Conjugated Cationic Polythiophene Polyelectrolyte Induced aggregation of Silver Nanoparticles and Its Application to SERS

S. Kazim1,*, J. Pfleger1, M. Bondarev2, J. Vohlidal2, M. Prochazka3, E. Jager1, P. Stepanek1,
1Institute of Macromolecular Chemistry, AS CR, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic
2Charles University in Prague, Faculty of Sciences, Hlavova 2030, Prague 2, Czech Republic
3Charles University in Prague, Faculty of Mathematics and Physics, Ke Karlovu 5, Prague 2, Czech Republic
*e-mail: samrana_kazim@yahoo.co.in

Conjugated polyelectrolytes (CPEs) show interesting optical, electrical and redox properties together with good solubility in water and water-miscible solvents, making possible processing of these polymers from aqueous solutions. This makes them suitable for various biosensor and optoelectronic applications. Solubility of CPEs in water also substantially simplifies preparation of their composites with noble-metal nanoparticles (NPs) that can show the effect of local enhancement of electromagnetic field, which can be evidenced by the surface enhancement of Raman scattering (SERS).

Recently we have prepared a new conjugated cationic polyelectrolyte with regioregular poly(alkylthiophene) backbone and ionic-liquid-like side groups: poly[3-{6-(1-methylimidazolium-3-yl)hexyl]thiophene-2,5-diyl bromide}, PMHT-Br. In the present communication we report on the morphology and optical properties of Ag NPs/PMHT-Br systems formed by aggregation of silver nanoparticles in the hydrosol.

Dispersions of aggregates have been studied by optical absorption, fluorescence, SERS, TEM, dynamic light scattering and zeta-potential measurements. Aggregation of Ag-NPs was found to depend on the concentration of PMHT-Br in the system. Optimum aggregation is achieved at components ratios providing a charge balance between Ag-NPs and PMHT-Br, at which Ag-NPs are nearly single-polymer-layer coated, their zeta potential is close to zero and they easily form aggregates in which their interparticle distances lie in the region-enabling occurrence of the desired plasmonic effect. At higher Ag-NPs/PMHT-Br ratios, Ag-NPs do not aggregate since they preserve their original negative zeta potential (borate-stabilized Ag sol) but effectively quench fluorescence of PMHT-Br. At lower Ag-NPs/PMHT-Br ratios, zeta potential of Ag-NPs is switched to positive values hence they do not aggregate either. Prevailing resonance enhancement of Raman scattering is observed for systems of non-balanced compositions. TEM images of the Ag-NPs/PMHT-Br systems together with the observed concentration dependent zeta potential of particles present in the system and Raman spectra and fluorescence quenching measurements have shown that electrostatic interactions of negatively charged Ag NPs with cationic PMHT-Br chains play key role in the formation of systems showing surface-enhanced optical effects.