Electronic Supplementary Material (ESI) for Analyst.

Supplementary Information

Plasmonic Nanoparticle-Film Calipers for Rapid and Ultrasensitive Dimensional and Refractometric Detection

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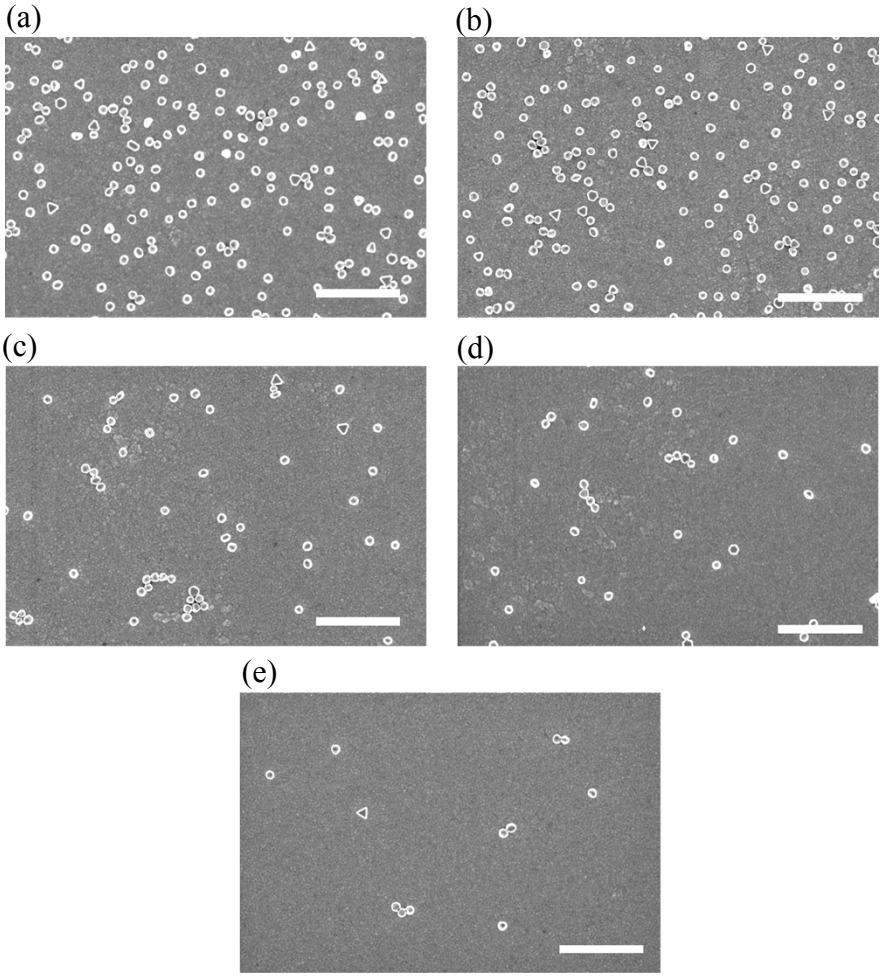

Fig. S1 SEM images of NP-film calipers prepared from 100-nm Au NP colloidal solution of (a) 1×, (b) 0.75×, (c) 0.5×, (d) 0.25×, and (e) 0.1× concentration. The spacer is AEEA. All of the scale bars are 1μm.

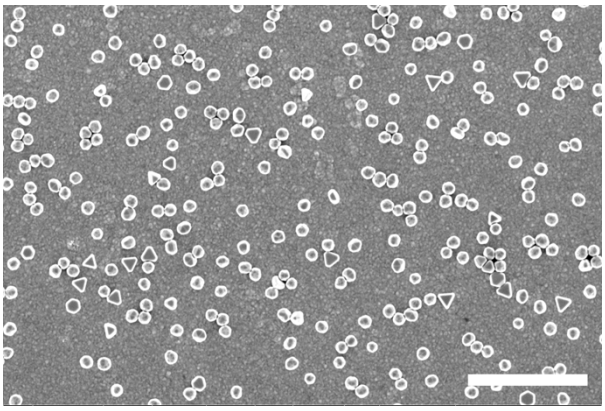

Fig. S2 SEM image of NP-film caliper using APTMS as the spacer. The concentration of Au NP colloidal solution is 1×. The scale bar is 1μm.

Discrimination between amino acids using NP-film calipers

The spatial molecular structures of these three thiol-containing amino acids are similar, especially those of Cys and Hcy. Because their molecular weights are quite close (Cys: 121.16 g/mol; Hcy: 135.18 g/mol; GSH: 307.32 g/mol), it is rather difficult to discriminate among them using conventional plasmonic sensors to measure changes in refractive index. Fig. S3a reveals the molecular structures of these three amino acids; their spatial lengths differ only on the angstrom scale. We took advantage of the plasmonic gap mode, which is highly sensitive to variations in the gap spacing, to test whether our caliper system could discriminate between these three amino acids. We used SAMs of the three amino acids as gap spacers in the 100-nm NP-film calipers; the ellipsometric thicknesses of the Cys, Hcy, and GSH monolayers were 6.1, 7.2, and 8.6 Å, respectively. Because of their different spatial lengths, the immobilized NPs were separated from the film at distinct distances (Fig. S3b). The short incubation time (30 min) and the presence of other functional groups (e.g., carboxyl) prevented the molecules from stretching and standing normal to the surface; therefore, the loose monolayers of these thiol-containing amino acids were not as thick as those predicted for amino-terminated alkanethiols having the same number of carbon atoms in their chain.[1, 2] SE data revealed that the plasmonic wavelengths of the three systems were shifted measurably (Fig. 6a and 6b). In the tan(Ψ) spectra (Fig. 6a), the plasmonic wavelength of the Cys system was the highest (ca. 825 nm) among the three systems, due to Cys being the shortest molecule. In addition, the Cys system exhibited the most-pronounced coupling of the plasmonic gap mode, leading to the deepest drop in the signal in the tan(Ψ) spectra. The plasmonic wavelength of the Hcy system underwent an obvious blue-shift (to ca. 816 nm) relative to the signal of the Cys system. Although an Hcy molecular spacer is thicker than a Cys molecular spacer

by approximately 1.1 Å, the plasmon wavelength shifted by approximately 7 nm, indicating that the NP-film caliper is a highly sensitive biosensor with angstrom-scale capability. Moreover, when the gap spacer was the thicker GSH molecule (length: ca. 8.6 Å), the plasmon wavelength shifted further, down to 802 nm. The resulting gap spacing–dependent wavelength shift, approximately 9 nm/Å (Fig. 6c), is superior to those reported previously (ca. 5–7 nm/Å).[3] We observed similar phenomena in the cos(Δ) spectra (Fig. 6b). The wavelengths of the spectral peak were located at different regimes when using Cys, Hcy, and GSH as the gap spacer molecules. In addition, because the density of NPs was associated with the concentration of Cys, Hcy, and GSH, the dip in the tan(Ψ) spectra was less pronounced when the amino acid solutions had been diluted (Fig. S3c), with the peak intensity in the cos(Δ) spectra decreasing as well (Fig. S3d).

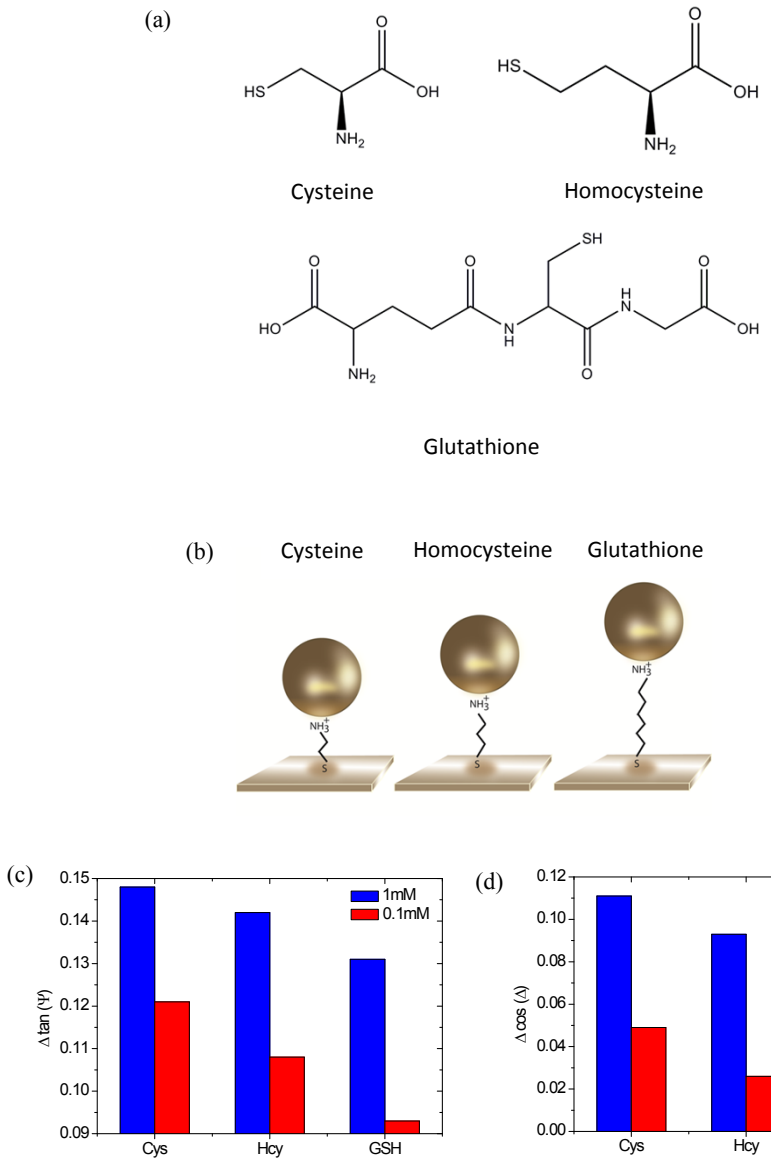

Fig. 6 (a) Chemical structures of Cys, Hcy, and GSH. (b) Schematic representations of SAMs of Cys, Hcy, and GSH as spacers between the NPs and the film. The spatial lengths of Cys, Hcy, and GSH determined the gap spacings in these NP-film calipers. (c, d) Changes in SE (f) tan(Ψ) and (g) cos(Δ) spectra of NP-film calipers featuring Cys, Hcy, and GSH as spacers (prepared at 1 and 0.1 mM).

Reference

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