Electronic Supplementary Information

Controlled Preparation of $Au/Ag/SnO_2$ Core-Shell Nanoparticles Using a Photochemical Method and Applications in LSPR based Sensing

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Experimental Section

Chemicals and Materials

Hexadecyltrimethylammoniumbromide (CTAB) (98%), sodium borohydride (99%), gold(III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$) (99.9%) and sodium stannate trihydrate ($Na_2SnO_3 \cdot 3H_2O$)(95%) were purchased from Sigma-Aldrich. Silver nitrate ($AgNO_3$) and L-(+) -ascorbic acid were purchased from Alfa Aesar. De-ionized water was used in all the experiments.

Synthesis of Gold nanorods (Au NRs):

Au NRs were prepared by using a previously reported seed-mediated growth method.[1] The seed solution was first prepared by adding 250 μL of 0.01 M $HAuCl_4$ to 10 mL of 0.1 M CTAB solution in a plastic tube. 0.6 mL of freshly prepared ice-cold 0.01 M $NaBH_4$ solution was quickly added and mixed by gentle shaking for 2 min. The resultant brownish yellow solution was kept at room temperature for at least 2 h before used as the seed solution. In the seed-mediated growth step, 2.0 mL of 0.01M $HAuCl_4$ and 0.27 mL of 0.01 M $AgNO_3$ were added into 40 mL of 0.1 M CTAB solution and mixed by gentle shaking. 0.8 mL of 1.0 M HCl, 0.32 mL of 0.1 M freshly prepared L- (+) -ascorbic acid solution, and 96 μL of seed solution were then added into the mixture sequentially. The reaction mixture was left undisturbed at least 6 h for longitudinal overgrowth. Finally, CTAB capped Au NRs with longitudinal plasmon resonance band at 763 nm were obtained.

Preparation of Gold nanospheres (AuNSs):

20 nm CTAC capped AuNSs were prepared according to a previously reported three-step procedure.[2] Citrate-stabilized Au seeds with diameter of 3.5 nm were first prepared by the following steps. The mixture of sodium citrate (250 μL, 0.01 M) and $HAuCl_4$ (50 μL, 0.05M) was diluted with 9.4 mL of H_2O in a round bottom flask, followed by injection of ice-cold $NaBH_4$ (300 μL, 0.1 M) and mixed by vigorously stirring for 2 min. The obtained solution was kept in room temperature for at least 3 h before use. Au NSs with a diameter of 8 nm was subsequently prepared. $HAuCl_4$ (45 μL, 0.05 M) and freshly prepared L- (+) -ascorbic acid (50 μL, 0.1M) were added into CTAC solution (9 mL, 0.08 M). After mixing, 1 mL of previously obtained Au seed (3.5 nm) was injected. The mixed solution was stirred for 10 min to grow AuNSs with a diameter of 8 nm. At last, the resultant 8 nm AuNSs were used as seeds for the growth of CTAC capped Au NSs. $HAuCl_4$ (225 μL, 0.05 M) and L- (+) -ascorbic acid (250 μL, 0.1M) were added into 45 mL of CTAC (0.08 M) and mixed by gently shaking. 5 mL of 8 nm Au NSs solution was then added into the mixture under vigorously stirring, which was continued for 10 min. The mixture solution was kept at room temperature for 3 h before use. Finally, Au NSs with averaged diameters of 20 nm were obtained.

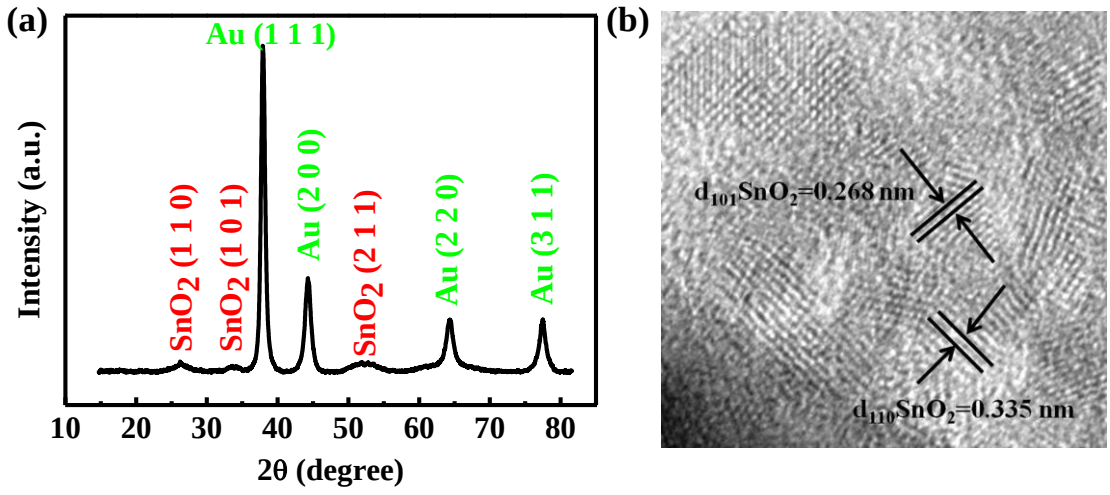

Figure S1 (a) XRD pattern of AuNR/SnO_2. (b) HRTEM image of AuNR/SnO_2, which was focused on the SnO_2 shell.

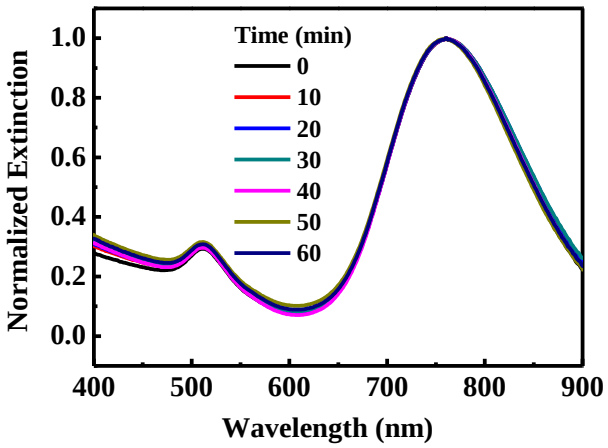

Figure S2 UV-Vis extinction spectra of Au NR reacted with $AgNO_3$ under UV light irradiation.

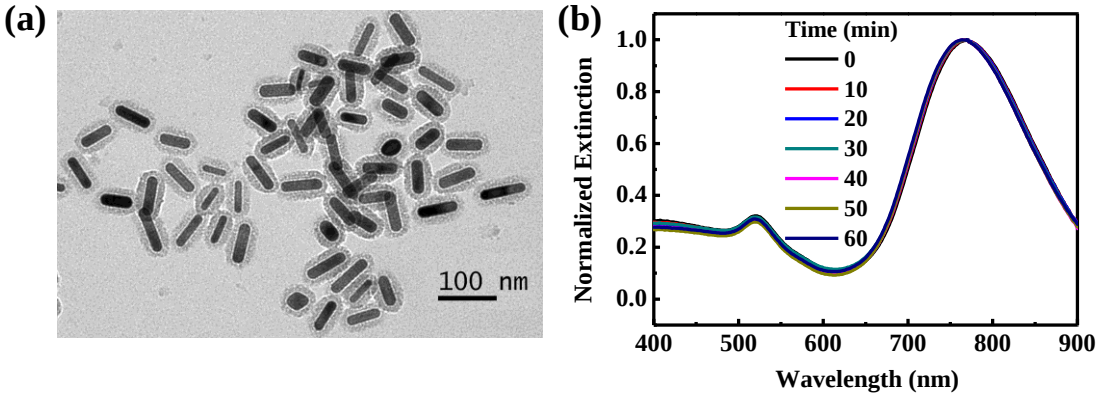

Figure S3 (a) TEM image of AuNR/SiO_2; (b) UV-vis extinction spectra of the AuNR/SiO_2 and $AgNO_3$ mixture solution under irradiation by UV light.

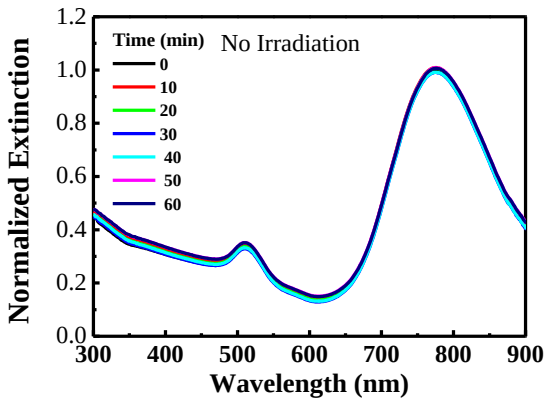

Figure S4 UV-vis extinction spectra of the AuNR/SnO_2 and $AgNO_3$ mixture solution without any light irradiation.

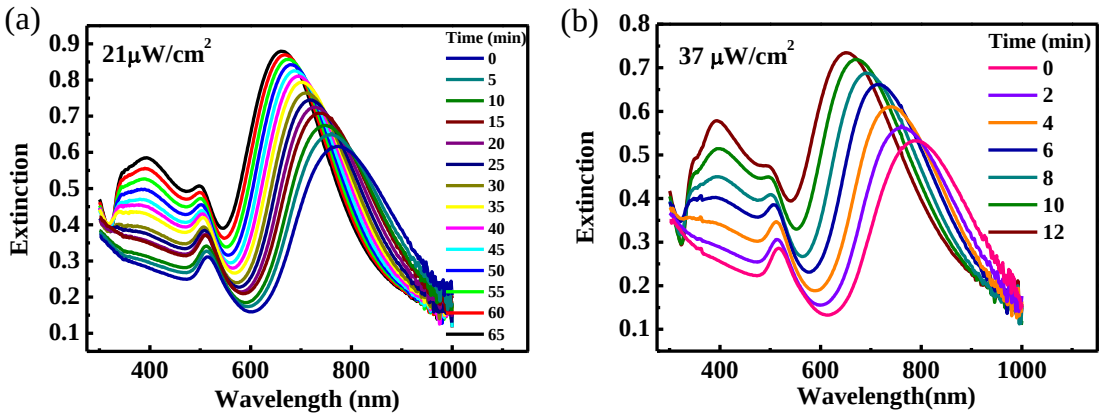

Figure S5 UV-vis extinction spectra of the mixture of Au/SnO_2 and $AgNO_3$ irradiation with UV light at intensity of 21μW/cm^2 and 37 μW/cm^2

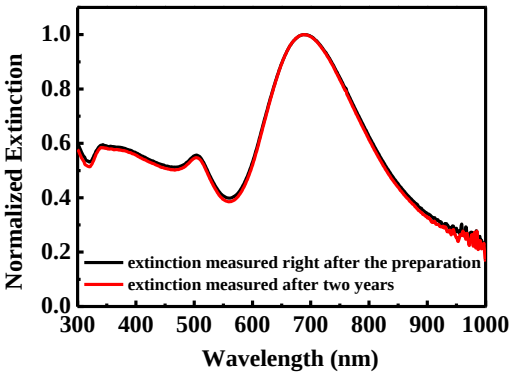

Figure S6 Extinction spectra of one $Au/AgNR/SnO_2$ sample measured right after preparation and after storage for two years.

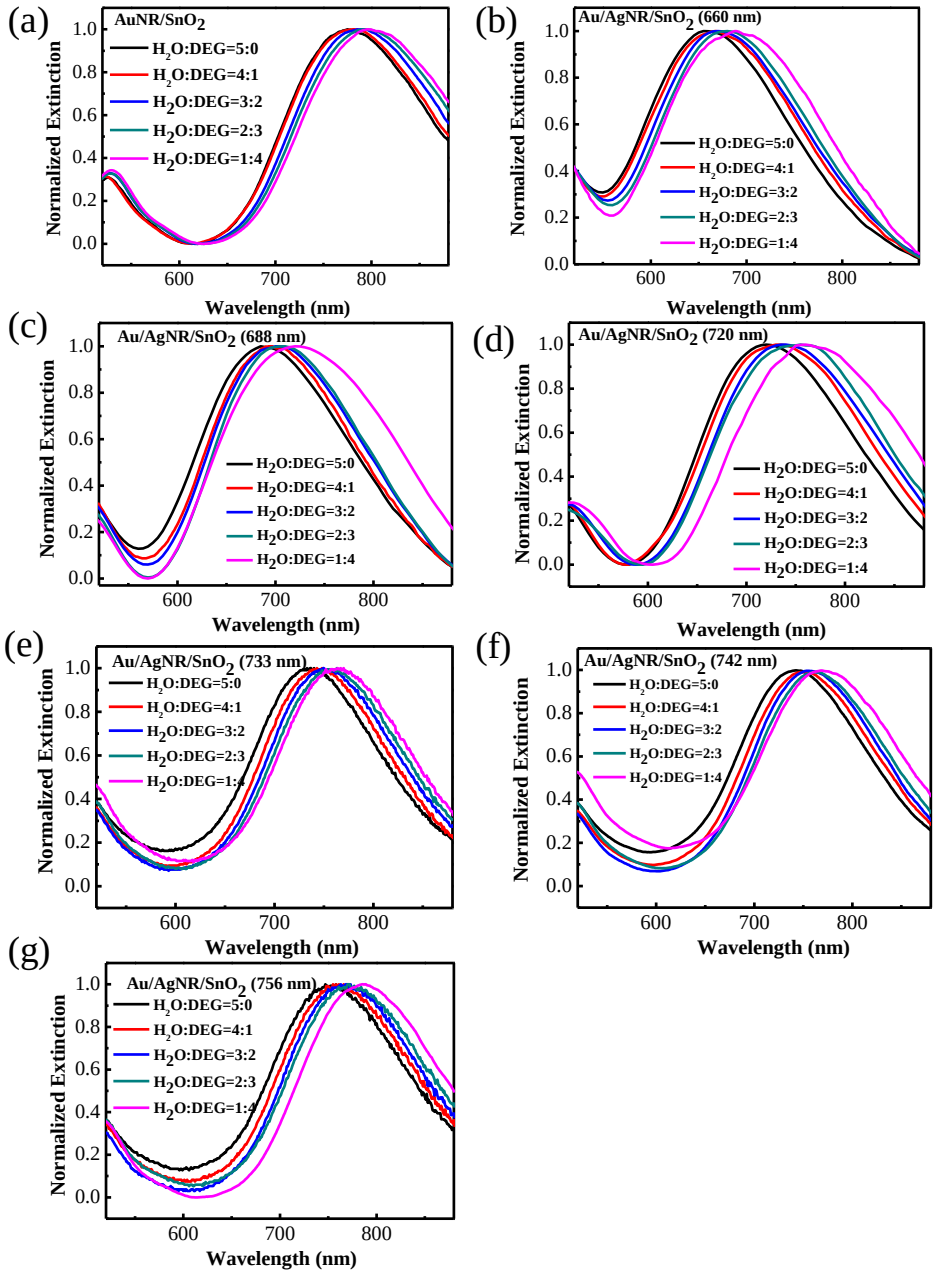

Figure S7 Normalized extinction spectra of AuNR/SnO_2 (a), Au/AgNR/SnO_2(660nm) (b), Au/AgNR/SnO_2(688nm) (c), Au/AgNR/SnO_2(720nm) (d), Au/AgNR/SnO_2(733nm) (e), Au/AgNR/SnO_2(742nm) (f) and Au/AgNR/SnO_2(756nm) (g) in water-DEG liquid mixture solvent of varying volume ratios.

Reference:

1. B. Nikoobakht and M. A. El-Sayed, *Chem. Mater.*, 2003, **15**, 1957-1962.

2. X. Kou, Z.. Sun, Z. Yang, H. Chen and J. Wang, *Langmuir*, 2009, **25**, 1692-1698.