**Supporting information**

# Localized surface plasmon resonance sensor based on wavelength-tunable spectral dips

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## Mechanisms of multiple dip formation.

The Ag NR ensemble on $TiO_2$ involves NRs with various aspect ratios. Irradiation at wavelength $\lambda_1$ excites three different types of NRs: (1) NRs of $\lambda_{m=1} = \lambda_1$, (2) NRs of $\lambda_{m=2} = \lambda_1$, and (3) NRs of $\lambda_{m=3} = \lambda_1$, where $\lambda_{m=x}$ is the resonance wavelength of the $x$th-order plasmon ($x$ = 1 for dipole and $x \geq 2$ for multipole) (Figure S2). All those NRs are oxidized and shortened by the excitation. Oxidation of (1) NRs of $\lambda_{m=1} = \lambda_1$ , (2) NRs of $\lambda_{m=2} = \lambda_1$, and (3) NRs of $\lambda_{m=3} = \lambda_1$, gives rise to dip formation at $\lambda_1$ (dip 1), $\lambda_2$ (dip 2, $\lambda_2 > \lambda_1$), and $\lambda_3$ (dip 3, $\lambda_3 > \lambda_2$), respectively. $\lambda_2$ is dipole resonance wavelength of NRs of $\lambda_{m=2} = \lambda_1$, and $\lambda_3$ is dipole resonance wavelength of NRs of $\lambda_{m=3} = \lambda_1$. Note that dipole peaks are much more prominent than multipole peaks, so that the dips observed are due only to dipole resonance. Explanation in further detail is given elsewhere (*J. Phys. Chem. C* 2013, 117, 2435−2441).

As we previously reported, even order plasmon modes ($m$ = 2, 4, ...) of the NRs are optically forbidden at perpendicular incidence ($\theta = 0°$), because the electrical polarizations are canceled out in integration along the long axis. Therefore, we irradiated the sample with light at oblique incidence ($\theta = 30°$) to obtain the largest number of dips.

## Figures

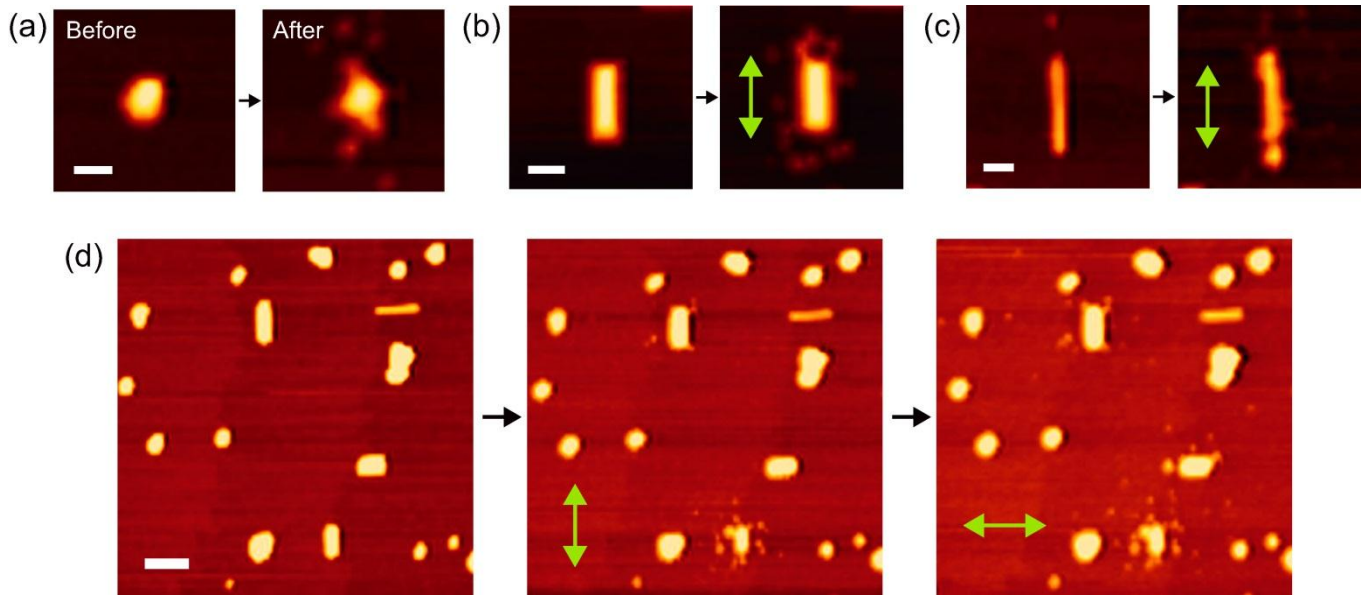


**Fig. S1** Typical AFM images of (a) a Ag NS before and after irradiation with 560 nm light (3 mW $cm^{-2}$, 30 min), (b) a Ag NR before and after irradiation with 900 nm light (10 mW/$cm^2$, 60 min) for excitation of the longitudinal dipole plasmon mode ($m$ = 1), and (c) a Ag NR before and after irradiation with 800 nm light (10 mW $cm^{-2}$, 60 min) for excitation of the longitudinal multipole plasmon mode ($m$ = 3). The size of NS (a) and the aspect ratio of NRs (b, c) decreased by oxidation. The small satellite Ag NPs deposited around the mother NPs after irradiation are NPs redeposited due to recombination of $Ag^+$ ions released from the mother NPs into adsorbed water with electrons transferred from the mother NPs to $TiO_2$. (d) AFM images at the same area before (left) and after sequential irradiation with perpendicularly polarized 900 nm light for excitation of the longitudinal mode, which indicate the aspect ratio- and polarization-selective oxidation of the Ag NRs. Green arrows indicate the direction of incident electric field. Scale bars are 50 nm in (a-c) and 100 nm in (d).

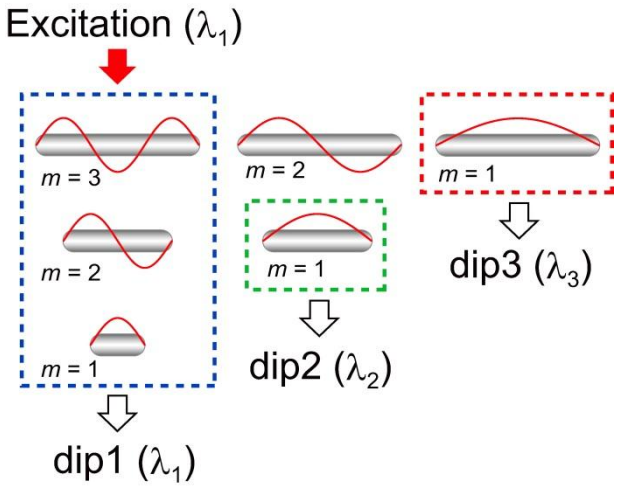


**Fig. S2** Mechanism of the formation of extinction dips at $\lambda_1$, $\lambda_2$, and $\lambda_3$ by excitation of the dipole ($m$ = 1) and multipole ($m$ = 2, 3) plasmon mode of Ag NRs at $\lambda_1$.

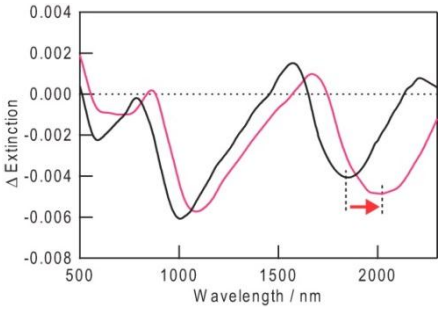


**Fig. S3** (Black line) Difference spectrum of Ag NRs on $TiO_2$ in air ($n$ = 1) after formation of dips by polarized light at 1000 nm. (Red) Difference spectrum of Ag NRs on $TiO_2$ in the sucrose solution in $D_2O$ ($n$ = 1.41). Arrow indicates dip shift for dip2.

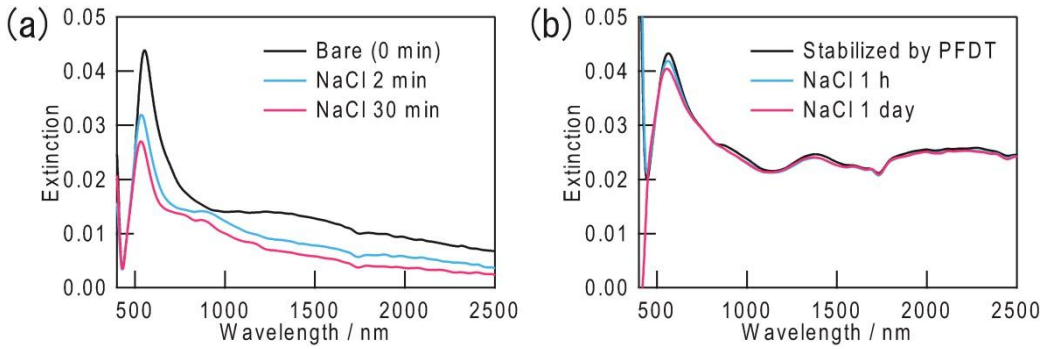


**Fig. S4** Spectral changes of the Ag NRs-$TiO_2$ sample (a) without and (b) with a PFDT SAM during immersion in 0.9 wt% NaCl aqueous solution.