Supporting Information for

Light-Directed Growth/Etching of Gold Nanoparticles via Plasmonic Hot Carriers

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1. *Simulation details.*

1.1 FDTD simulations

FDTD method is used for simulating the scattering spectra of the Au NPs on Si substrate. The mesh setting for Au sphere and its surrounding medium inside the TFSF is 1 nm. In x and y directions, a broad band (450-850 nm) plane wave is applied with perfectly matched layer (PML) boundary condition. The scattering spectra are recorded by an analysis group located outside the total field scattering field (TFSF) source.

1.2 COMSOL simulations

COMSOL is applied to simulate the temperature changes of Au NPs in $HAuCl_4$ solutions on Si or Glass substrate during laser irradiation with 3D model geometry. We employ plane wave incidence and time-dependent heat conduction equation as follow:

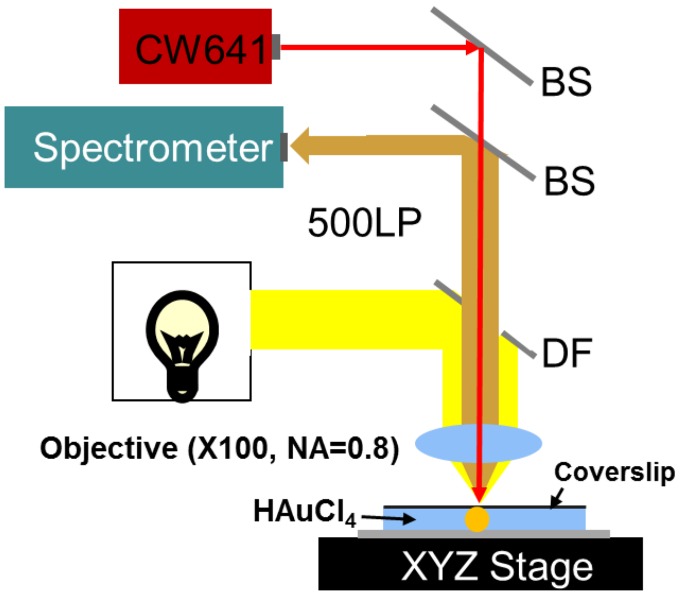
$$\rho(\vec{r})c(\vec{r})\frac{\partial T(\vec{r},t)}{\partial t} = \nabla \cdot [k(\vec{r})\nabla T(\vec{r},t)] + q(\vec{r},t)$$

Where $\vec{r}$ and t is the coordinate and time, $T(\vec{r},t)$ is the local temperature, and $\rho(\vec{r})$, $c(\vec{r})$, $k(\vec{r})$ are the material's mess density, specific heat capacity, thermal conductivity respectively. $q(\vec{r},t)$ is the heat produced by the total power dissipation of electromagnetic field which is measured in W/m^3.

The ambient boundary condition is defined as a constant temperature 293.15 K. The maximum meshing sizes of the Au NP, water, Si and Glass are set as 2 nm, 16 nm, 12 nm, and 12 nm, respectively. The material properties are listed in the table below:

Table S1. Materials properties adopted for COMSOL simulations.

Materials	Density[Kg/m^3]	Thermal conductivity [W/(m•K)]	Heat capacity [J/(Kg•K)]
Water	1.0	internal	4200
Au (JC)	19320	318	129
Si (Aspnes)	2329	130	700
Glass	1.45	1.3	940



Scheme S1. Experimental setup for the irradiation and spectroscopy.

2. Extra Supporting figures

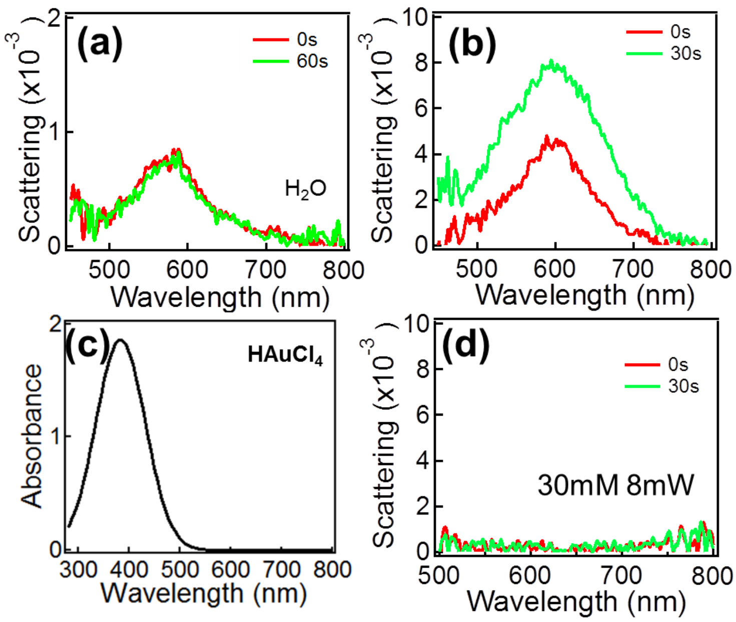


Figure S1. Control experiments on the optical growth mechanism. Scattering spectra of Au NPs before and after laser irradiation (a) in pure water, (b) in $HAuCl_4$ solution (10 mM) but residue citrate ligands on Au were removed via O_2 plasma, (c) Absorbance spectra of $HAuCl_4$ (10 mM) solution. (d) Scattering spectra of Si substrate (immersed in 30mM $HAuCl_4$ solution) irradiated by 641 nm laser (8 mW).

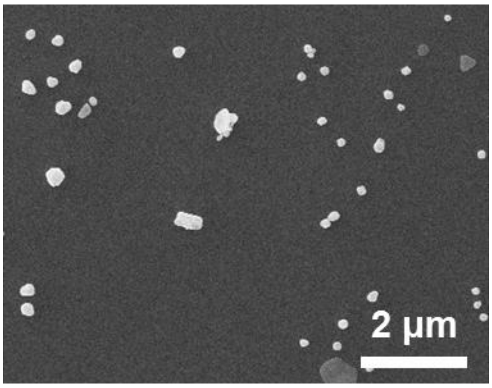


Figure S2. SEM images of Au NPs generated by irradiating $HAuCl_4$ (10 mM) with 446 nm laser on Si substrate.

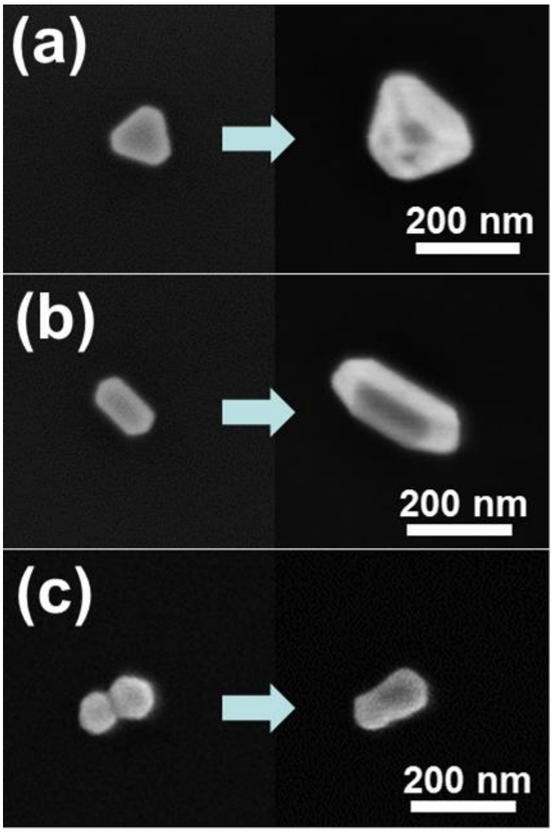


Figure S3. Generality of plasmon-mediated optical growth. SEM images of Au NPs before and after 641nm laser irradiation (4 mW, 30 s) with the presence of $HAuCl_4$ (10 mM). (a) Au nanoplate, (b) Au nanorod, (c) Au nanodimer.

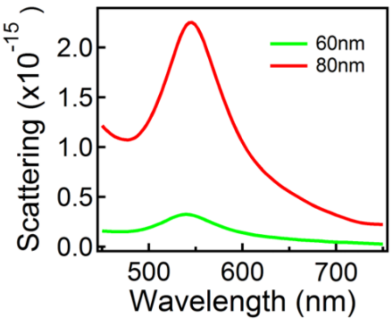


Figure S4. Scattering spectrums simulated by FDTD method of 80 nm and 60 nm Au NPs on Si substrate.

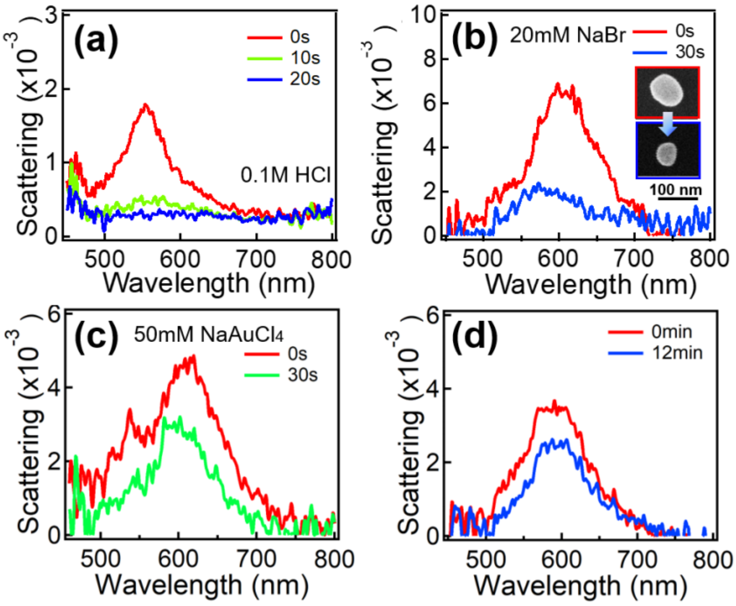


Figure S5. Scattering spectra of Au NPs before and after the irradiation under different conditions. (a) in 10 mM $HAuCl_4$ solution containing 0.1 M HCl. (b) in 1 mM $HAuCl_4$ solution containing 20 mM NaBr. (c) in 50 mM $NaAuCl_4$ solution (pH=6). (d) The scattering spectra of Au NPs before and after thermally heated at 60 ˚C in $HAuCl_4$ solution (20 mM) for 12 mins.

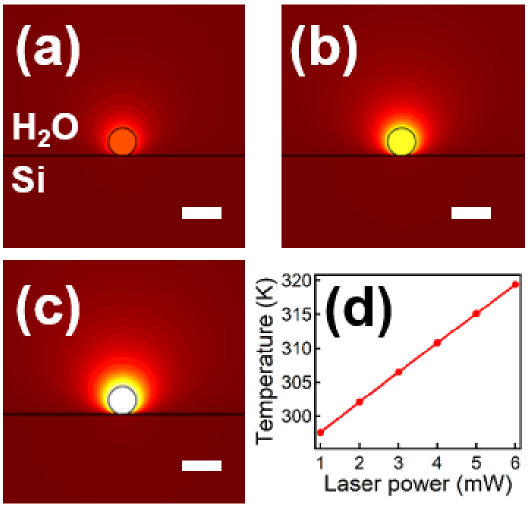


Figure S6. COMSOL simulations of the temperature distribution around the Au NP when irradiated with 641 nm laser and different powers on Si substrate in H_2O. (a) 2 mW. (b) 4 mW. (c) 6 mW. (d) Change of surface temperature with laser power. Scale bars are 100 nm

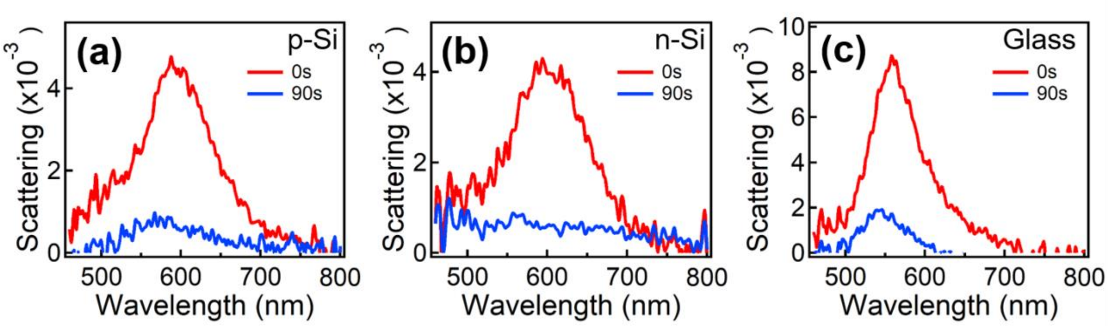


Figure S7. Scattering spectra of Au NPs before and after the irradiation on different substrates. (a) p-type Si, (b) n-type Si, (c) Glass. The laser power is 6 mW and the $HAuCl_4$ concentration is 20 mM.

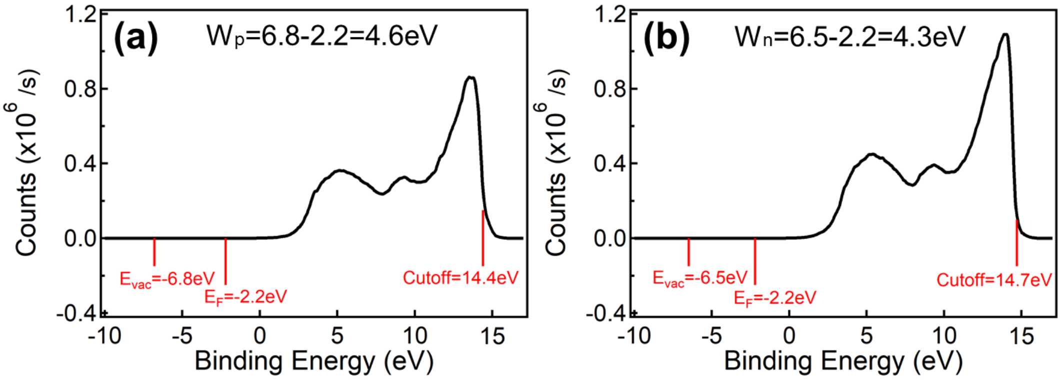


Figure S8. UPS spectra of (a) p-type and (b) n-type Si.