

Molecular Condensation and Highly Sensitive Detection of Organic Molecules based on a Thermo-responsive Polymer Micro-assembly formed by Plasmonic Optical Trapping.

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Localized surface plasmon (LSP) enhances the electromagnetic fields of resonant light confined to nanoscale volumes near the noble metallic nanostructures, and hence LSP is a powerful candidate for a nano-optical sensing technique of molecules. In particular, surface-enhanced Raman scattering (SERS) has attracted much attention due to the use for highly sensitive detection and analysis of organic molecules adsorbed on the plasmonic nanostructures. Recently, we propose an alternative detection method of organic molecules by plasmon with nano-molar sensitivity [1]. A key technique of this method is plasmonic optical trapping.

An optical gradient force is exerted on nanoparticles such as polystyrene nanospheres and quantum dot polarized in the gradient of electromagnetic field, resulting in optical trapping of them. By using the enhanced electromagnetic field by plasmon, the nanoparticles were efficiently trapped on the plasmonic nanostructures (plasmonic optical trapping; POT). We have demonstrated POT of macromolecules such as thermo-responsive polymer (poly(*N*-isopropylacrylamide) ; PNIPAM).[1] Poly-(*N*-isopropylacrylamide) (PNIPAM) is a representative water-soluble thermo-responsive polymer. PNIPAM can homogeneously dissolve in water at room temperature, taking a hydrated random-coiled structure. Upon raising temperature above a lower critical solution temperature (LCST = 32 °C), the polymer exhibits coil-to-globule structural transition accompanied by dehydration of the polymer chains. The dehydrated globules aggregate with each other due to hydrophobic interactions, and consequently forming polymer-rich domains in solution (phase separation). It is reversible process.

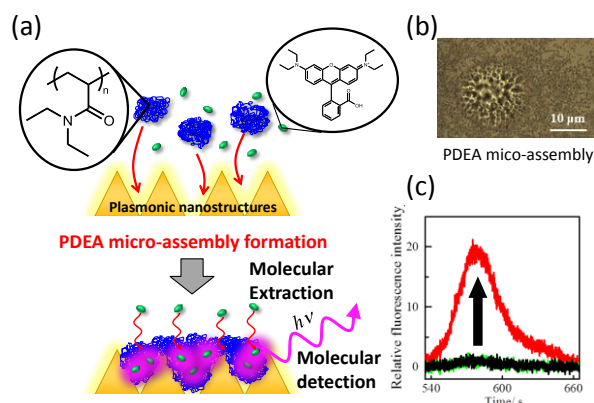


Fig. 1 (a) a schematic illustration of our analytical method. (b) an optical micrograph of PDEA micro-assembly formation. (c) fluorescence spectrum of rhodamine B extracted in a PDEA micro-assembly.

POT of PNIPAM rapidly formed a dehydrated micro-assembly on a plasmonic surface upon resonant excitation. The PNIPAM micro-assembly can extract organic molecules dissolved in aqueous solutions, leading to an increase of the concentration within the micro-assembly. Accordingly, we can detect spectroscopic (fluorescence/Raman) signals from the extracted molecules with high sensitivity. We developed a novel highly sensitive detection method based on this concept for a small amount of fluorescent and non-fluorescent organic molecules [2].

Analyte molecules were dissolved in a PNIPAM or poly(*N,N*-diethylacrylamide) (PDEA) aqueous solution. Gold nanopyramidal dimer arrays on a glass substrate were used for the plasmonic nanostructure. The substrate was fabricated by an angle-resolved nanosphere lithography technique. Upon resonant excitation of plasmon using 808 nm laser light, the electromagnetic field was estimated to have been enhanced by a factor of $\sim 10^4$ in $|E|^2/|E_0|^2$. Analytes in the polymer micro-assembly are detected using microspectroscopic systems.

During near-infrared laser irradiation for plasmon excitation, a micro-assembly of polymer was formed on the plasmonic substrate immediately. The assembly formation was a reversible process in response to plasmon excitation, caused by a combination of the enhanced optical force and of the local temperature elevation in solution by photothermal effect of the plasmonic nanostructures. This hydrophobic PNIPAM assembly formed by plasmonic excitation will be useful for extraction of organic molecules dissolved in aqueous solution. Figure 1 shows fluorescence microspectroscopy during plasmon excitation in Rhodamine B/PNIPAM dilute solution. Before plasmon excitation, Rhodamine B in solution weakly emitted (gray line in the figure). Upon plasmon excitation, the fluorescence intensity became increase, clearly indicating the molecular extraction of Rhodamien B into the polymer assembly. Furthermore, by using Raman microspectroscopy, the extracted non-fluorescent molecules (*o*-, and *p*-chlorophenol) were also successfully detected in this method.

In conclusion, we demonstrated the novel analytical tool of organic molecules dissolved in solution by means of POT combined with Fluorescence/ Raman microspectroscopies. The polymer assembly was caused by not only the enhanced optical force but also the local temperature elevation at the nanogaps. The hydrophobic thermoresponsive polymer assembly formed by controlling physical behaviors was worked for the molecular extraction field. This extraction method will be potentially a versatile tool for contacting organic molecules with plasmonic active site, opening a new way to novel plasmonic analytical method and plasmonic photochemical reactions.

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References:

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