Abstract

This work is aimed at the preparation and morphological and spectroscopic characterization of the interphase nanocomposite (NC) two-dimensional (2D) self-assembled systems of Ag and Au nanoparticles (NPs). The NPs were functionalized with the following ligands with terpyridine end–groups: 2,2′:6′,2″-terpyridine (tpy), 4'-(2-thienyl)-2,2':6',2"-terpyridine (T-*tpy*), α,ω-bis(terpyridyl)-2,2'-bithiophene (*tpy-2T-tpy*) and α,ω-bis(terpyridyl)-2,2':5',2"-terthiophene (*tpy-3T-tpy*).

The morphological analysis of transmission electron micrographs proves the preservation of the average interparticle distance in closely spaced NP pairs, independent of the ligand. The value of the total average interparticle distance increases in the order: tpy < T-*tpy* < *tpy-2T-tpy* < *tpy-3T-tpy*, while the average occupied area fraction in the same order decreases. The morphological descriptors (i.e. interparticle distance and occupied area fraction) were found to correlate with the shift of the SPE (surface plasmon extinction) maxima of NCs (tpy > T-*tpy* > *tpy-2T-tpy* > *tpy-3T-tpy*).

The results show that the shift of SPE band maximum depends on the degree of surface plasmon delocalisation rather than on the value of the average interparticle distance in closely spaced NP pairs. The smaller are the islands formed by closely spaced NPs, the smaller is the shift of the SPE maximum and vice versa.

The SERS study of the prepared NCs proved the existence of two forms of the surface complexes – with and without the MLCT (metal-to-ligand charge transfer) transition in Ag and/or Au/tpy and Ag and/or Au/T-*tpy* NCs. The existence of surface complexes with MLCT transition was not proved for the systems derived from bis(tpy) NCs.

Key words: plasmonic nanoparticles, self assembled monolayers, SERS, TEM, image analysis, 2,2′:6′,2″-terpyridine