Summary of dissertation

The main topic of the dissertation is design and physicochemical characterization of nanocomposites based on surface – decorated metal nanostructures covered by electrochemically reduced graphene oxide. The proposed hybrid systems of different hydrophilicity were tested for possible applications as electrochemical catalysts and platforms for ultra – sensitive SERS detection.

Great advantages of hybrid systems are new properties due to the intermolecular interactions between the components resulting in synergy effects. Metal nanoparticles capped with Keggin – type polyoxometalates (POMs) show unique optical and electrochemical properties due to the redox activity of stabilizing ligands. Polyoxometalates (POM) have the ability to stabilize metal nanoparticles and to facilitate the electron transfer at the same time. This class of inorganic ions show intrinsic electrocatalytic properties towards the reduction of hydrogen peroxide in acidic solutions, but their stability at neutral pH is rather weak.

The tendency of POM to undergo hydrolysis can be beneficial in electrochemical applications since products of partial POM degradation are electroactive. Due to the fact that electrochemical transformation of POM ions into smaller units leads to exposure of metallic surface, nanoparticles with partially hydrolyzed stabilization agents can exhibit better SERS performance compared to pristine POM-MNPs units.

Keggin – type structures chemisorb irreversibly on carbon and metal surfaces, disclose high proton and electron conductivity and have the ability to adopt a wide range of redox states which makes them attractive catalysts. This class of inorganic ions was used in this thesis as ligands stabilizing metal nanoparticles. The ability of POM to adsorb on solid surfaces helped to control the size of metal cores during synthesis.

In this dissertation I focused on obtaining and characterization of gold and silver nanostructures stabilized with Keggin – type polyoxometalates covered by layers of hexagonal carbon rings rich in structural defects obtained by the electrochemical reduction of graphene oxide. The presented hybrids were tested as electrochemical sensors for hydrogen peroxide and SERS platforms for molecule showing fluorescence (Rhodamine 6G).

An important achievement of this dissertation was to demonstrate that the POM structures do not significantly change after chemisorption regardless the type of metal core used (Au/Ag) and the POMs (SiW or PMo units). However, infrared and Raman spectra of POM-coated nanometallic particles indicated different interaction between POMs and metal core depending on catalyst layer.

The phenomenal catalytical performance of gold and silver nanostructures decorated with polyoxometalates were significantly expanded in its nanocomposites with partially reduced graphene oxide. The justification of synergy observed for hybrid systems were discussed based on spectral data. All hybrid systems were examined as possible SERS supports. The observed differences were rationalized by various SERS mechanisms.