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Title: *Colloidal noble-metal nanocrystals and their bimetallic alloys with controlled composition and structure: synthesis, characterization, properties*

**Abstract**

The development of nanotechnology continuously expands the range of synthesized nanoparticles (NPs) containing various types of cores and surface stabilizing compounds. Designing and synthesizing NPs with controlled composition and structure, in particular multicomponent systems, is still an open task. Even the simplest bimetallic systems are characterized by new special features absent in single-component systems, determining,
e.g. the crystal and electronic structure. An important aspect of obtaining non-agglomerating colloids with designed properties is the use of suitable stabilizers (e.g. carboxylates, amines, thiols, phosphines) that can interact with NPs in a specific manner.

This work focuses on the synthesis of silver and palladium nanoparticles and their Pd/Ag alloys. They were obtained from newly synthesized for this purpose aliphatic carboxylate salts of these metals and their amine adducts, which were characterized by
a number of experiments, including spectroscopic (FTIR, UV-Vis, NMR, XRD) and thermal (DSC, TGA) methods.

Coordination of characteristic ligand functional groups was determined using infrared spectroscopy (FTIR). The results for silver complexes show that silver laurate has a bidentate (dimeric) bridge coordination structure, while in the silver bis(amine) carboxylate this coordination changes to chelating. 1H and 13C NMR spectroscopic studies in solution allowed to determine that there are two types of amine ligands in the silver bis(amine) carboxylate complexes weakly and strongly interacting with silver carboxylate, which are rapidly exchanged. Information on the crystal structure of the complexes was obtained on the basis of X-ray diffraction studies (XRD) which revealed the layered molecular arrangement
and the interpenetration of aliphatic chains. Thermal studies have confirmed the obtaining
of pure products that can be effectively used in the synthesis of nanoparticles.

Similarly, previously unknown in the literature palladium (II) carboxylate complexes and their corresponding bis(amine) carboxylate adducts were obtained, and their structure was proposed. Infrared studies suggested the emergence of monodentate coordination. The structural analysis was supplemented with NMR studies, especially with the use of 1H-1H COSY experiments, thanks to which the chemical structure of the obtained complexes was detailed. The results of solid state 13C CP-MAS NMR studies confirmed that in the obtained complexes the palladium ion has square-plane coordination, which is formed by two nitrogen atoms
of amino groups and oxygen atoms of two carboxylate groups. Further crystallographic studies by XRD show the layered arrangement of molecules and interpenetration of aliphatic chains both in palladium (II) carboxylates complexes and in their amine adducts, as is the case
in analogous silver complexes.

The synthesis and detailed characterization of Ag and Pd precursors was aimed
at understanding the conditions for the preparation of single-component silver and palladium nanoparticles and bimetallic Pd/Ag alloy NPs by the thermal decomposition method. Appropriate functionalisation of the nanoparticle surface with weakly interacting aliphatic carboxylate and amine groups turned out to be crucial for their potential use. The acquired knowledge allowed to obtain bimetallic Pd/Ag NPs alloys with a given composition, which enabled the construction of a hydrogen sensor that works effectively as a function of hydrogen concentration at room temperature. The presence of silver improves durability of hydrogen absorption-desorption cycle and changes the sensitivity range of the sensor by blocking excessive H2 absorption.