

# Cryochemistry of nanometals

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## 1. Introduction

The development of nanotechnologies is one of the most promising prospective of nowadays (Poole&Owens, 2003). Nanoscience has been established as a new interscience field of research. It can be defined as a whole knowledge on fundamental properties of nanosized objects. The results of nanoscience are realized in nanotechnology as new materials and functional facilities. At present time nanochemistry becomes one of the main growing directions of nanoscience objects (Sergeev, 2006; Ozin&Arsenault, 2005). Understanding the peculiarities controlling the size, shape and self-organization of nano- and subnanosized particles and the properties of materials including such particles is the main problem of nanochemistry. Another problem is connected with the existence of size effect. As size effect we can define the qualitative changes in physical and chemical properties and chemical activity depending on the number of atoms and molecules in nanosized particle. The existence of such dependences is a particular feature of nanochemistry.

The use of low temperatures temperature technique (4-100 K) enlarges the possibilities of nanochemistry and opens new prospects in creation of bulk and film materials with new conducting, protecting and sensor properties. Low temperatures and matrix isolation methods are used for stabilization of highly energetic and very active metal species as atoms, clusters and nanoparticles. Using metal atoms, clusters and nanoparticles the effect of reacting particles size (number of atoms) on their chemical activity and properties of reaction products can be revealed. This effect is the intrinsic feature of nanochemistry, which is the base of production of new compounds and materials with unusual properties. (Sergeev, 2001; Sergeev&Shabatina, 2002; Shabatina&Sergeev, 2003; Shabatina&Sergeev, 2007).

The main scope of this work is to combine the unique properties of metal atoms, clusters and nanoparticles with different organic and inorganic substances, particularly liquid crystals and polymers using methods of cryochemistry. The joint and separate condensation of metals (Ag, Mg, Cu, Pb, Sm and Eu) and different active and inert organic and inorganic compounds on the cooled surfaces and in cooled liquids have been made. The problems of stabilization and of activity and selectivity in competitive reactions of metal species are discussed.

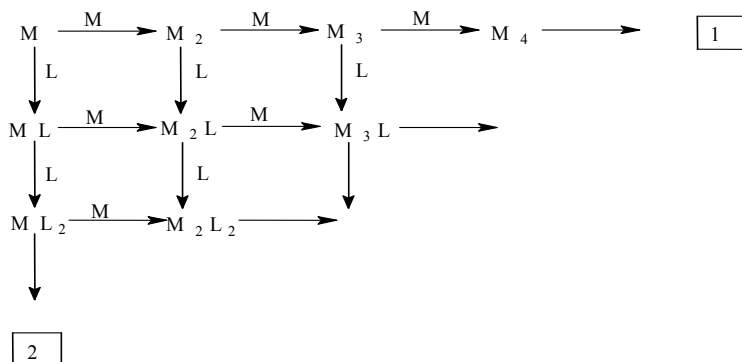
## 2. Size effects in reactions of metal atoms and clusters stabilized in matrices of noble gases and hydrocarbons

Low temperatures and matrix isolation methods are used for stabilization of highly energetic and very active metal species as atoms, clusters and nanoparticles. The scheme of our cryochemical synthesis and some methods of characterisation of film samples obtained are presented in Fig.1. Low temperatures can be used also for study of unusual chemical reactions of metal species. The effect of reacting particle's size (size-effect) on their chemical activity and properties of reaction products is of great interest. As size effect we can define the qualitative changes in physical and chemical properties and chemical activity depending on the number of atoms and molecules in nanosized particle. For metal species of several nanometers in size, containing up to 10 nm in size (10-1000 atoms) the dependence of the reaction rate possesses not monotonous character (Sergeev, 2003). The existence of such dependencies is a particular feature of nanochemistry at low temperatures and is based on changing of electronic and geometry structure of metal species by raising the number of atoms formed the particle. Analyzing of such dependencies is of great importance for understanding of the nature of size effects, which can be considered as structural-size effects.

Metal atoms and small metal particles possess high chemical activity (Klabunde, 1994). The interaction between separated metal atoms and ligand molecules can be described by the following scheme including parallel and consecutive reactions, where M is metal atom and L is ligand molecule [5]. Aggregation of metal atoms (the reaction pathway 1) and their reactions with ligand molecules (the reaction pathway2):

The problem of producing of the exact compound can be solved for the reactions of naked clusters in the gas phase using double mass-spectral selection method under molecular beam conditions. For metal species of several nanometers in size, containing up to 100 atoms the dependence of the reaction rate ordinary possesses not monotonous character.

It is important to note, that physical and chemical properties of metal atoms and small clusters in the gas phase and stabilized in inert gas matrices, for example, argon under low temperatures are practically the same. This fact allowed us to discover the size effects in chemical reactions of metal atoms and clusters in condensed phase. One of the exiting examples is the interaction of magnesium atoms and clusters with carbon tetrachloride in low temperature film co-condensates of different metal concentration. It is important that the reaction doesn't occur for bulk metal at ambient temperatures. In low temperature co-condensates according to the results:





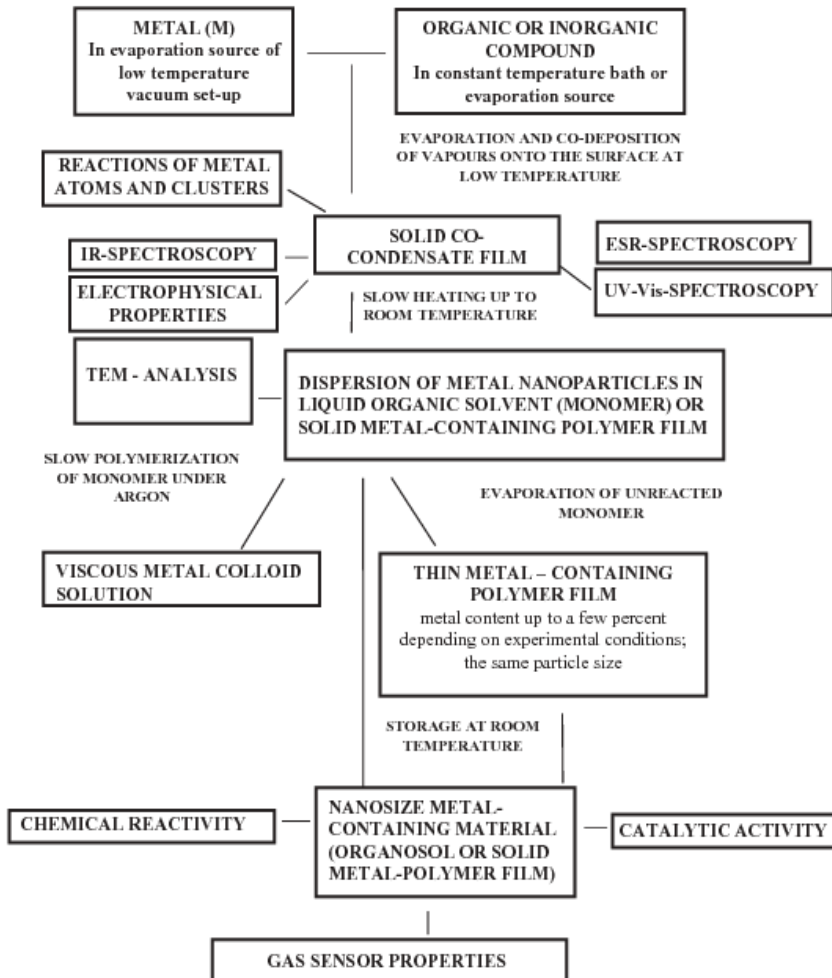


Fig. 1. Cryochemical synthesis of nanosize materials encapsulated into inorganic, organic and polymeric matrices (Sergeev & Shabatina, 2008)

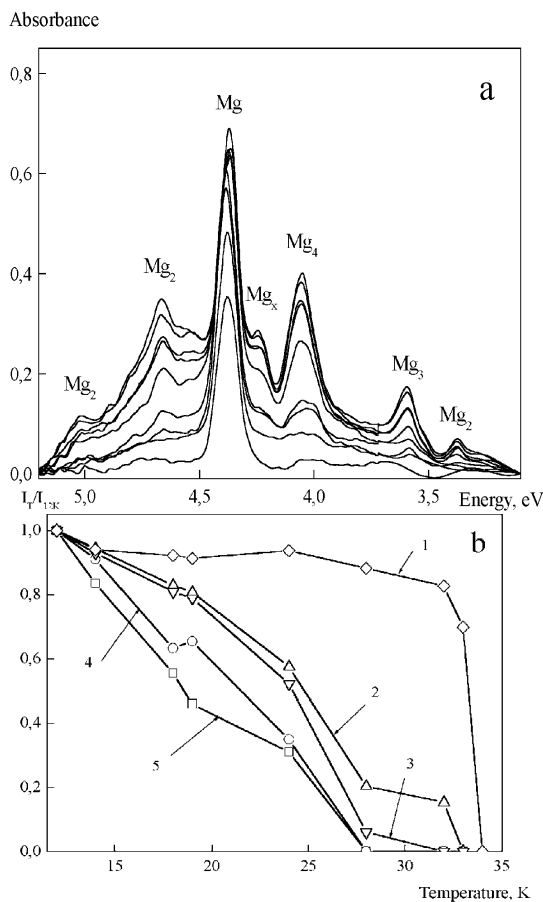


Fig. 2. The changes in UV-visible spectra in the temperature range 12–35 K in the system Mg : CCl<sub>4</sub> : Ar = 1 : 100 : 1000 (a) and normalized integral intensity of magnesium particles absorption at different temperatures: (1) Mg, (2) Mg<sub>4</sub>, (3) Mg<sub>x</sub>, (4) Mg<sub>3</sub>, (5) Mg<sub>2</sub>. (b) (Mikhalev et.al, 2004)

The relative activity of samarium species in reaction with carbon dioxide at different temperatures show the higher activity of samarium clusters as compared with samarium atoms.

Evidently the effect of metal particle size on its reactivity is of primary importance for the development of nanochemistry. From our viewpoint of no less importance is to compare the chemical activity of uni-size particles of different chemical nature, of different substances. The data of Table 1 allowed us to compare the activity of atoms and clusters of two different metals - magnesium and samarium and for each metal particles of the same size with two different ligands  $\text{CO}_2$  and  $\text{C}_2\text{H}_4$ . It was shown that in double systems:  $\text{Mg-CO}_2$  and  $\text{Mg-C}_2\text{H}_4$ ,  $\text{Sm-CO}_2$  and  $\text{Sm-C}_2\text{H}_4$  both metals react with both ligands  $\text{CO}_2$  and  $\text{C}_2\text{H}_4$ , but in triple systems  $\text{Mg-CO}_2\text{-C}_2\text{H}_4$  and  $\text{Sm-CO}_2\text{-C}_2\text{H}_4$  both metals react performable with carbon dioxide molecules. These results reveal the problem of activity and selectivity in competitive reactions of metal species (Sergeev, 2001).

| Metal             | Ligand  |   |  |
|-------------------|---|---|--|
| specie            | $\text{CO}_2$   | $\text{C}_2\text{H}_4, \text{C}_2\text{D}_4$  | $\text{CH}_3\text{X}, \text{X}=\text{Cl}, \text{Br}$                   |
| Mg                | $\text{Mg}^+\text{CO}_2^-$ at matrix annealing                                    | cycle<br>$\text{Mg}(\text{C}_2\text{H}_4)_2$<br>at matrix annealing   | $\text{CH}_3\text{MgX}$ at irradiation<br>( $\lambda=280 \text{ nm}$ ) |
| $\text{Mg}_{2-4}$ | $\text{Mg}^+\text{CO}_2^-$ at co-condensation                                     |   | $\text{CH}_3\text{MgX}$ at irradiation                                 |
| $\text{Mg}_x$     | $\text{Mg}^+\text{CO}_2^-$ at matrix annealing                                    |   | ( $\lambda>300 \text{ nm}$ )   |
| Sm                | $\text{Sm}^+\text{CO}_2^-$ , $\text{CO}$ ,<br>$\text{SmCO}_3$ at matrix annealing | complexes<br>$\text{Sm}(\text{C}_2\text{H}_4)\text{-(C}_2\text{D}_4)$ and<br>$\text{Sm}(\text{C}_2\text{H}_4)_2\text{-(C}_2\text{D}_4)_2$ | methane  |
| $\text{Sm}_2$     | $\text{Sm}^+\text{CO}_2^-$ , $\text{CO}$ ,<br>$\text{SmCO}_3$                     |   | at co-condensation   |
| $\text{Sm}_x$     | co-condensation   |   |  |

Table 1. Reaction products of magnesium and samarium with ligands at 10–40 K

### 3. Competitive interactions of metal species with organic molecules in low temperature co-condensates.

Cryochemical synthesis allowed us to obtain new compounds and complexes for series of d- and f-metals (Shabatina, 2007). The competitive interactions of atoms and dimers of europium and samarium with alkylcyanobiphenyls and cyanophenylpyridines and metastable complexes have been obtained and characterized by FTIR, UV-Vis and ESR-spectroscopy (Shabatina et al., 2005, Vlasov 2005). The formation of two sandwich-like

complex structures with different stoichiometric metal to ligand ratio  $ML_2$  and  $M_2L_2$  were shown by combination of spectral data with the results of DFT-B3LYP modeling of the system. The solid state transformation of mononuclear lanthanide complex to the binuclear one was established by heating of the system up to 173-243 K.

The reactions of silver and copper atoms and clusters were studied using mesogenic alkylcyanobiphenyl compounds as stabilizing matrix and carbon tetrachloride as the third active reagent (Shabatina, 2003; Timoshenko, 2005). In framework of these investigations the following tasks were solved: to carry out the cryosynthesis of new metal atom and cluster complexes and to study their thermal stability; to establish the competitive reactions and relative chemical activity of metal species of different size with the reagent molecules added to the system; to establish of intermediate reaction products and propose the reaction mechanism. It was shown the competition in reactions of silver atoms and clusters with carbon tetrachloride and complexation with cyanobiphenyl molecules. The triple Ag- $CCl_4$ -5CB co-condensate systems of different reagent's ratios from 1:1:100 to 1:10:1000 have been studied by ESR-technique in temperature range 77-350 K. There are three reaction pathways for silver atoms and small clusters existing in cocondensate samples at different temperatures. It was established the competitive formation of silver atoms complexes of  $\pi$ -type with two cyanobiphenyl molecules, formation of  $\sigma$ -type complexes with two different ligands 5CB and  $CCl_4$ , and aggregation of the silver atoms and small clusters resulting in formation of silver nanoparticles. The preferred reaction channel was dependent upon the reagent ratio, and, first of all, on carbon tetrachloride contents in the system. By heating up of the co-condensate system silver complexes undergo decomposition and freed silver atoms aggregated with formation of additional amount of metal nanoparticles. The formation of  $AgCl \cdot CCl_3$  complex was shown also for triple Ag- $CCl_4$ -5CB system and also for double Ag- $CCl_4$  system. Depending on carbon tetrachloride content in the system and temperature we can obtain performable stabilized in matrix metal clusters or paramagnetic chloro-containing products (Fig.3).

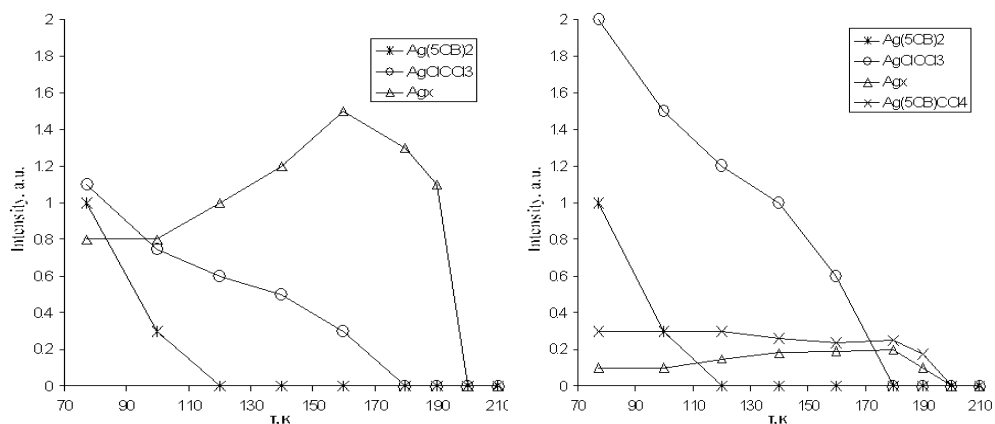
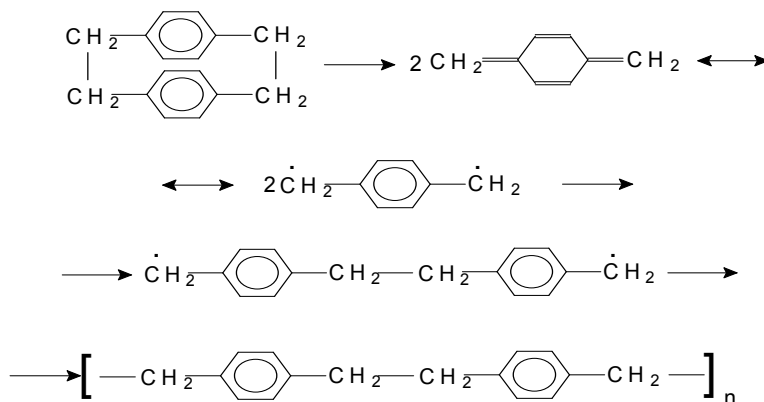


Fig. 3. Temperature dependence of the relative yields of paramagnetic products of metal atoms and clusters reactions in Ag/5CB/ $CCl_4$  co-condensate.  $\Delta$ - Agx,  $\odot$ -AgCl- $CCl_3$ ,  $\boxtimes$  - Ag(5CB) $_2$ ; x-Ag(5CB) $CCl_4$ .

#### 4. Encapsulation of nanometals in thin polymer films

Low temperature technique was used also for encapsulation of metal particles of definite size in polymer films. Metal atom aggregation was prevented by sterical hindrance of polymer matrix cage (Sergeev, 2005). In this case we have used different monomers which can polymerize just at low temperatures. One of them is highly reactive para-xylylene monomer, obtained via pyrolysis of para-di-xylylene. The process is presented by the following scheme:



Polymeric films containing of aggregates of metal atoms were obtained by joint and layer-by-layer condensation on cooled surface (Sergeev et.al, 1995, Sergeev 2006). Co-condensate samples were polymerized by heating up to 110-130 K or by light irradiation at 80 K. The polymer poly-para-xylylene films with incorporated metal particles could be withdrawn from the reaction vessel and studied by different physical and chemical methods. The particle size histogram demonstrates rather narrow size distribution over the range 2-8 nm. The average diameter of the particles was estimated as 5,5 nm. The nanosize particles of Zn, Cd, Ag, Mg and Mn were also incorporated in poly-para-xylylene films.

We have developed also cryochemical and chemical synthetic methods for incorporating of metal particles into polyarylamide gels (Sergeev et.al, 1998; Sergeev et.al, 1999; Sergeev, 2006). It is interesting to compare properties of Ag-MA and Pb-MA polymer stabilized sol systems. Lead particles in contrast to silver do not initiate methylacrylate (MA) polymerization. The behavior of bimetallic Ag-Pb-MA system with the respect to MA polymerization resembled the properties of Pb-MA system rather than for Ag-MA system, bimetallic system does not initiate polymerization of MA monomer. Thus, bimetallic system possesses nonadditive changes of individual nanoparticle properties. Probably, the presence of lead in the system inhibits silver-induced polymerization of MA. It is important that lead particle size didn't exceed 5 nm for both Pb/MA and Ag/Pb/MA systems. The diameter of silver nanoparticles formed under the same conditions is 10-15 nm.

Polymer films including metal nanoparticles open new possibilities for synthesis of the materials with promising properties. High sensitivity for ammonia and water vapors



was shown for films containing lead nanoparticles (Sergeev et.al, 1997). Such films were proposed as new ammonia sensors having a response exhausted 3-4 orders of magnitude in their electrical conductivity (Bochenkov, 2002; Bochenkov 2005). As an example of the importance of cryosynthesis conditions, the microstructures of two samples containing nearly the same amounts of lead, but deposited at different rates are presented in Fig.4. The microstructure influences the electrical properties, thus, only sample (b) was found to be sensitive to humidity. After deposition and controlled annealing, the particles can be oxidized totally or partially to form a highly porous sensitive layer. A careful control over the deposition parameters, such as the condensation rate, evaporation rate and substrate temperatures allows us to obtain condensates with the required structure and also opens up the possibility of chemical modification of the surface and grain boundaries.

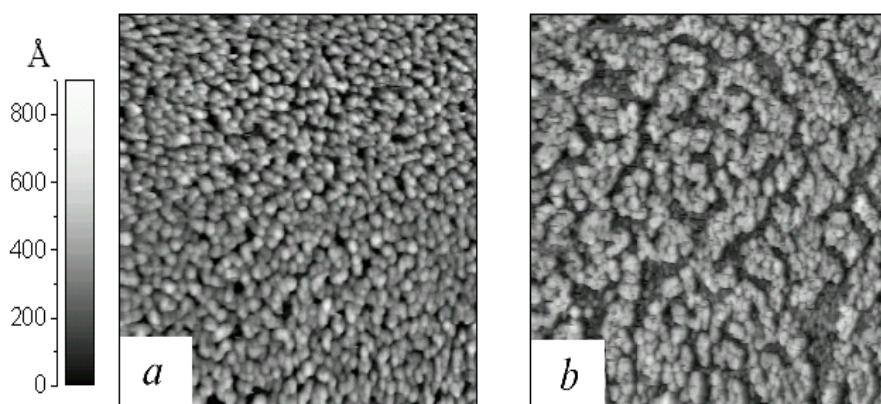


Fig. 4. AFM images of Pb condensates, deposited at 80 K after annealing to room temperature and exposure to the air. Scan area is 5mm 5 m m. (a) 34.3 ML deposited at 0.05 ML/s, no conductance onset during the deposition was observed. (b) 28.1 ML deposited at 0.20 ML/s, the conductance onset was observed. (Bochenkov, 2005)

## 5. Metal-mesogenic nanosystems formed by cryocondensation technique

New metal-mesogenic hybrid nanosystems were obtained based on silver, copper and mesogenic alkylcyanobiphenyls derivatives, which formed diversely organized solid and liquid crystalline phases with different type of molecular organization. In temperature range 80-300 K the controlling of metal particles size in range 2-30 nm and their morphology and aggregation processes were made (Shabatina, 2002; Shabatina, 2003a). Metal containing cyanobiphenyl film samples ( $l=20-50 \mu\text{m}$ ) were obtained by reagent's vapor co-condensation on the cooled surfaces of quartz, KBr or  $\text{CaF}_2$  or polished copper under molecular beam conditions. IR, UV-Vis and ESR spectroscopic studies of the samples were realized in situ, in vacuum, using special spectral cryostats. The systematic IR-, UV- and ESR-study of specific interactions were carried out for low temperature co-condensates of mesogenic cyanobiphenyls and cyanophenylpyridines with transition metals of the first group (Ag, Cu)

at 80-350K. The spectroscopic data combining with the results of quantum chemistry calculations showed for alkylcyanobiphenyl system the formation of sandwich-like silver complex at low temperatures and the structure with head-to-tail arrangement of two ligand molecules was proposed. It was established that annealing of the samples up to 150-200 K led to complex thermal degradation and metal nanocluster formation. The kinetics of complex thermal degradation and metal cluster's growth were studied by ESR technique. It was shown the kinetics retarded character revealed the existence of activation energy distribution for complex thermal degradation. The main value of process activation energy was estimated as 30 kJ/mole, the silver cluster formation was shown also for UV-irradiation of the samples at low temperatures. UV-Vis spectroscopic study of silver/CB and copper/CB systems at 80 K showed the appearance of new absorbance band at 360 and 420 nm due to complexes formation. These bands disappeared at 200 K and the new wide bands with maxima at 440 and 560-600 nm were detected at 200-300 K for silver and copper co-condensates, correspondingly. The aggregation of metal atoms and/or small clusters via complex decomposition and formation of nanosize metal particles could cause it.

Low temperature layer-by-layer co-condensation of silver, mesogenic compound 4-pentyl-4-cyanobiphenyl (5CB) and 4-octyl-4-cyanobiphenyl (8CB) and para-xylylene monomer followed by heating of the obtained film sample resulted in encapsulation of such hybrid metal-mesogenic system into polymer film. Transmission electron and probe microscopic study (TEM, AFM) of the samples show the existence of two kinds of metal particles stabilized in nematic (orientationally ordered) alkylcyanobiphenyl matrix at elevated temperatures. These were globular silver particles with diameter of 15-30 nm and highly anisometric rod-like metal particle with length more than 200 nm. The preferential growth of rod-like metal particles regulated by the increase in metal to ligand ratio. The use of smectic (layered organized) phases of higher homology 4-octyl-4-cyanobiphenyl (8CB) led to the formation of flat quasi-fractal aggregates.

## **6. Conclusions. Prospects of thin films containing nanosized metal particles in nanochemistry, catalysis and electronic materials**

This survey of literature data and of the results obtained by the authors of the review shows that the methods of cryochemistry and cryonanochemistry make it possible to carry out and control self-assembling processes of metal atoms to form subnano- and nanosized aggregates, perform competitive chemical interactions of atoms, small clusters and nanosized metal particles with different organic and inorganic substances. At present time the effective approaches of cryochemistry are being developed aimed on stabilization of metal atoms, dimmers, trimmers and higher clusters and metal particles in inert gas matrices and polymer films and by certain organic substances layers at different substrates. The use of low temperatures and controlled condensation of reagent vapors allowed us to obtain and stabilize metal particles of 1 nm and less in size. Such hybrid organic-inorganic film materials can find their applications in catalysis and as highly sensitive chemical sensors.

The accumulation of data on the reactions of the variety of different metals for a wide range of temperatures in condensed systems, including solid co-condensate films, will allow one to reveal the fundamental peculiarities of nanochemistry, and at first the manifestation of size effects and clearing its nature for the competitive reactions of metal species and the

periodicity in the variation of reactivity of these objects. This information together with the comparative analysis of characteristics of ligand-free and ligand-stabilised metal nanoparticles makes it possible to separate the effects of metal core and stabilizing organic shell effects on the chemical and catalytic activity of the system at different temperatures. This approach should be coupled with the quantum chemical modeling of the systems under investigation.

The development of cryonanochemistry is aimed on the elaboration of new methods for synthesis of nanostructured film materials with the unique electronic, optical, magnetic, electrophysical and mechanical characteristics. It is necessary to carry out highly selective catalytic, photo- and thermo -induced chemical transformations as the basis in the production of nanodevices and surface modification processes. The quest of promising applications is associated with the development of methods for the formation of ordered assembles of metal particles of definite sizes and shapes incorporated in thin polymeric films, liquid crystals, carbonaceous and biological systems. The use of low temperature vapor condensation technique offers a possibility of the direct introduction of metal atoms and clusters into organic and polymer films without using additional chemical reagents and solvents. This can result in the development of environmentally clean methods for the synthesis of nanostructured film materials with special properties. Of great importance is the use of such methods for production of multifunctional hybrid films based on chemically modified metal particles and biologically active substances, which includes the development of new systems for medical diagnostics and target delivery of drug substances.

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## **Polymer Thin Films**

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This book provides a timely overview of a current state of knowledge of the use of polymer thin film for important technological applications. Polymer thin film book covers the scientific principles and technologies that are necessary to implement the use of polymer electronic device. A wide-ranging and definitive coverage of this emerging field is provided for both academic and practicing scientists. The book is intended to enable readers with a specific background, e.g. polymer nanotechnology, to become acquainted with other specialist aspects of this multidisciplinary field. Part A of the book covers the fundamental of the key aspect related to the development and improvement of polymer thin film technology and part B covers more advanced aspects of the technology are dealt with nano-polymer layer which provide an up-to-date survey of current research directions in the area of polymer thin film and its application skills.

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