Nanocomposites and nanomaterials

Nanohybrids of thermoresponsive polymer with embedded gold nanoparticles: spectroscopy and modeling study

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Nanohybrids of thermoresponsive polymer with plasmonic nanopacticles are attracting considerable interest due to wide range of applications including sensing, photovoltaics, nanomotion, photothermal therapy, and drug delivery. Here we report on a versatile study of novel star-like dextran-graft thermoresponsive poly(N-isopropylacrylamide) (D-g-PNIPAAm) copolymers with incorporated gold nanoparticles. The synthesized nanohybrids can additionally used for detection of different analytes by surface enhanced methods (SERS). The application of the thermoresponsive polymer can appreciably extend the set of the analytes by demonstration of physical trapping going through lower critical solution temperature point.

Au nanoparticles were synthesized in-situ in water solution of star-like copolymer D-g-PNIPAAm [1]. It was established by dynamic light scattering and UV-vis methods that Au nanoparticles of size 5-10 nm are incorporated into polymer matrix and don't change size when polymer matrix undergoes conformational transition. The lower critical solution temperature (LCST) for nanosystem Au/D-g-PNIPAAm was higher than for individual D-g-PNIPAAm (34,3°C and 33,8°C, respectively). At higher temperature the aggregation process of macromolecules was observed.

The D-g-PNIPAAm nanohybrids were studied by Raman and optical absorption spectroscopy. Two broad bands ($\Delta\Gamma$~50 cm^{-1}) at about 135 and 265 cm^{-1} were observed in Raman spectrum of aqueous suspension of D-g-PNIPAAm. The performed calculation with the B3LYP density functional and Stuttgart_RSC_1997_ECP basis set showed that these bands could be assigned with Au-Au vibrations. Upon heating above LCST of PNIPAAm to 40^0C we observed the appreciable shift and the change of the intensity of number of the bands assigned with C-O stretching vibrations, C_α-H bending vibrations, amide I and amide II vibrations. That is explained by change of conformation of PNIPAAm and bond linking it to dextran.

[1] V. Chumachenko, N. Kutsevol et al. J. Mol. Liq. 2017. V.235. 77-82.