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THE FORMATION OF JANUS PARTICLES FOR SERS

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Surface-enhanced Raman scattering is a sensitive and selective technique for detection of the presence of low-abundance biomolecules in biological and chemical systems performed on metal-covered substrates. The production of the substrates is usually organized by distribution of silver or gold nanoparticles on the surface as well as using lithography. We provide an alternative approach of production the substrate which allows us to form polymer spheres half-covered with silver by Redox reaction in silver nitrate solution.

Introduction

Surface-enhanced Raman spectroscopy (SERS) has been attracting a lot of interest since it was investigated in 1974 due to its capability to 10^6-10^{14} times intensify the Raman signal of a target analyte. The phenomenon of SERS is defined by localized surface plasmon resonance (LSPR) which is generated by incident light when it interacts with the metal surface of the substrate. The highest enhancement provide gold and silver substrates as the incident beam is influenced by a highly-conductive surface. LSPR is referred to so-known “hot-spots”, the areas of substrate where the SERS signal enhances extraordinarily. The “hot-spots” are generated on a highly-developed surface and their presence strongly depends on the composition, size, geometry and separation distance between the rough points of the metal surface. The main focus of current SERS substrates researches is on the production of a high-developed surfaces, which are mainly performed by dusting metal nanoparticles on Si surfaces and shells, or even by metal coverage of self-assembled polymer molecules, thus fabricating the roughness of the surface for a more intensive SERS signal.

The approach presented in this work provides to obtain not fabricated SERS substrates, but prepared in a solution of silver nitrate, where the required thickness of the polymer spheres coverage is regulated by the solution concentration. The resulting metal surface is naturally rough and irregular which is known to provide the SERS signal of a high intensity. Moreover, with the solutions of low concentrations, the mode of growing Janus particles turns on, thereby providing the material for substrate with more “hot-spots”. Besides, there are the techniques for the attachment temperature-sensitive polymers to the metal surface of polymer spheres which have a wide range of applications in intensification of the SERS signal and studying the conformational changes of thermosensitive polymers.

Method

We studied silver deposits formed on ion-exchange spheres in electroless field in $AgNO_3$ solution. The process of aggregation is caused by a redox reaction between Ag^+ ions in solution and metallic copper, which initiates the growth of silver over the spheres. The concentration of solution is 0.1-0.2 wt%, and it is not sufficient for the polymer spheres to be covered completely. Therefore, the Janus particles, half-covered silver spheres are formed.

The particles provide a good enhancement activity either themselves or with polyelectrolyte coverage. Hence, we suggest two techniques, where the first one is “layer by layer” coverage with several double layers of polyethylenimine (PEI) and poly(N-isopropylacrylamide), or PNIPAM. The second method is based on the binding of n-isopropylacrylamide (NIPAM) into the silver layer whilst the process of the metal reduction on the polymer sphere surface. PNIPAM is thermosensitive polymer and with the temperature above 32 °C undergoes a reversible lower critical solution temperature (LCST) phase transition from a swollen hydrated state to a shrunken dehydrated state, losing about 90% of its volume. This allows the improved spheres to attach the molecules of analytes from the solution of lower concentrations, thereby providing the intensification of the SERS signal.

Conclusion

The identification of molecules of low concentrations like proteins in biological liquids or prohibited compounds in water solutions requires a high level of precision in medicine, criminalistics or trading. Consequently, there is a demand for the SERS method to be developed as a cheaper and accurate one. The suggested technique of a SERS substrate preparation is accessible and simple to carry out. It also allows to create half-covered Janus particles which provide additional LSPR at the edges of silver caps. Moreover, a charged surface of silver spheres is capable to attach polyelectrolytes with thermosensitive qualities, thus endowing the spheres with more powerful qualities.

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