

Localized Surface Plasmon Resonance Sensor Based on Silver Nanoprisms Coated with Alkylthiol Monolayers

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1. Introduction

Metal nanoparticles show interesting optical properties that offer potential applications to analytical chemistry. Localized surface plasmon resonance (LSPR) is unique phenomenon for the metal nanoparticles and leads to the appearance of strong absorption peaks in visible to near-infrared region. The peaks are very sensitive to surrounding dielectric environment, and therefore this property has been used to develop chemical and biological sensing systems as LSPR sensing.

Spherical [1], prismatic [2,3], bipyramid [4] and nanoshell-shaped [5] metal nanoparticles have previously been used as LSPR sensing platforms. Particularly, metal nanoprisms can be efficient platforms because these are very sensitive to changing of surrounding dielectric environment. However an intrinsic problem with the nanoprisms is the instability of their vertices and these must be coated with robust protective materials for preservation of their morphology. It has recently been reported the fabrication of the metal nanoprisms coated with silica shells [2] and chitosan polymer [3] for LSPR sensing. Although these strategies are useful, it remains possible that the high-density coating materials reduce the sensitivity for changes in dielectric environment.

In this study, we report the fabrication of silver nanoprisms coated with ultrathin films consisting of alkylthiol self-assembled monolayers on solid supports, which exhibit morphological stability and high sensitivity to their dielectric surroundings.

2. Experimental

An aqueous colloidal solution of the silver nanoprisms was synthesized as follows. An aqueous solution of silver nitrate (1 mM, 100 mL) was added to an equivalent volume of aqueous solution containing 0.2 mM of sodium tetrahydroborate and 5 mM of trisodium citrate under stirring and cooling in an ice-bath to produce the aqueous solution of citrate-capped silver nanoparticles with diameter of about 10 nm. A typical photoreaction was carried out by irradiating the colloidal solution with 150-W halogen lamp, leading the conversion from silver nanoparticles to nanoprisms [6]. And then obtained aqueous solution was centrifuged three times (10000 rpm, 10 min) to remove smaller silver nanoprisms and residual silver nanoparticles.

A schematic diagram for the fabrication of alkylthiol-coated silver nanoprisms on solid supports is shown in Fig. 1. Typically, amino group-modified glass plate was immersed in an aqueous colloidal solution of negatively charged silver nanoprisms for 60 min to electrostatically adsorb silver nanoprisms onto the amino group-modified glass plate (denoted as AgPr/Glass). After washing the AgPr/Glass with sufficient water, the plate was immersed in an anhydrous ethanol solution of 1 mM of hexadecanethiol to form self-assembled monolayers of hexadecanethiol onto the surface of silver nanoprisms (denoted as HDT/AgPr/Glass). Finally, prepared HDT/AgPr/Glass were washed with sufficient anhydrous ethanol.

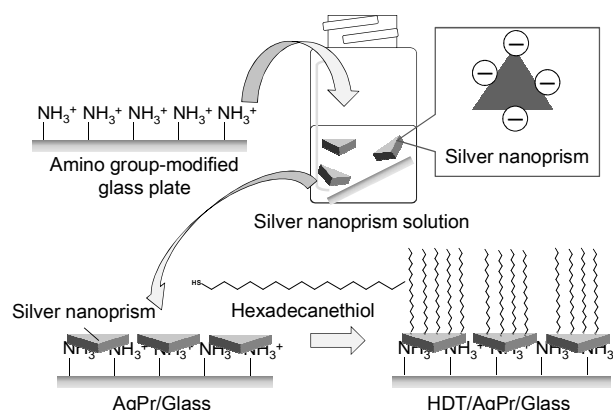


Fig. 1 Schematic diagram for fabrication of HDT/AgPr/Glass.

3. Results and Discussion

Absorption spectra for the colloidal aqueous solutions of silver nanoprisms before and after centrifugation processes are shown in Fig. 2(A). Before centrifugation, appreciable absorption peaks at around 670 and 920 nm derived from LSPR excitation of the silver nanoprisms were observed. These results indicated that at least two types of prisms with different sizes were synthesized by irradiation of halogen light. After centrifugation, the peak at 670 nm was almost disappeared and the peak at 920 nm was still remained, indicating that smaller nanoprisms were almost removed.

From TEM image of silver nanoprisms obtained after

centrifugation is shown in Fig. 2(B). We have confirmed the formation of silver nanoprisms with about 120 nm edge-length.

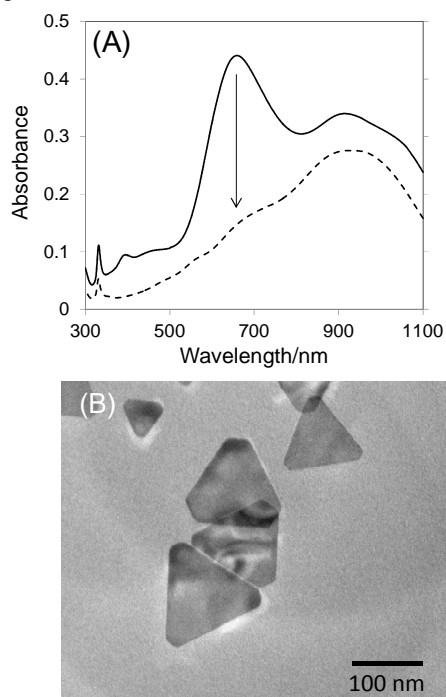


Fig. 2 (A) Absorption spectra for aqueous colloidal solutions of silver nanoprisms before(—) and after(---). (B) TEM image of obtained silver nanoprisms.

Transparent absorption spectra for HDT/AgPr/Glass measured in air and toluene solvent are shown in Fig. 3. From the spectrum measured in air, we have confirmed that the spectral shape for HDT/AgPr/Glass were similar to that for silver nanoprisms dispersed into aqueous solution. These results suggest that the monodispersed silver nanoprisms were immobilized onto the glass plate without aggregation. For the spectrum in toluene solvent, the peak from LSPR excitation was drastically shifted to longer wavelength region as compared with that in air [peak wavelength in air (refractive index (n) = 1.000): 903 nm and that in toluene (n = 1.497): 1065 nm]. By proceeding consecutive spectral measurement cycles in air and toluene solvent, we have confirmed that the wavelength changes in LSPR peak were reversible. These results suggest that the silver nanoprisms on glass plate have good morphological stability and high sensitivity to their dielectric surroundings (~330 nm per refractive index unit).

In order to evaluate the effect of hexadecanethiol monolayers as protective agent, we have performed same experiments as described above for AgPr/Glass (without modification of hexadecanethiol monolayers). As a result, the LSPR peak showed irreversible and stepwise reduction and blue-shift as proceeding measurement cycles. These results imply that the morphology of silver prisms is unstable upon dipping in toluene solvent.

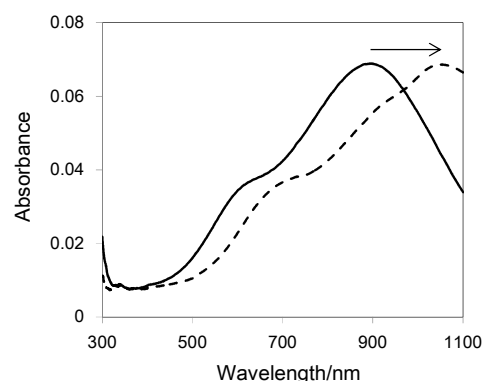


Fig. 3 Absorption spectra for HDT/AgPr/Glass in air(—) and toluene solvent(---).

4. Conclusion

We have succeeded to fabricate plasmonic sensor based on silver nanoprisms coated with hexadecanethiol monolayers which exhibit morphological stability and high sensitivity to their dielectric surroundings. These can be excellent plasmonic nanosensor chips in near-infrared region.

References

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