Supplementary Information

The exclusive response of LSPR in uncapped gold nanoparticles towards silver ions and gold chloride ions

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Experimental details:

Materials: Gold trichloride ($AuCl_3$, Sigma Aldrich), tetraethyl orthosilicate (TEOS, SD Fine-Chem Limited (SDFCL)), ammonia solution (30%, Merck Millipore), (3-aminopropyl)-trimethoxysilane (APTMS, Sigma Aldrich), sodium borohydride ($NaBH_4$, SDFCL), sodium hydroxide (NaOH, SDFCL), trisodium citrate dihydrate (Merck Limited), hydrochloric acid (HCl, 37%, Merck Millipore), ethanol (HPLC grade, Commercial Alcohols). All chemicals were used as it is without any further purification.

Preparation of gold nanoparticles: The precursor (solution I) is prepared by taking 0.0303 g of $AuCl_3$ and adding 2 ml of ultrapure water to it followed by addition of 8.8 μl of HCl (37% w/w). Reductant solution (solution II) is prepared by adding 0.0400 g of NaOH (powdered crushed pellets) and 0.0376 g of $NaBH_4$ to 20 ml of ultrapure water. To prepare 3 nm AuNPs, 0.1 ml of solution I is diluted with 9.6 ml of ultrapure water followed by addition of 0.3 ml of solution II

under vigorous stirring conditions. The stirring is continued for 2 minutes followed by heating at 70 ^{0}C for 3 minutes. To prepare 7 nm AuNPs, the procedure is same only difference being addition of 1.1 ml of solution II instead of 0.3 ml.

The citrate capped gold nanoparticles (diameter = 10 nm) are prepared using Turkevich method by adding 2 ml of trisodium citrate (1 wt% in water) to 38 ml of $HAuCl_4$ (0.5 mM) solution boiling at 100 ^{o}C.

Preparation of APTMS functionalized silica nanoparticles: A modified Stober process proposed by Nozawa et al is used to prepare silica nanoparticles of 130 nm diameter.[1] For APTMS functionalization, 100 mg of the silica particles are added to an ethanolic solution (30 ml) of APTMS (0.3 ml) followed by stirring and heating (70 ^{0}C) for 2 hours under argon atmosphere. The functionalized silica particles are cleaned via repeated centrifugation and re-dispersion (in ethanol) process and dried in argon atmosphere.

Preparation of AuNP decorated silica nanoparticles: For attaching AuNPs (3 or 7 nm) over the silica nanospheres, functionalized silica (20 mg) is added to 10 ml of AuNP solution and mixture is sonicated for 5 minutes. Thereafter, the mixture is left undisturbed for 15 min and The product is cleaned via centrifugation and redispersion in ethanol. To attach 10 nm AuNPs over silica, the procedure is same only difference being amounts of silica and AuNP solution taken (24 mg of functionalized silica added to 40 ml of AuNP solution).

Characterization of samples: Transient absorption spectroscopy was carried out for AuNP film (with absorbance 0.01) on glass substrate samples. The output (800 nm, 1.5 W) of an amplified laser (1 kHz, 100 fs, Libra, Coherent) is used to generate the pump wavelength for transient absorption experiment. The pump light (400 nm) is achieved by frequency doubling the 800 nm light on a β-BBO crystal. A typical power of 2 μJ/pulse was maintained at the sample. A portion of the 800 nm light is focused on a translating CaF_2 crystal, housed inside TA spectrometer (ExciPro, CDP), to generate the white light continuum (350-800 nm). The probe light is split into probe and reference part to eliminate shot to shot fluctuation. A magic angle condition of 54.7^o was maintained to eliminate rotational anisotropy. The transmitted light is detected by a spectrometer (Horiba CP140-104) coupled with CMOS detector. A chirp correction file was generated by measuring the coherent signal from the solvent. The full width at half maxima of the corresponding cross correlation functions (after fitting in Surface Minor Pro) ranges between 100-200 fs in the entire probe wavelength. The spectra were background subtracted and chirp corrected by using same software. No appreciable photo-degradation was observed.

The extinction, transmission and reflection spectra of nanoparticle solutions and thin films were measured using PerkinElmer Lambda 950 UV-Vis spectrometer. TEM imaging was performed on JEOL 2100F FEG transmission electron microscope while SEM images were obtained using JEOL JSM-7600F. Open circuit voltage (V_{oc}) measurements were performed using a potentiostat/galvanostat (Metrohm Instruments-302 N) in a conventional three-electrode cell

configuration with AuNP coated FTO-glass (with 2 cm^2 area) acting as working electrode, platinum wire as counter electrode and Ag/AgCl as the reference electrode. KCl (0.1 M) was used as electrolyte during V_{oc} measurements.
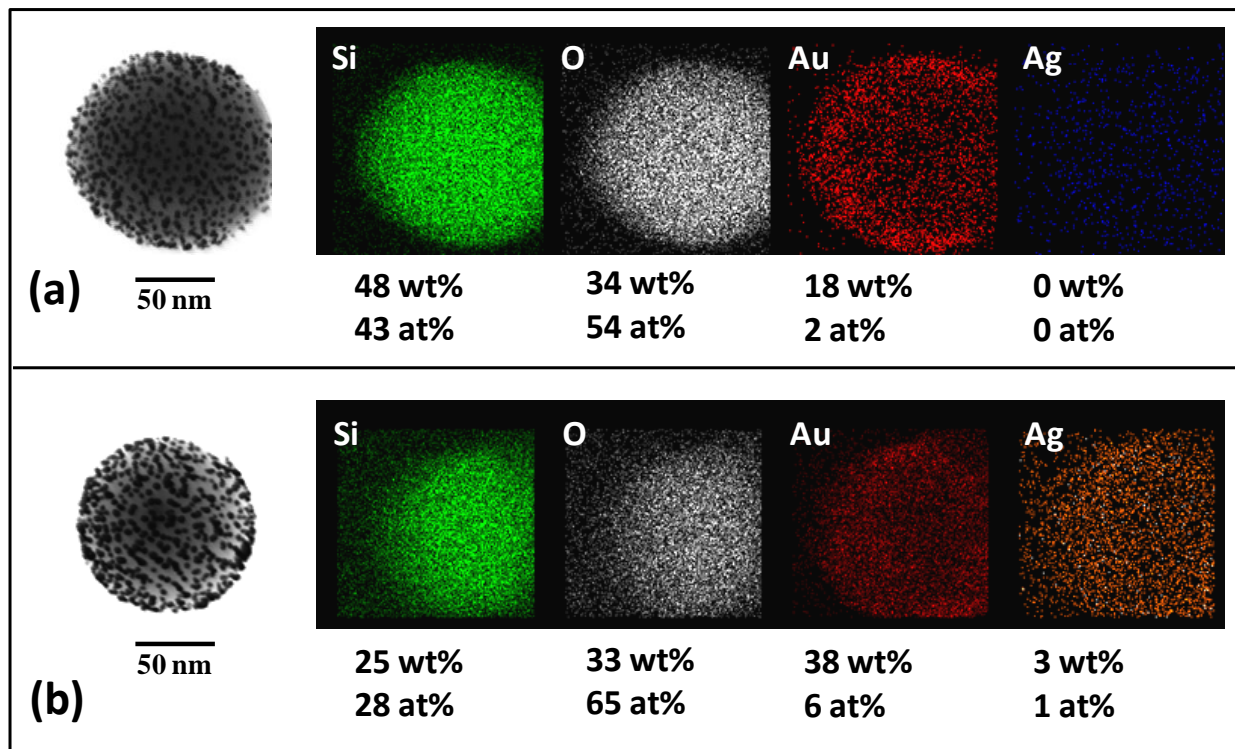

Fig. S1 EDX elemental color maps of SA3 particles taken in STEM mode (JEOL JEM 2100F) for (a) non-treated case, and (b) AgNO$_3$ treated case. (*Note: Weight percent of gold in (b) is considerably greater compared to (a) since silica particle in (b) is smaller in size.*)
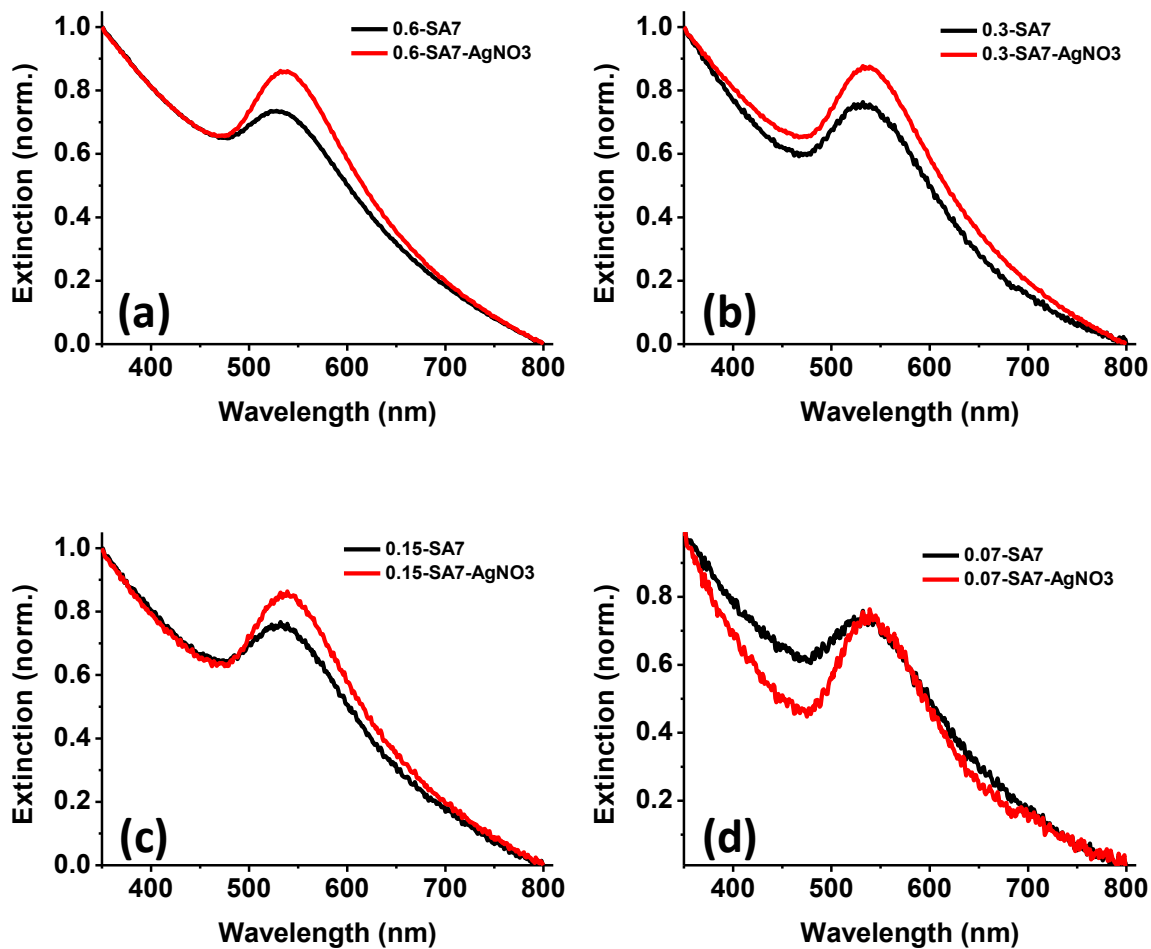
Fig. S2 Normalized extinction spectra (UV-visible spectra after normalization) of silica@AuNPs (AuNP diameter = 7 nm) at various particle concentrations before and after treatment with 10 mM AgNO$_3$. SA7 particle concentration is (a) 0.6 mg/ml, (b) 0.3 mg/ml, (c) 0.15 mg/ml, and (d) 0.07 mg/ml. the signal to noise ratio is high at/below 0.07 mg/ml concentration.
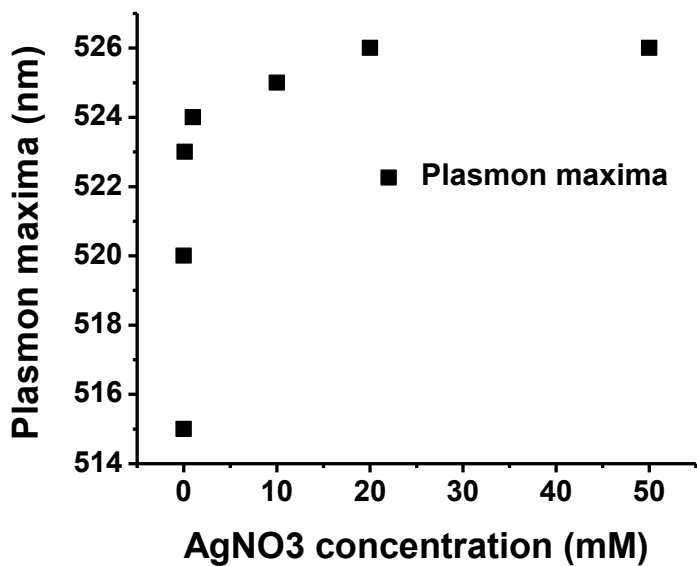
Fig. S3 Variation of plasmon maxima (3 nm AuNP monolayer over glass substrate) with concentration of $AgNO_3$. The plasmon shift saturates by 50 mM of $AgNO_3$ concentration.
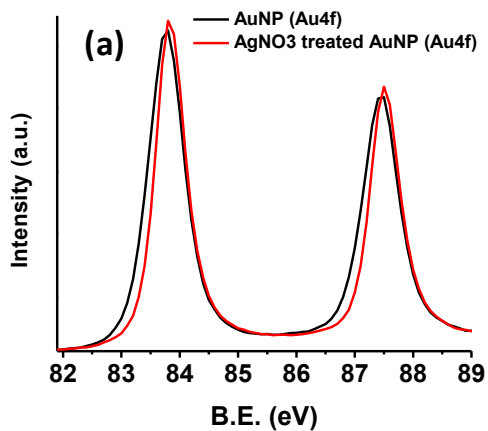

Fig. S4 XPS data shows blue-shift of $Au4f_{7/2}$ and $Au4f_{5/2}$ peaks after treatment of AuNP/glass (or Au3 system) with $AgNO_3$.
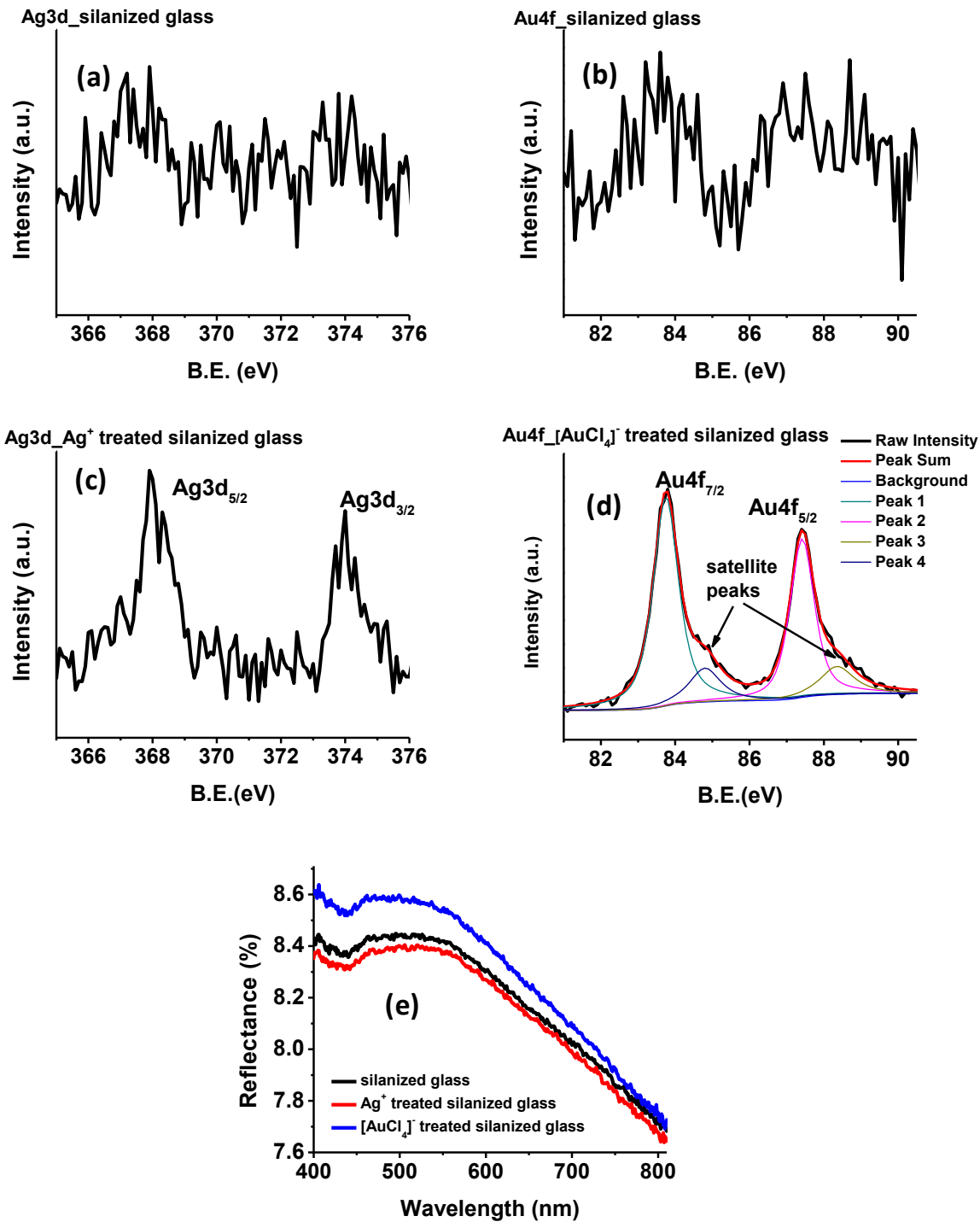
Fig. S5 XPS data shows (a) no presence of Ag in silanized glass substrate, (b) absence of Au silanized glass substrate, (c) presence of Ag in $AgNO_3$ treated silanized glass and (d) presence of Au in $AuCl_3$ treated silanized glass. (e) UV-Vis reflectance spectra shows absence of LSPR peak in $AgNO_3$ and $AuCl_3$ treated silanized glass substrate. XPS and UV-Vis studies suggest formation of Ag and Au atomic clusters on glass substrate after treatment with $AgNO_3$ and $AuCl_3$.

Effect of different ionic salts of Ag and Au on LSPR of SA3 particles

We also tested the effect of different salts of Ag and Au on LSPR of SA3 nanoparticles (Fig. S6, also refer Fig. 2b for comparison). It is found that anion attached to Ag or Au in salt does not affect the red-shift of LSPR and value of red-shift in LSPR of SA3 particles is same for different ionic derivatives of Ag and Au. For case of treatment of SA3 particles with $AgNO_3$ and Ag_2SO_4, the red-shift is nearly same (7 nm and 8 nm for $AgNO_3$ and Ag_2SO_4, respectively). Similarly, red-shift of LSPR after treating SA3 particles with $AuBr_4^-$ ions matches the value of red-shift for case of treatment with $AuCl_4^-$ ions. Even though $AuBr_4^-$ reduces easily (standard reduction potential = 0.858 V) compared to $AuCl_4^-$ (standard reduction potential = 0.93), the ease of reduction of $AuBr_4^-$ does not translate into greater shift in LSPR of SA3 due to anti-galvanic reaction.
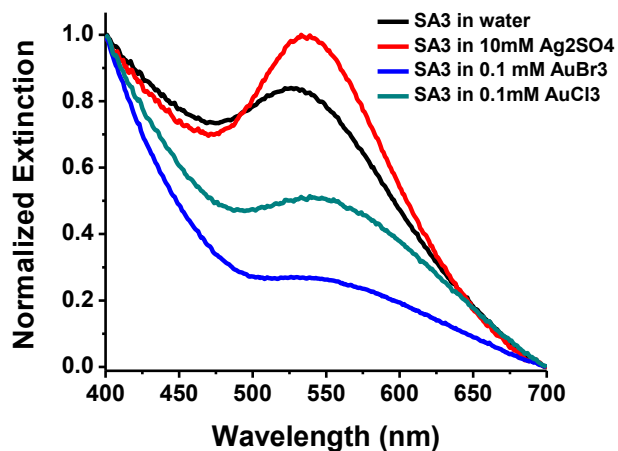

Fig. S6 Experimental extinction spectra (UV-visible spectra after normalization) of silica@AuNPs (AuNP diameter = 3 nm) showing red-shift in LSPR of SA3 particles after treatment with Ag_2SO_4, $AuBr_3$ and $AuCl_3$ solutions. The LSPR red-shifts by 8 nm, 18 nm and 18 nm for Ag_2SO_4, $AuBr_3$ and $AuCl_3$ ionic solutions, respectively.

TEM images suggesting formation of Ag and Au via nucleation around AuNPs and over aminosilanized silica

In order to confirm formation of Ag around AuNPs via anti-galvanic reaction, we did high resolution TEM imaging of SA3 particles. We observe AuNPs surrounded by crystalline features which have lighter contrast compared to AuNPs (Fig. S7a). Such crystalline features are likely to be Ag which deposit around spherical AuNP via anti-galvanic reaction. Since, lattice type and constant for Ag (0.407 nm) and Au (0.406 nm) is nearly same, we can not distinguish the respective elements by measuring distance between the lattice planes which are observed in high resolution TEM images. Due to ultrasmall Ag and Au features, attempts at elemental determination in EDX-STEM mode of imaging could not distinguish the Ag and Au over silica as reliable elemental determination was hindered by slightest drift of EDX spot. However, formation of Au dots over aminosilanized silica particles after treatment with freshly prepared 0.1 mM solution of $AuCl_3$ is seen in TEM images which confirms the finding from XPS studies. Thus, results from TEM imaging supplement the results from XPS study and confirm the formation of Ag and Au clusters around AuNPs and over the functionalized silica surface after treatment of SA3 particles with respective ionic solutions (Fig. S7b and S7c).
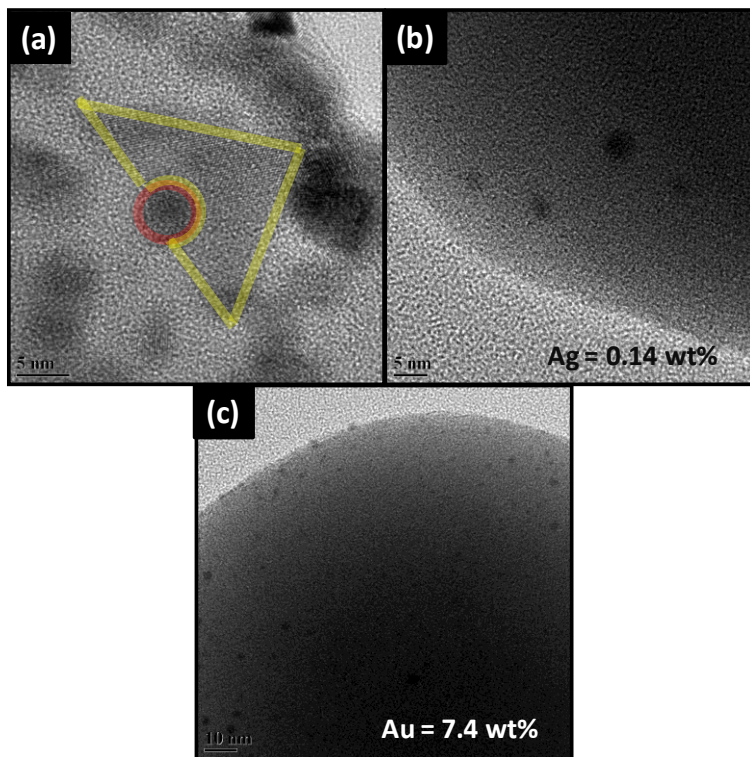

Fig. S7 (a) High resolution TEM image showing suspected formation of Ag (inside yellow boundary) around an AuNP (red circle) over silica after treatment of SA3 particles with AgNO3 solution. (b) and (c) TEM images showing formation of ultrasmall dots of Ag and Au seen over silica particle after treatment of aminosilanized silica with $AgNO_3$ and $AuCl_3$ solution, respectively.

Relation between LSPR and lifetime

The extinction cross-section of nanoparticle is given by[2]

$$\sigma_{ext} = \frac{9V\varepsilon_m^{3/2}}{c} \frac{\omega\varepsilon_2(\omega)}{[\varepsilon_1(\omega) + 2\varepsilon_m]^2 + [\varepsilon_2(\omega)]^2}$$

where,

$V = volume\ of\ spherical\ nanoparticle;$

$\varepsilon_m\ is\ dielectric\ constant\ of\ surrounding\ medium;$

$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)\ is\ the\ dielectric\ constant\ of\ nanoparticle;$

$c\ is\ the\ speed\ of\ light;$

$\omega\ is\ the\ frequency\ of\ incident\ light$

The dielectric constant of plasmonic nanoparticle depends

The dielectric constant of plasmonic nanoparticle is size dependent and following equation:[3]

$$\varepsilon(R,\omega) = \varepsilon_{bulk}(\omega) + \frac{\omega_p^2}{\omega(\omega + i\gamma_0)} - \frac{\omega_p^2}{\omega(\omega + i\gamma)}$$

where,

$R = radius\ of\ nanoparticle$

$\varepsilon_{bulk}(\omega)\ is\ bulk\ dielectric\ constant\ of\ material$

$\omega_p^2 = ne^2/(\varepsilon_0 m_{eff})$ is the bulk plasma frequency of material where 'n' is concentration of electrons

$\gamma\ is\ damping\ term\ dependent\ on\ fermi\ velocity\ (v_F)\ and\ radius$ [2]

$$\gamma(R) = \gamma_0 + i\frac{v_F}{R}$$

$\gamma\ can\ be\ expanded\ into\ addition\ of\ inverse\ of\ various\ electron\ relaxation\ times\ as$ [2]

$$\gamma = \sum_i (\tau_i)^{-1} = (\tau_{e-e})^{-1} + (\tau_{e-ph})^{-1} + (\tau_{e-d})^{-1}$$

$\tau_{e-e}\ is\ electron - electron\ relaxation\ time, \tau_{e-ph}\ is\ electron - phonon\ relaxation\ time\ and$

$\tau_{e-d}\ is\ the\ electron - defect\ relaxation\ time$

When the particle is excited by pump frequency, the electrons in particle are excited above Fermi energy and are called hot electrons. These hot electrons relax via various modes. Initially, there is non-Fermi distribution of electrons and they relax via electron-electron scattering ($\tau_{e\text{-}e}$). Thereafter, electrons lose their energy to lattice via electron-phonon ($\tau_{e\text{-}p}$) and electron-defect ($\tau_{e\text{-}d}$) scattering. The lattice finally relaxes via phonon-phonon scattering ($\tau_{p\text{-}p}$) loosing heat to surroundings.

References

1.   Nozawa, K.; Gailhanou, H.; Raison, L.; Panizza, P.; Ushiki, H.; Sellier, E.; Delville, J. P.; Delville, M. H., *Langmuir* 2005, **2**1, (4), 1516-1523.
2.   Link, S.; El-Sayed, M. A., *The Journal of Physical Chemistry B* 1999, **103**, (21), 4212-4217.
3.   Myroshnychenko, V.; Rodriguez-Fernandez, J.; Pastoriza-Santos, I.; Funston, A. M.; Novo, C.; Mulvaney, P.; Liz-Marzan, L. M.; Garcia de Abajo, F. J., *Chemical Society Reviews* 2008, **37**, (9), 1792-1805.