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The supramolecular approach to the phase transfer of carboxylic calixresorcinarene-capped silver nanoparticles



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ABSTRACT

The octacarboxylic derivative of tetrapentylcalix[4]resorcinarene (**1**) was used as stabilizer for preparation of silver nanoparticles (AgNPs) hydrosol. The calixresorcinarene-capped nanoparticles Ag@**1** are stably dispersed in an aqueous colloid solution and have an average diameter of 4–6 nm (TEM). The interaction of the macrocycle **1**, possessed the receptor properties, with the cationic surfactant cetyltrimethylammonium bromide (CTAB) leads to the hydrophobization of AgNPs hydrosol. It was shown, that macrocycle **1** in its individual solution forms the hydrophobic associate with 8 mol of CTAB (¹H NMR, 2D NOESY). Various and complicated influence of CTAB/macrocycle molar ratio on the hydrophobization of AgNPs and their transfer into organic phase was demonstrated. The initial Ag@**1** and modified Ag@**1**-CTAB were characterized by UV-vis and FTIR spectroscopy, DLS, and TG/DSC methods. It was shown that the efficiency of water/organic phase transfer depends on the macrocycle/surfactant molar ratio. The presented supramolecular approach can be useful to form the ordered nanostructures through supramolecular modification and self-organization of hybrid metal nanoparticles.

1. Introduction

Now the research area that is located at the crossroads of materials research and nanosciences is rapidly emerging. The hybrid metal nanoparticles are one of the most intensively investigated nanomaterials due to their unique electronic and optical properties. The modification of metal nanoparticles' surface is used to improve their stability, dimensions, sensor properties, surface energy, biocompatibility and so on [1]. The appropriate modification of the nanoparticles' surface changes the surface composition, structure and morphology of a material and may yield to a controlled assembly and/or to the transferring of nanoparticles to the aqueous/organic media [2]. The method of phase transfer represented an effective way for functionalizing metallic nanoparticles with suitable ligands towards the creation of close-packed, ordered arrays and nanoparticulate thin films. Also phase transfer has always been an important approach for the preparation of organosols of noble metals, since the methods for direct synthesis of noble metal nanoparticles in non-polar organic media were limited due to the poor solubility of the corresponding metal ion precursors [3].

There are some ways for modification of the hydrophobicity/

philicity on metal nanoparticles surface such as ligand exchange, ligand chemical modification, or addition of layers of molecules that stabilize the particles in the desired phase [2,3]. The last one is used in the process of noncovalent modification of noble metals nanoparticle's surface as a result of the formation of ionic associates of nanoparticles ligands with opposite-charged organic molecules and surfactants [4–9].

Earlier the modification of metal nanoparticles' surface through the formation of inclusion complexes of the hydrophilic macrocycles on the nanoparticle's surface has been reported [10–14]. This approach leads to the successful transfer of metal nanoparticles in aqueous or organic phase depending on scientific task. For example, the inclusion complexes of α -cyclodextrin and *p*-sulfonated calix[4]arene with octadecanethiol were used for capping of AuNPs and AgNPs, respectively [10,11]. These particles are well-soluble in the aqueous solution. The displacement of macrocycle's molecules from supramolecular complex by addition of chloroform leads to the hydrophobization of NPs surfaces [10,11].

Another case of host-guest complex formation aimed to the change of NPs surfaces properties is the interaction of AgNPs stabilized by oleic acid, dispersed in hexane, with aqueous alkaline solution of *p*-sulfo-

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