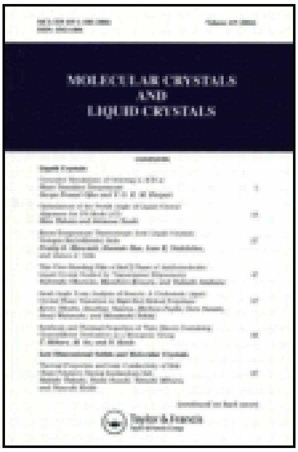

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*Ordered aggregates including nanosized silver particles (*d = *6.0 ± 1.5 nm and* d = *2.5 ± 0.5 nm) stabilized by cholesterol and thiocholesterol forming from metal sols and by cooling from the isotropic state are obtained. The composition, morphology and structure of the aggregates are determined by FTIR, UV-Vis spectroscopy, transmission electron microscopy, and electronic diffraction. The optical properties of the silver–thiocholesterol and silver–cholesterol systems are studied.*

Keywords Nanoparticles; optical properties; ordered aggregates; thiocholesterol/cholesterol

1. Introduction

Nanohybrid systems including metal particles stabilized by organic ligands or introduced into the organic or polymeric matrixes attract the interest of researchers due to their unique quantum-size properties and the possibility of their application in such fields as microelectronics, optics, catalysis, information recording systems, and data storage systems [1–5]. The physical and chemical properties of nanohybrid systems depend both on the size and shape of the structural elements (nanoparticles), and on the manner of their organization into the joint structure [6,7]. Development of synthesis methods of nanohybrid aggregates having different order of the particles of the same size is an important task in modern nanochemistry. For the synthesis of nanoparticles having a certain size it is necessary to physically or chemically isolate nanoparticles from one another and from the external environment to prevent aggregation [8]. The stability of such systems is achieved through the introduction of functionalized organic ligands (long chain) aryl- and alkylthiols, organic amines, alcohols, and (others) capable of specific interactions with the surface of the nanoparticles. Additional supramolecular organization of the ligand molecules allows the use of the obtained nanoparticles for the formation of 1*D*-, 2*D*-, and 3*D*-ordered

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aggregates. Such aggregates could differ in their properties from the individual particles [9].

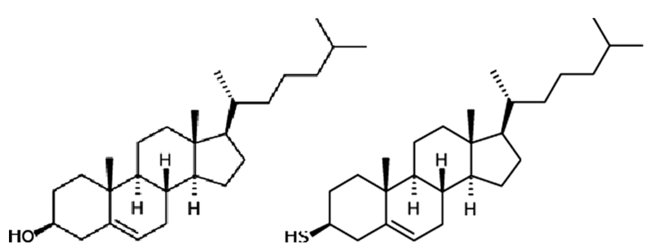
2. Experimental Methods

To obtain stabilized silver particles, a method based on the transfer of the Ag^+ complex from water into organic medium in a two-phase (liquid–liquid) system followed by reduction with sodium boron hydride in the presence of tetra-*n*-octylammonium bromide and stabilizing organic thiol ligand was used [10]. In the procedure modified by us, silver nitrate was used as a source of silver ions, cholesterol or thiocholesterol (Figure 1) were used as stabilizing ligands. The samples were obtained by the following way. Three solutions were prepared: solution I is a silver nitrate water solution obtained from 0.0191 g ($1.124 \cdot 10^{-4}$ mole) of silver nitrate and 3.75 ml of water solution II is a solution of 0.2734 g ($5.0 \cdot 10^{-4}$ mole) of tetra-*n*-octylammonium bromide (TOAB) in 10 ml of toluene, and solution III is a water solution of 0.0472 g ($1.25 \cdot 10^{-3}$ mole) of sodium boron hydride in 3.125 ml of water. Solution II was added into solution drop wise under continuous stirring. After addition, the mixture the organic layer was separated for further synthesis and cholesterol or thiocholesterol (the ratio of the ligand and silver concentrations was 1:1) were added under continuous stirring. Solution III was added very quickly into the solution obtained and the mixture with ethanol was placed into the refrigerator at $-18°C$ for the precipitation of nanoparticles. The precipitate obtained was centrifuged and washed with ethanol for the removal of excess reagents. The nanoparticles obtained were resolvated into toluene for carrying out the spectroscopic studies.

The FTIR spectra of the samples were registered on an FTIR-spectrometer "IRAR" (FIAN, Moscow); the optical spectra were recorded on a Specord M40 spectrophotometer (Carl Zeiss, Germany). The qualitative and quantitative composition of the samples was investigated by electron diffraction and chemical analysis on an ICP-MS spectrometer. The structure of the samples formed and the size of the stabilized silver particles were investigated by transmission electron microscopy.

3. Results and Discussion

The triple systems silver–cholesterol–toluene and silver–thiocholesterol–toluene obtained at the first stage were characterized by FTIR and optical spectroscopy. In the IR spectra of the samples the band characteristic of O–H vibrations at



(a) (b)

Figure 1. Molecular structure of cholesterol (a) and thiocholesterol (b).

$\nu = 3490–3500\,cm^{-1}$ and δ-deformation vibrations of OH-group at $\nu = 1090–1140\,cm^{-1}$ and of S–H vibrations at $\nu = 2540–2590\,cm^{-1}$ are almost absent and mostly the bands characteristic of CH_3, CH_{2-} and S(O)-CH_2 group vibrations at $\nu = 2920–2880\,cm^{-1}$ and $\nu = 1415–1440\,cm^{-1}$ are present, which is evidence of the practically covalent interaction of the ligand thiol/hydroxyl group with the surface of the silver nanoparticles, and of the formation of stabilizing ligand layer on the surface of the metal particles [11,12]. In the optical spectra of toluene solutions, an intensive band of plasmon resonance of silver nanoparticles is observed at 420–450 nm (Fig. 2a).

Removing of toluene from the samples led to the formation of dispersions of stabilized nanoparticles and of regular structures depending on metal concentration and chemical nature of functional group of stabilizing ligand. In Figures 3 and 4, electronic micrographs of silver nanoparticles stabilized by cholesterol and thiocholesterol in diluted toluene sols are shown.

In the case of cholesterol stabilizing ligand silver nanoparticles possess linear dimension of $d = (6.0 \pm 1.5\,nm)$ and after removing of toluene form on the support surface two-dimensional layer with a characteristic hexagonal order. Earlier, the formation of hexagonal ordering of two-dimensional nanostructures was observed for gold nanoparticles in [13–15]. In the case of the silver–thiocholesterol system, the formation of nanosized hybrid aggregates including small silver particles with

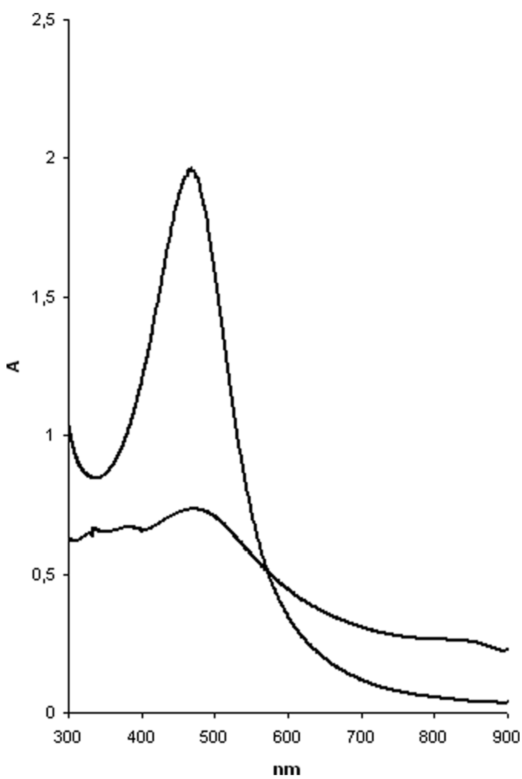
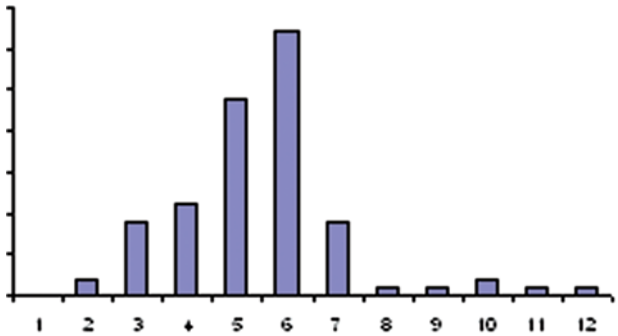
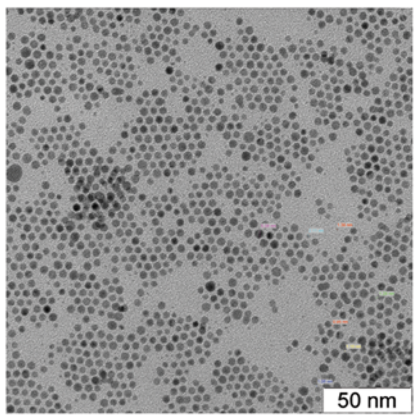


Figure 2. The optical absorbance spectra of thiocholesterol stabilised silver nanoparticles plasmon resonance for: toluene solutions (a) and film samples formed in mesophase (b).



(a)



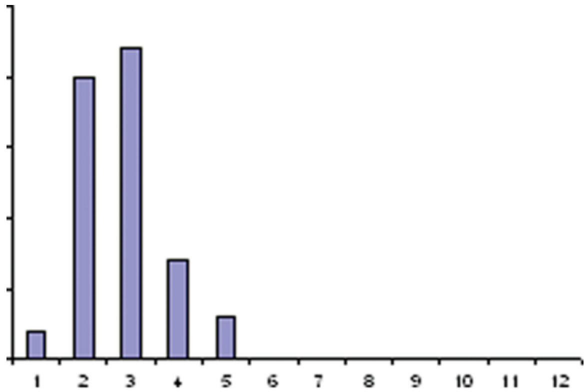
(b)

Figure 3. TEM picture for silver nanoparticles stabilised by cholesterol and histogram of size distribution. (Figure appears in color online.)

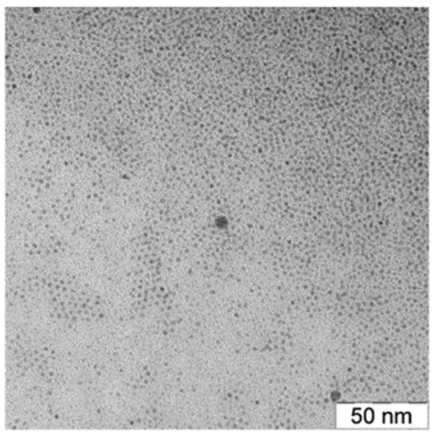
linear dimension $d = (2.5 \pm 0.5)$ nm, which are stabilized by ligand in monotropic cholesteric phase (heated up to 70°C and cooling down to 25°C) nanotubular/nanowhisker aggregates, were detected (Fig. 5). Silver nanoparticles joined into ordered ensembles with chain arrangement of individual metal particles are clearly seen. The size of the individual particles in this case almost does not change compared to the silver nanoparticles precipitated from the thiocholesterol–toluene mixed system, reaching $d = (2.5 \pm 0.5)$ nm. The linear dimension of the aggregates reaches more than 10 μm at the thickness of 20–30 nm, which practically coincides with the thickness of one or several molecular helical structures of the mesogenic ligand formed in the cholesteric mesophase. In the optical spectra of the samples (Fig. 2b), along with the plasmon absorption of individual nanoparticles at $\lambda = 450$ nm, the long wave absorption at 770–900 nm, which is characteristic for chain silver nanoparticles aggregates also appears [16].

4. Conclusions and Perspectives

Thus, in our work, regular 2D surface structures with hexagonal ordering of monosized silver nanoparticles ($d = 6.0 \pm 1.5$ nm) stabilized by cholesterol and hybrid

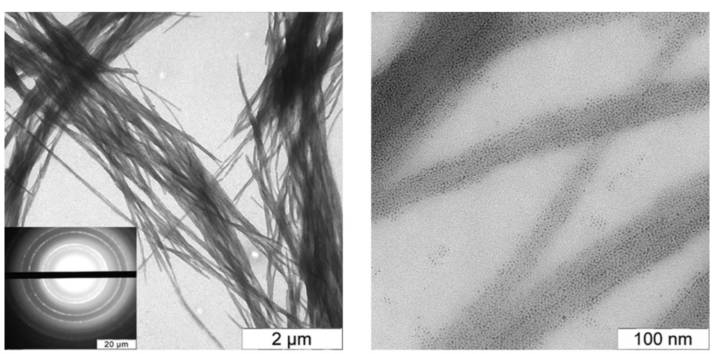


(a)



(b)

Figure 4. TEM picture for silver nanoparticles stabilized by thiocholesterol and histogram of size distribution. (Figure appears in color online.)



(a) (b)

Figure 5. TEM picture for silver nanoparticles tubular aggregates stabilized by thiocholesterol (after 24 hours at 25°C): general view (a) and internal structure (b).

tubular silver–thiocholesterol nanoaggregates including monosized nanoparticles ($d = 2.5 \pm 0.5$ nm) and having joint linear dimensions more than 10 μm. This system possesses optical properties differing from the plasmon absorption of individual silver nanoparticles obtained. Such systems could be of interest for the creation of new optical and electro-optic devices with adjustable light absorption and light reflection.

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