Electronic Supplementary Information: Characterization of ultra-thin nanoporous gold films for improving performance of SPR biochemical sensors

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Experimental and calculation details

Materials

Sputtering targets of chromium (99.999% pure Cr), Au (99.999% pure Au) and $Au_{35}Ag_{65}$ alloy purchased from Trillion Metal Co., Ltd. were used to deposit metal films. Nitric acid (68 wt% HNO_3) was purchased from Sinopharm Group Co., Ltd. and used to dissolve the component of Ag. 1-mm-thick slide glass substrates (BK7, n = 1.522 @ 633 nm) were purchased from Matsunami Glass Co., Osaka, Japan.

Ultra-thin NPG film-modified SPR chip fabrication

A sputtering-dealloying combined method is employed to prepare the ultra-thin NPG (UTNPG) film according to the following steps: (i) a 3-nm-Cr layer was sputtered on the cleaned glass substrates to strengthen the adhesion of the upper layer to the glass substrates; (ii) a 50-nm-Au layer was sputtered on the Cr layer to protect the Cr from dissolution in HNO_3 during the following dealloying process; (iii) an ultra-thin Au-Ag alloy film was successively sputtered on the Au layer; (iv) the films-covered glass substrates were immersed in HNO_3 at room temperature to dissolve the Ag component from the alloy film, accompanied with the self-assembly of Au atoms on the substrate. After the dealloying, the substrates were removed out of the HNO_3 and thoroughly rinsed with deionized water and completely dried with nitrogen gas.

Fresnel equation and Bruggeman effective medium approximation

A four-layer (glass/Au/UTNPG/dielectric) Fresnel formula express as:

$$R_{TM} = |r_{1234}|^2 = \left|\frac{r_{12} + r_{234}e^{i2k_2d_2}}{1 + r_{12}r_{234}e^{i2k_2d_2}}\right|^2, \tag{S1}$$

with

$$r_{234} = \frac{r_{23} + r_{34}e^{i2k_3d_3}}{1 + r_{23}r_{34}e^{i2k_3d_3}} \tag{S2}$$

$$r_{ij} = \frac{n_jk_i - n_ik_j}{n_jk_i + n_ik_j}, i = 1, 2, 3; j = i + 1 \tag{S3}$$

$$k_i = \frac{2\pi}{\lambda}\left(n_i^2 - n_1^2 sin^2\varphi\right)^{1/2}, i = 1, 2, 3, 4 \tag{S4}$$

where $\varphi = \pi/4 + \sin^{-1}\left(\sin(\theta)/n_1\right)$ is the total internal reflection angle at the metal/glass interface of the SPR chip; θ is the incident angle between the collimated beam and the normal of the prism's refracting face; n_i is refractive index (RI) of the *i*th layer of the SPR chip, and the first layer is the glass substrate; k_i is the wavevector component in the direction normal to the interface; r_{ij} is the Fresnel reflection coefficient at the interface between the ith layer and the jth layer; d_2 is the thickness of the Au film; d_3 is the thickness of the UTNPG film.

In the calculation process, the glass RI (n_1) is RI of BK7 glass. The complex RI of Au film (n_2) is obtained from the published literature.[S1] n_3 is the effective complex RI of the UTNPG film according to the Bruggeman approximation (Eq. S5),[S2] and n_4 is the RI of air or water.

$$f_1\frac{n_2^2 - n_3^2}{n_2^2 + 2n_3^2} + f_2\frac{n_4^2 - n_3^2}{n_4^2 + 2n_3^2} + f_3\frac{n_a^2 - n_3^2}{n_a^2 + 2n_3^2} = 0, \tag{S5}$$

where f_1, f_2, and f_3 are volume fractions of the Au skeleton and the pores and the adsorbed analyte, respectively; n_a is the RI of the adsorbed analyte.

It is needed to note that the effective complex RI of NPG is usually modeled by the Bruggeman effective medium approximation and the Lorontz-Drude (L-D) model. The L-D model can quantitatively describe the electrodynamic response of the material and is more suitable for evaluating the RI of NPG compared to the Bruggeman approximation in the mid-infrared (mid-IR) region.[S3] In the mid-IR region, the complex permittivity of NPG is well described with a 3-oscillator L-D model, while the permittivity of dense gold is expressed with a standard-2 oscillator L-D model.[S4] Due to the fact that the Bruggeman approximation models the effective permittivity of NPG by assuming the medium as a system of gold inclusions into a void matrix,[S5] there is a significant difference in the permittivity of NPG estimated using the L-D model and the Bruggeman approximation in the mid-IR region. However, in the visible near-infrared region, the permittivity of NPG can also be described with a 2-oscillator model.[S4] In this case, the complex permittivity of NPG obtained from the L-D model and Bruggeman approximation are close to each other, as shown in Fig. S1. The L-D parameters are from Table 1 in Ref. 4. This demonstrates that the complex permittivity (or refractive index) of NPG can be predicted by using the Bruggeman effective medium approximation. A similar result has been reported in the literature[S6].

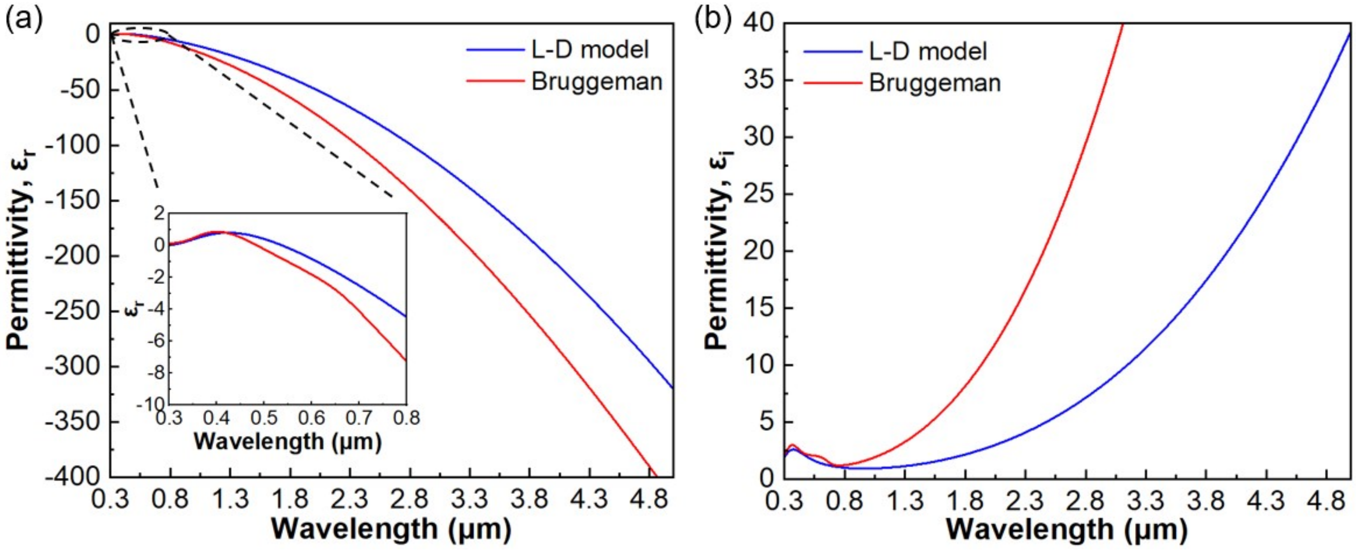

Fig. S1 Comparison of the (a) real and (b) imaginary parts of the permittivity of NPG determined by the L-D model and the Bruggeman effective medium approximation.

EDS spectra

Fig. S2 presents the EDS spectra before and after the dealloying process, including Ag (the composition of the Au-Ag alloy film), Au (the composition of the UTNPG film and the 50-nm-Au layer) and other elements (the compositions of the glass substrate). Because the detection depth of EDS is much larger than the thickness of the UTNPG and Au, the elemental compositions of the glass substrate were also detected. The residual silver in the UTNPG film is too little to be detected (Fig. S2b), implying that the complete dealloying was achieved.

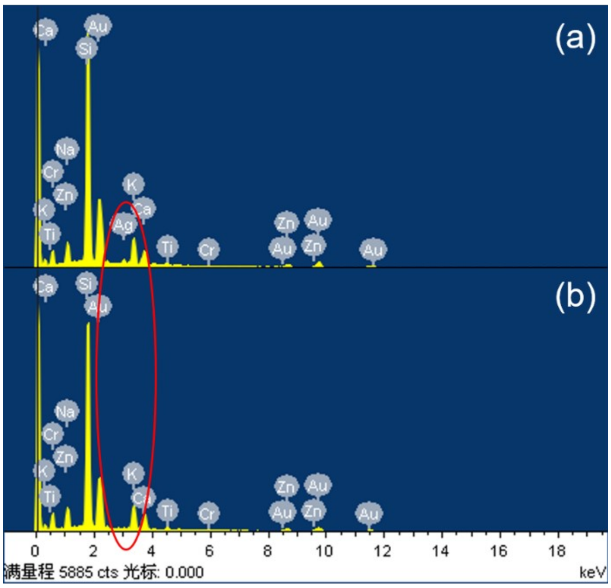

Fig. S2 EDS spectra of sensor chips with (a) the ultra-thin Au-Ag alloying film sputtering and (b) dealloying (i.e., UTNPG film)

Surface plasmon dispersion relation calculation for the UTNPG film-modified SPR chips

The UTNPG film-modified SPR (UTNPG-m-SPR) sensor chip consists of a glass substrate, a 50-nm-Au film and a UTNPG film. The surface plasmon traveling at the interface between the UTNPG film and the dielectric cladding can be excited by prism coupling and the propagation constant (β) can be obtained based on Eq. (S6):[S7]

$$\beta = \beta_0 + \Delta\beta = \frac{2\pi}{\lambda}\sqrt{\frac{\varepsilon_{NPG}\varepsilon_d}{\varepsilon_{NPG} + \varepsilon_d}} + \Delta\beta \tag{S6}$$

where β_0 is the propagation constant of the surface plasmon at the interface between dielectric cladding and NPG with infinite thickness, and $\Delta\beta$ is the contribution of the finite thickness of the UTNPG film and Au layer and the presence of the prism. λ is the wavelength of the incident light, and ε_d and ε_{NPG} are the real parts of the dielectric constant for the dielectric cladding and the UTNPG film, respectively. It is difficult to calculate β directly through Eq. (S1) due to many disturbance factors for $\Delta\beta$. Here, β was obtained by solving the resonance wavelength/frequency of the sensor chip at different incident angle (φ). Specifically, the SPR spectra under different φ at a certain porosity are obtained based on the Fresnel formula (Eq. S1-S4) and the resonance wavelength λ_R corresponding to each φ is obtained. By this way, β can be expressed by $\beta = \sin\varphi \cdot n_{glass}\omega/c$, where $\omega = 2\pi c/\lambda$.

Thicknesses of as-prepared ultra-thin Au-Ag alloy films

The simulated spectra of SPR sensors with different thicknesses of ultra-thin Au-Ag alloy films were calculated based on the four-layer (glass/Au/Au-Ag/air) Fresnel formula (Fig. S3a). The complex RI of Au-Ag alloy is obtained from the literature.[S8] The thickness of Au-Ag alloy films in No. 1 and No. 2 were estimated to be 4.2 nm and 11.3 nm, respectively, by fitting the $\Delta\lambda_R$ that is closest to the experiment data (Fig. S3b), which is similar to the UTNPG film in No. 1 and No. 2 (i.e., 4.5 nm for No. 1 and 11.9 nm for No. 2).

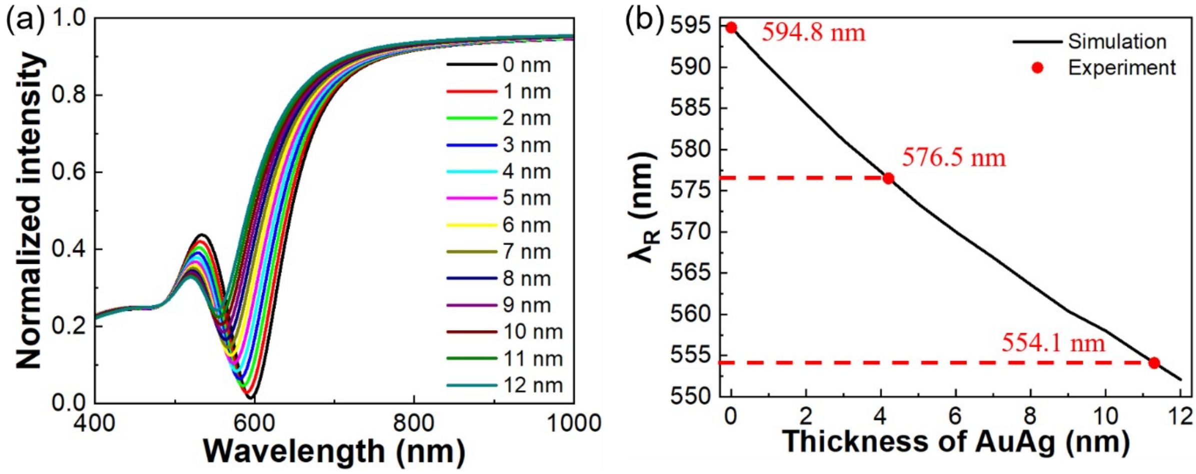

Fig. S3 (a) The simulated spectra of SPR sensor with different thicknesses of ultra-thin Au-Ag alloy films; (b) fitting the $\Delta\lambda_R$ to the experiment data.

Ellipsometry

The thickness of the UTNPG film in No. 1 was determined by an ellipsometer (M-2000DI, J.A. Woollam Co., Inc.) and its built-in fitting model. The substrate was set as BK7, layer 1 was set as Au and layer 2 was set as the effective medium approximation (EMA) based on Bruggeman analysis mode. The thickness of layer 2 was fitted to be 3.28 nm with the mean squared error (MSE) of 21.065.

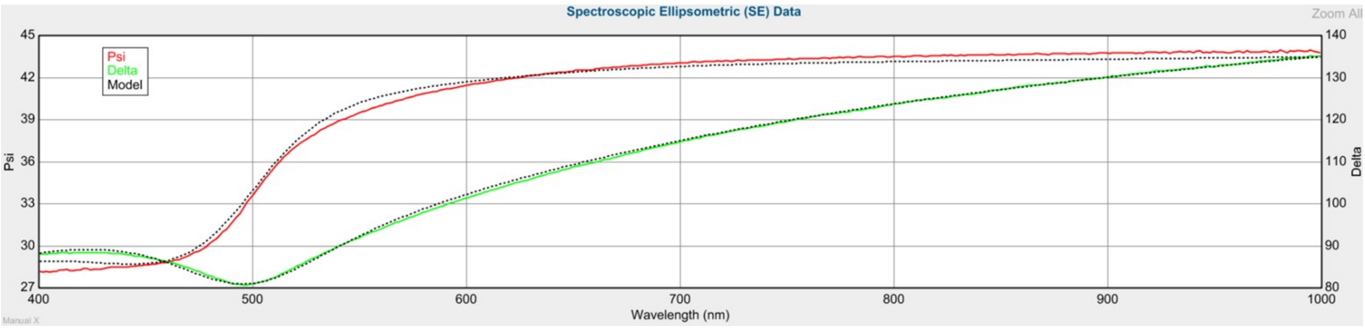

Fig. S4 Ellipsometry data for the UTNPG film in No. 1

Sensing properties and sensitivity enhancement of UTNPG-m-SPR sensors

Table S1 The RI of different concentrations of cysteamine solutions measured by an Abbe refractometer

[C]	0 nm	1 nm	10 nm	100 nm	1 μM	10 μM	100 μM	1 mM	10 mM
First test	1.3324	1.3326	1.3326	1.3322	1.3324	1.3324	1.3322	1.3322	1.3323
Second test	1.3324	1.3322	1.3325	1.3326	1.3323	1.3323	1.3323	1.3324	1.3325
Third test	1.3326	1.3324	1.3324	1.3325	1.3324	1.3322	1.3326	1.3323	1.3326

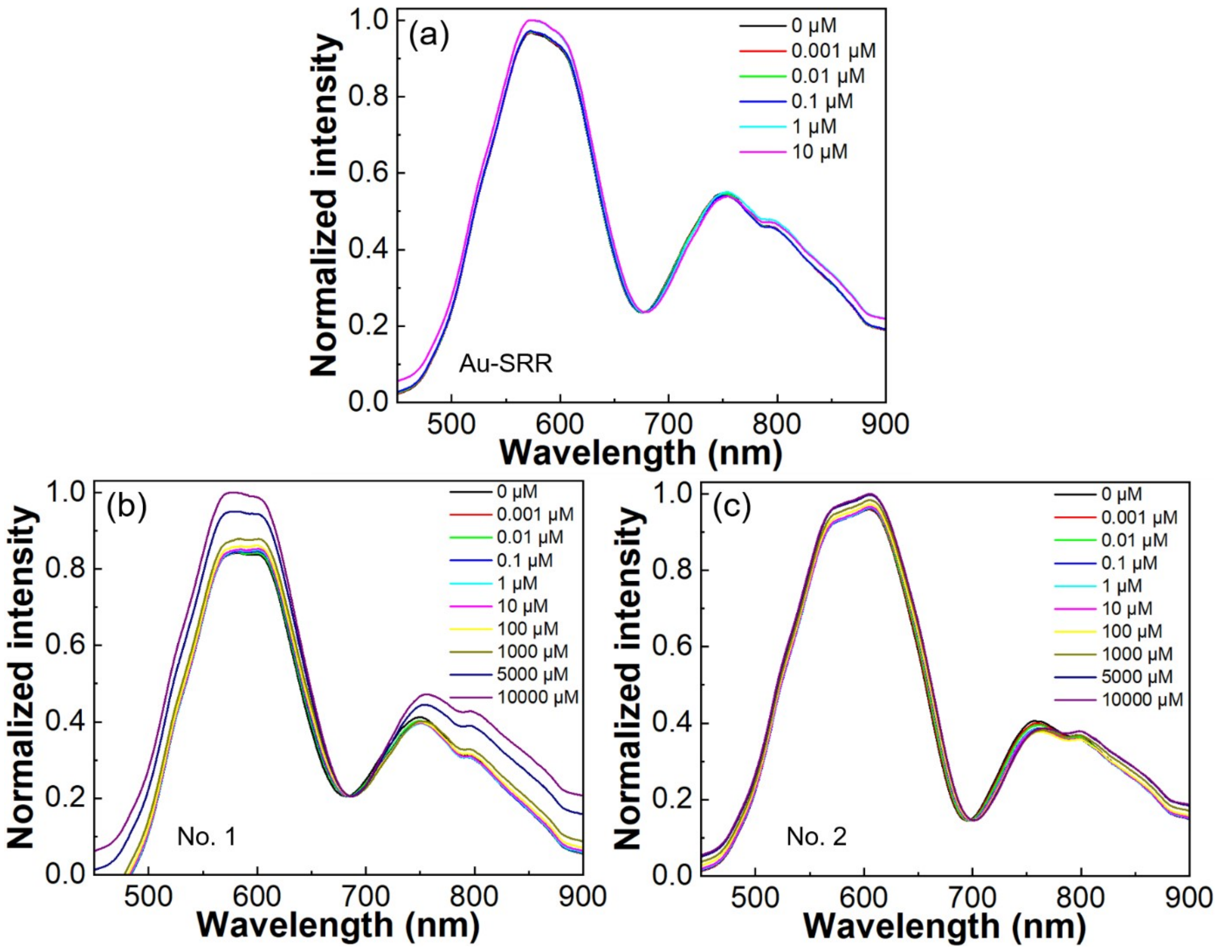

Fig. S5 The spectra measured at each cysteamine solution concentration for (a) Au-SPR, (b) No. 1 and (c) No.2

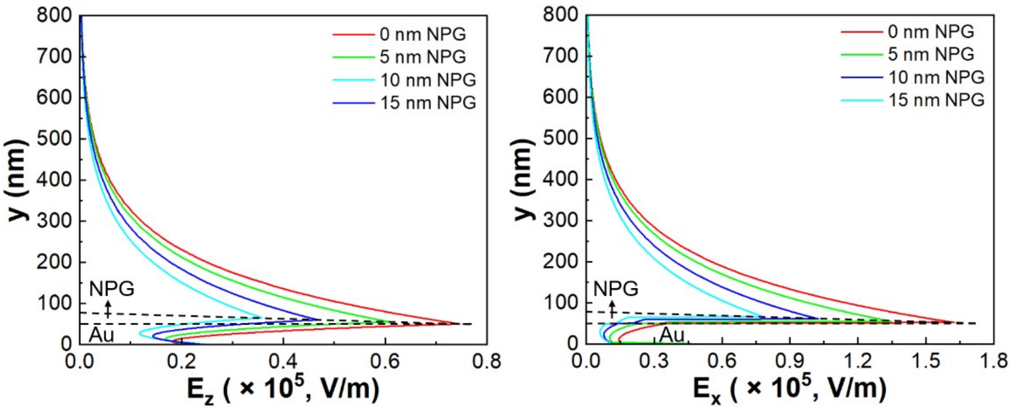

Fig. S6 The electric field distribution of z and x components (i.e., E_z and E_x)

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