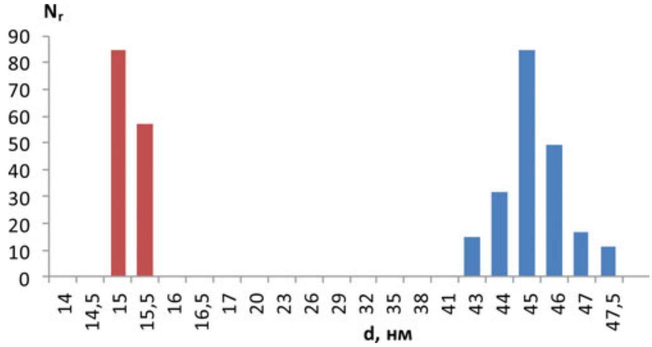

Figure 4. Histogram of size distribution for silver nanoparticles stabilised in nematic mesophase of 5CB, red – cross size of nanoparticles, blue - linear length of nanoparticles.

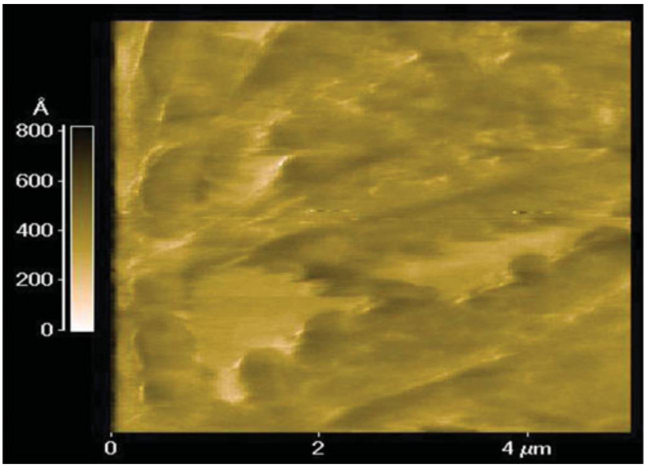

Figure 5. AFM image (tapping mode) of the sample of hybrid metal-mesogenic nanosystem Ag/8CB (1/10) in smectic phase.

results results of thermal analysis, polythermal polarisation spectroscopy and electronic and atomic force microscopy.

The data presented in Fig. 6 show the formation of nanoparticles with different morphology and size, stabilised by mesogenic ligands depending on the phase state of mesogenic matrix and metal concentration in the system. The shape of the particles is in general the result of competition of general tendency of minimization of particle's surface energy and elastic energy of liquid crystal. Rapid heating (more than 100 K/min)of the co-condensate Ag/5CB sample to the temperatures of isotropic phase existence (T> 318 K) – region I - led to the formation and stabilization of global nanoparticles with d = (15 ± 10) nm in size. Transition to the nematic phase of 5CB gives us anisometric metal nanoparticles and their orientationally ordered assemblies - region III. In the biphase region II, including coexistance of isotropic phase with fluctuations of nematic ordering – the formation both isotropic globular and anisometric rods is possible. The maintaining of the samples at 273–283 K –and increasing of the metal content in the sample from 1 up to 10 w/w % - region IV - led to preferential growth of

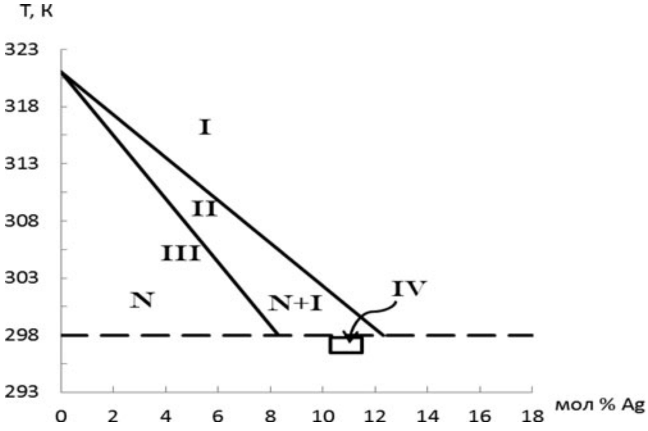

Figure 6. The scheme of phase-structural states for Ag/5CB hybrid nanosystem: I – isotropic phase. II – two phase region : isotropic phase including the fluctuations of nematic ordering; III – nematic phase. 1V – the temperature region in nematic phase close tophase transition from crystal to nematic; V – solid phase at 150–200 K.

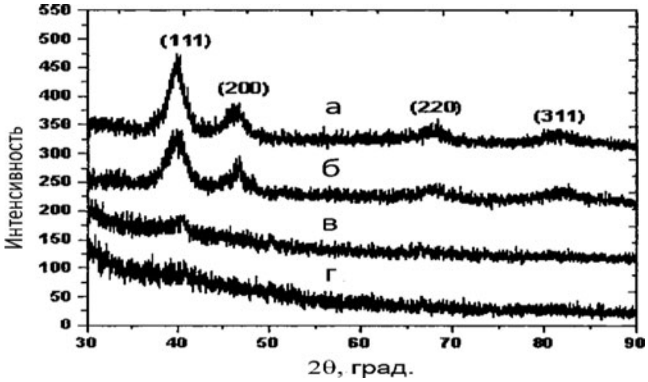

Figure 7. X-ray data for sample of hybrid metal-mesogenic nanosystem Ag/5CB (1:10), encapsulated in polymer (PPX) film at 450 K (a), 300 K (b), 250 K(c), 200 K (d).

rod-like metal nanoparticles with higher l/d ratio more than 10. Small metal nanoparticles of 1–2 nm in size are formed in diluted systems in the solid phase at 150–200 K.

3.3. Hybrid metal –mesogenic nanosystems encapsulated in polymer films and their properties

The layer-by-layer co-condensation of vapors of para-xylylene monomer, metal silver and cyanobiphenyl ligand followed by controlled heating or UV- irradiation of the sample led to the formtion of hybrid metal-mesogenic compositions with varied from 1 up to 10 w/w % of metal contents, encapsulated in poilymer film. The results of TEM study of the Ag/5CB samples encapsulated in poly-para-xylylene films (PPX) show, that increasing of metal contents in the sample up 10 w/w% led to the growth and stabilisation of elongated rod like metal particles with anisometric ratio l/d more than 10 (where l – length, d – cross diameter of particles). X-ray difractograms of the sample Ag/5CB (1:10), formed at 200 K with followed annealing up to 450 K, are shown on Fig. 7. The results obtained show the formation of metalnanoparticles with fcc cubic lattice, with lattice constant similar to crystal silver a = 0,408 n, crysgtallographic plaines were identified as (111), (200), (220) и (311).

The proposed method allows to encapsulate from several molecular layers up to several microns. In optical spectra of such hybrid metal containing mesogenic systems encapsulated in PPX fuilms at 300 K appear the plasmonic bands at 420–440 and 500–600 nm, characteristic for the formation of silver nanoparticles and their ordered aggregates. Rising metal concentration led to the formation of anisometric rod-like particles with multimodal plasmonic resonance related to the cross and linear resonance. Formation of rod like metal nanoparticles with anisometric ratio $l/d>10$ led to the increasing of plasmonic absorbance in longwave spectral range ($\lambda \geq 650$ nm).

At this case the value of dichroic ratio $D_{!!}/D_{\perp}$ in plasmonic band for samples Ag/5CB (1:10) uniformly oriented by magnetic field rises in 5 times in comparison with pure 5CB samples. Optical properties of the samples are stable during several months.

4. Conclusions and perspectives

Thus, the new approach was proposed and realized in this work for formation of highly ordered hybrid metal-mesogenic, based on the governed self-organisation of atomic-molecular systems obtained by low temperature condensation of metal and mesogenic components vapors followed by controlled annealing of the samples. The hybrid metal-mesogenic nanosystems have been obtained including metal (silver and copper) nanoparticles stabilized and organized by liquid crystalline matrix and their properties were studied in temperature 80–350 K. The conditions allowed the production of metal nanoparticles of different size and morphology were determined and methods of creation of their ordered nanostructures using of molecular self-organization and metal species self-assembly were developed.

Low temperature co-deposition of metal (Ag, Cu) and mesogenic alkylcyanobiphenyl component (5CB, 8CB) vapors led to the formation at the first stage of metastable biligand complexes of metal atoms with functional CN-group, stabilized in ligand matrices. Thermal degradation of the metastable complexes at 150–200 K led to the formation of small metal clusters, which initiate the growth of nanoparticles and their further aggregation and organization in anisotropic mesogenic matrix. The structural and dynamic properties of mesogenic matrix at different temperatures and different phase states controls metal atoms and small clusters self-assembling and aggregation and led to the formation of metal particles of different size and morphology and their ordered aggregates. The competition of the processes of matrix molecules self-association, metal atoms aggregation and complex formation between metal species of different size with ligand molecules and molecular aggregates determines the structure and physico-chemical properties of hybrid nanosystems formed in definite conditions. Highly ordered nanohybryd systems can be very promising for different applications in nanoelectronics and electro optics, possess unusual optical and sensor properties.

Acknowledgments

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