

# Site-Selective Growth of Ag Nanoparticles Controlled by Localized Surface Plasmon Resonance of Nanobowl Arrays

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**S1. Scanning electron microscopy (SEM) image of the Au nanobowl after the plasmonic chemical reaction illuminated by green light or blue light for a plasmonic chemical reaction.**

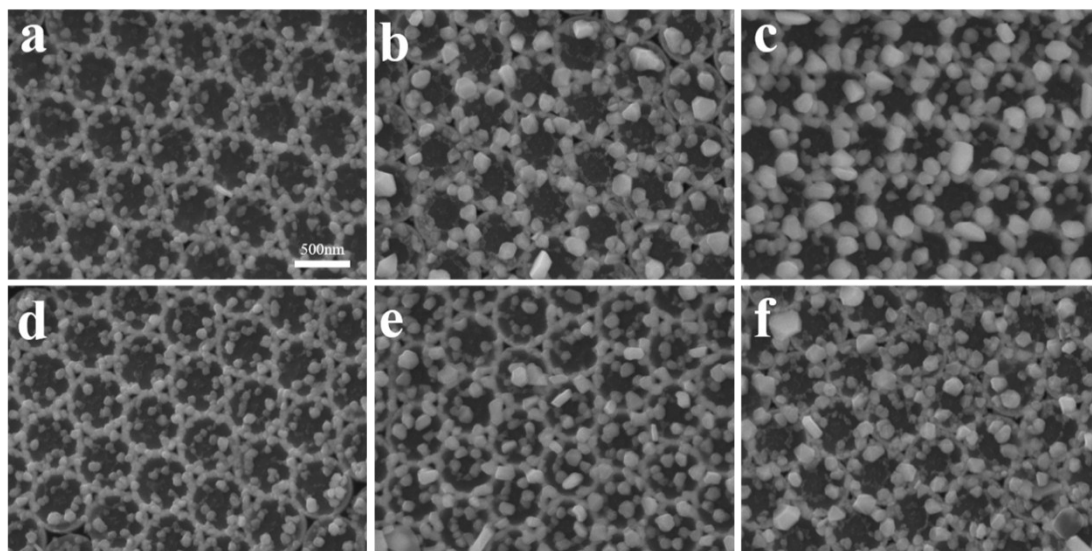


Figure S1. Scanning electron microscopy (SEM) image of the Au nanobowl after the plasmonic chemical reaction illuminated by (a-c) green light (520-530 nm) or (d-f) blue light (450-470 nm) for a plasmonic chemical reaction time of (a) (d) 10 min, (b) (e) 20 min, or (c) (f) 60 min. The scale bar in (a) represents a distance of 500 nm, which is the same for all SEM images. The light source is circularly polarized and vertically incident onto the sample surface.

When induced by green and blue light, the growth pattern for the Ag NPs differed from that induced by red light, as shown in Figure S1. The interstices (the triangular nanoholes formed between three neighboring nanobowls) are not the preferential position for the growth of Ag NPs, with the final pattern not showing a six-axis symmetrical structure. The growth position for the Ag NPs is close to the Au nanobowl wall. With increasing time, the Ag NPs grow inside the Au nanobowl. The FDTD simulation is performed to give detailed physical reasons for this observation, as shown in Figure S2.

## S2. The electric field distribution of Au nanobowl by blue and green light

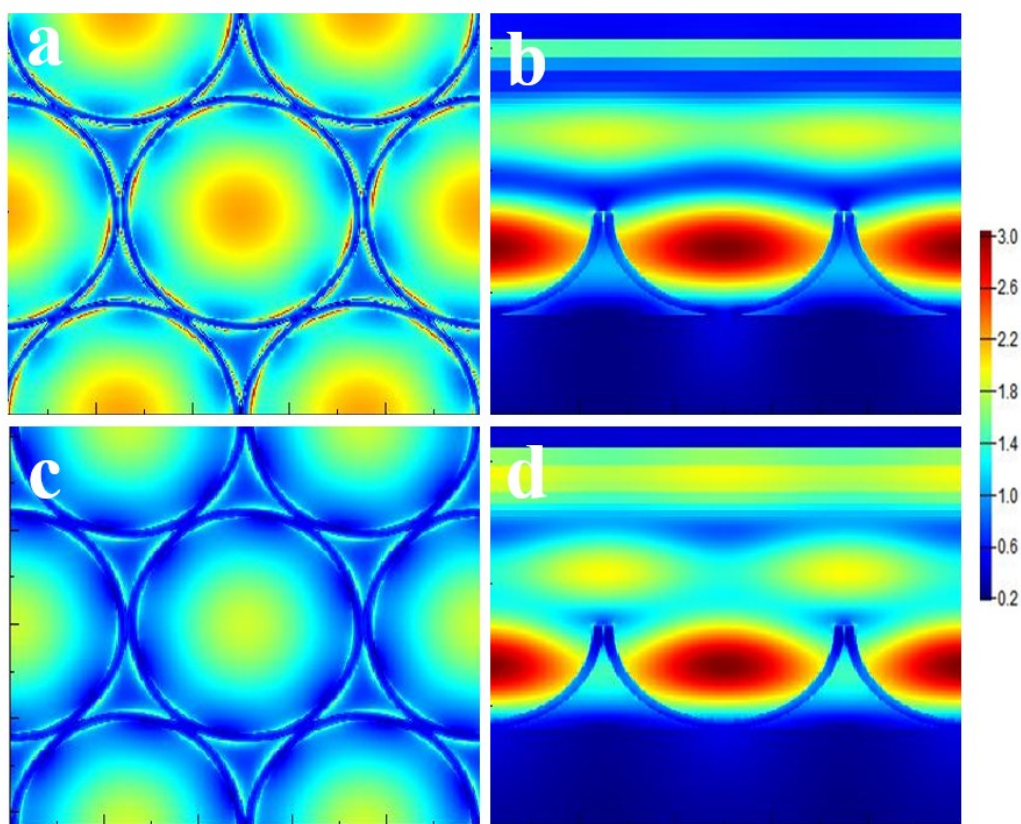


Figure S2. (a) and (b) correspond to the x-y plane and x-z plane, respectively. The blue (450-470 nm) light is circularly polarized with a vertical incidence. (c) and (d) correspond to the x-y plane and x-z plane, respectively. The green light (520-530 nm) source is circularly polarized with a vertical incidence, respectively.

When blue and green light are applied for Ag NP growth (as shown in Figure S1), theoretical simulation results for the hotspot distribution show a weak coupling electric field at the triangular nanoholes. The electric field is relatively strong inside the Au nanobowl. Therefore, the perfect six-axis symmetrical structure cannot form as induced by the red light. This result further proves that the electric field strength distribution is a key factor in the preparation of a perfect six-axis structure.

### S3. The EDS analysis map of six-axis symmetric structure

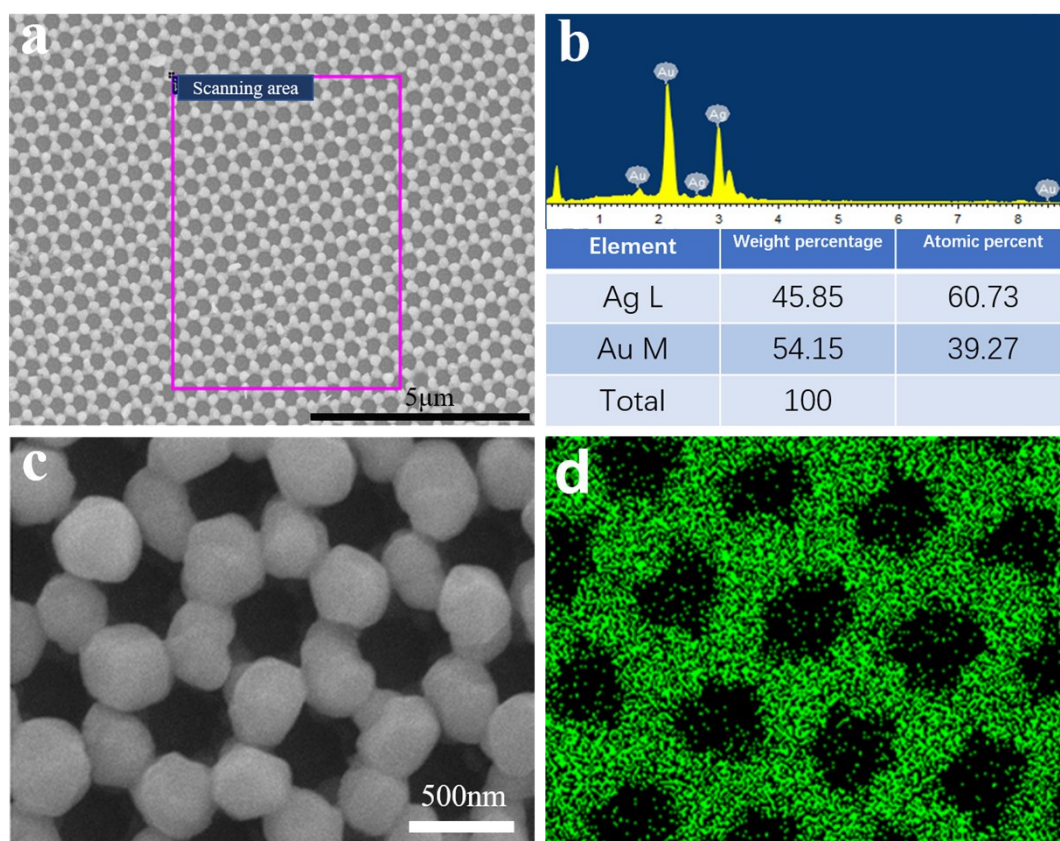


Figure S3. The energy-dispersive spectroscopy (EDS) image of the six-axis symmetric Ag NP array with  $t = 60$  min. The guide line in (a) (b) shows the scanning area and the element content. (c) and (d) show the analysis area and surface distribution of the elements, where green dots represent Ag.

#### S4. Analysis of average Ag NPs size under the condition of vertical incidence of circular polarization light

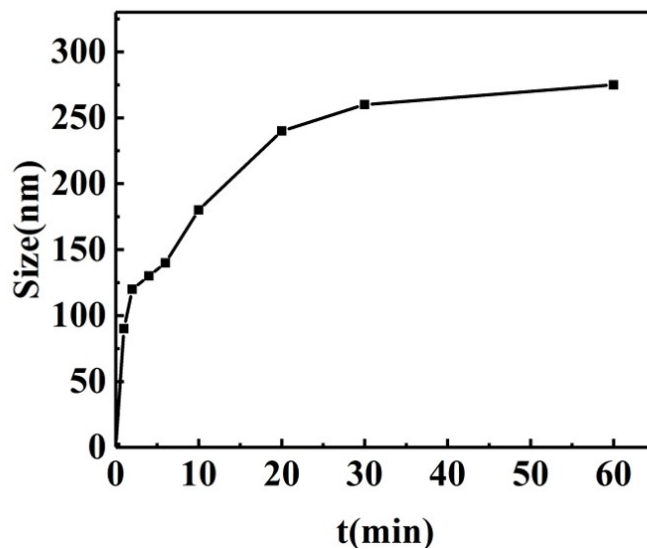


Figure S4. Average Ag NP size changes over time with vertically incident circular polarized light.

The size of the Ag NPs increases from 90 to 275 nm as the reaction proceeds for 60 min. The Ag NPs grow to 180 nm in 10 min, after which the Ag NP growth slows. After 30 min of reaction, the Ag NPs show saturated growth, with a diameter of 260 nm. The growth tends to stop at 60 min, after which the LSPR of the Au nanobowl was observed to gradually disappear with the growth of the Ag NPs, with the reaction reaching a thermodynamic equilibrium and maintaining a state of dynamic balance.

## S5. The effective propagation depth of LSPR of Au nanobowl

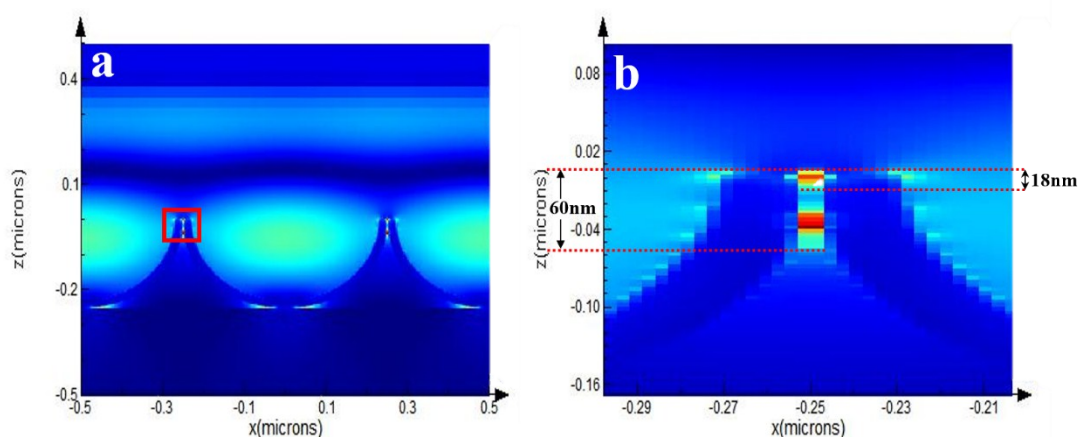


Figure S5. (a) and (b) Distribution of hotspots in the Z-direction of the Au nanobowl utilized in the FDTD simulation.

In general, the geometrical morphology of the structure is an important factors affecting LSPR. The distribution of hotspots in the Z-direction on the Au nanobowl array is shown in Figure S5. The distribution of hotspots in adjacent nanobowls is shown in Figure S5a. Figure S5b is the enlarged version of the red box area in Figure S5a. The hotspot depth is indicated in the figure. The hotspot at the top of the nanobowl is effective, and the propagation depth is less than 10 nm. Hotspots exposed to the surface of the Au nanobowl are defined as effective hotspots. Thus, the 20 nm SiO<sub>2</sub> coating could block the LSPR spectra. The electromagnetic coupling between the Au nanobowls is responsible for the site-selective growth of Ag nanoparticles, not the springhead of the continuous growth of Ag nanoparticles. The further deposition of Ag<sub>0</sub> on the particles is a natural process and occurs spontaneously. The growth rate and final size of silver nanoparticles mainly depend on three factors. The first is the number of nuclei for growth. The second is the concentration of Ag<sub>0</sub> monomer in solution, and the third is the diffusion coefficient of Ag<sub>0</sub> in the solution. Thus, the final size of Ag nanoparticles is not directly related to the hotspot depth of Au nanobowls.

### S6. Plasmon-assisted chemical reactions of Au nanobowl coated with SiO<sub>2</sub>

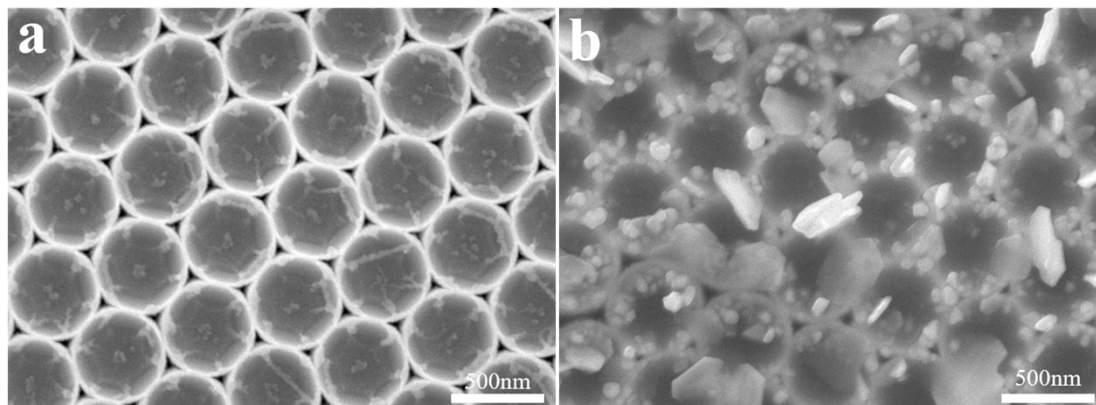


Figure S6. SEM images for the 20 nm SiO<sub>2</sub> sputtered onto the Au nanobowl (a) before and (b) after chemical reaction in silver nitrate/sodium citrate solution at 25 °C and illumination by a red LED lamp for 60 min.

## S7. Control experiment

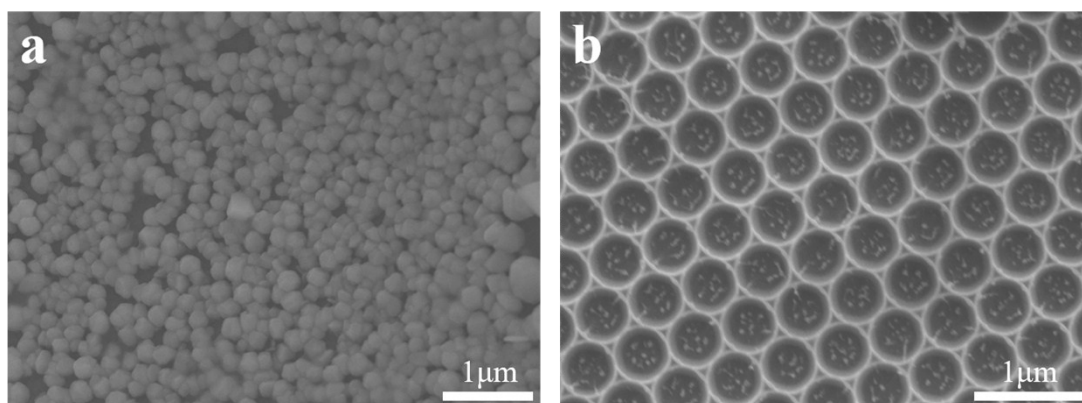


Figure S7. (a) Ag growth on a 25 nm Au flat film instead of a Au nanobowl, (b) reaction without any illumination from LED. The reaction time was always 60 minutes.

Two control experiments were carried out to confirm the results of our investigation. In the first control experiment, a 25 nm flat Au film on the silicon substrate was used to replace the Au nanobowl structure, and the reaction time was set at 60 min. Figure S7a shows that silver nanoparticles are uniformly distributed on the surface of the Au film. When Au is deposited onto the silicon substrate, the film is uniform all over the substrate, and the roughness distribution is random. Therefore, the hotspots are also random and uniform over the whole substrate, which results in similar sizes and random distributions of Ag nanoparticles. Figure S7b shows the sample after the reaction without any illumination from the red LED when the reaction time was again 60 min. We can see that there are no Ag nanoparticles on the structure of the Au nanobowl. These control experiments prove that light-controlled growth of Ag nanoparticles and Au nanobowl arrays induces the site-selective growth of Ag nanoparticles. To further prove the fundamental reason for the site-selective growth of Ag nanoparticles, we used monochromatic light of different wavelengths to



induce chemical reactions. The experimental results obtained with monochromatic light of different wavelengths and the corresponding analysis can be found in supporting information S1 and S2. Based on the above experimental results, we can conclude that the LSPR of Au nanobowls is the fundamental reason for the site-selective growth of Ag nanoparticles.

**S8. Analysis of average Ag NPs size under the condition of oblique  $50^\circ$  irradiation with linearly polarized light**

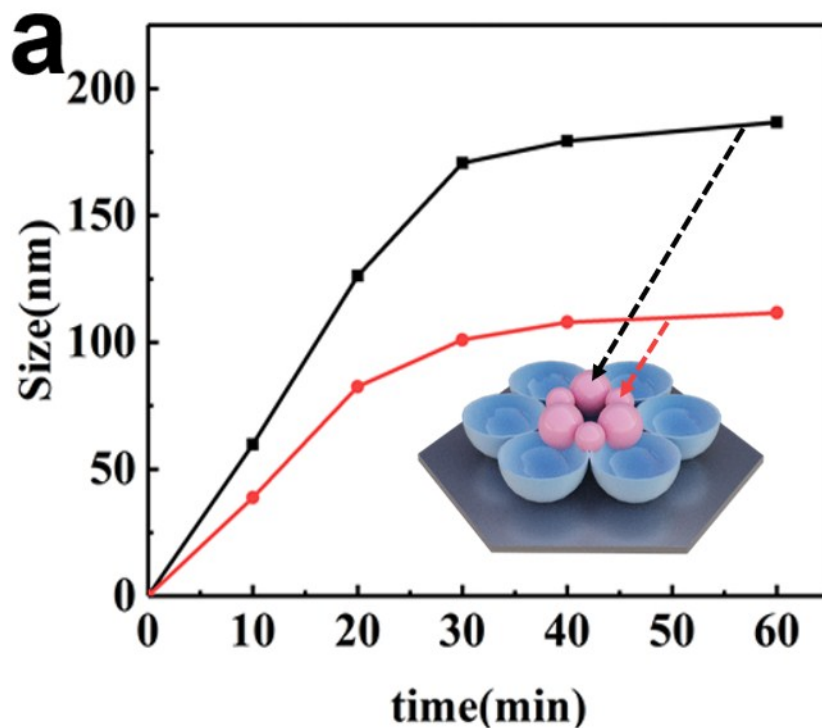


Figure S8. (a) The average Ag NP changes over time, corresponding to oblique  $50^\circ$  irradiation with linearly polarized light.

The black line shows the size evolution for the Ag NPs at location A. The red line shows the size evolution for the Ag NPs at location B. The Ag NPs at location A grow to 180 nm when the reaction proceeds for 60 min, whereas the nanoparticles at location B grow slowly to 106 nm.

### S9. Supplementary diagram of the fabrication process of nanobowl arrays

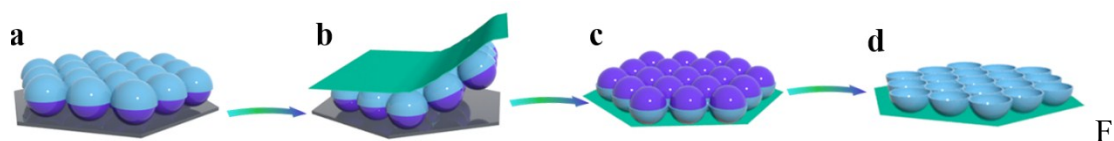


Figure S9. Schematic of the transfer process of nanobowl arrays. (a) Au was deposited onto the monolayer PS arrays via magnetron sputtering. (b) Tape was applied to the nanostructure. (c) Nanostructures were transferred onto the tape. (d) The ion etching treatment was carried out to remove the PS beads and obtain the nanobowl array.

The transfer process is shown in Figure S9. When the Au film was deposited onto the closely compact PS arrays in a magnetron control sputtering system, the nanobowl forms on each PS bead with the bottom facing up (Figure S9a). When the double side tape sticks to the nanobowl array, the nanobowls with the PS beads can easily be peeled off the original substrate because the interactions between the silicon substrate and the PS beads are weak van der Waals forces (Figure S9b). The PS/Au arrays were then transferred onto the tape with the PS beads facing up (Figure S9c). In the subsequent ion etching process, the PS beads were etched away, and the Au nanobowl array formed on the tape substrate (Figure S9d). The tape works as only the sticking layer, and there is no chemical reaction between the tape and the solution, Ag nanoparticles or Au nanobowl.

## S10. Absorption cross-section versus wavelength for Au nanobowl structure

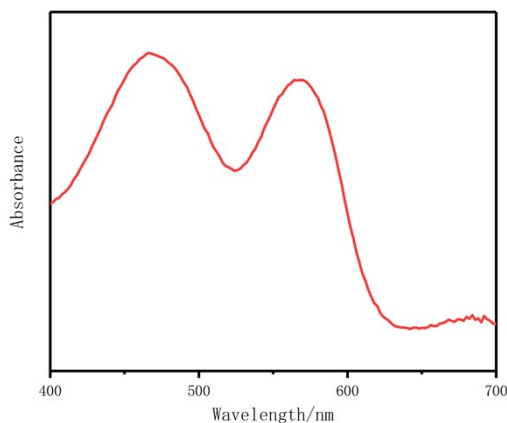


Figure S10. UV-vis absorption spectrum of the Au nanobowl.

According to previous studies, we know that the absorption spectra of different structures of gold have a wide range of adjustment, and the change of absorption spectra are extremely sensitive to the appearance of nanostructures.[3-5] Figure S10 shows the absorption spectrum in the visible light range of the Au nanobowl structure. It is obvious that the Au nanobowl have two distinct absorption peaks in the visible light range. The absorption peak at 466 nm belongs to the absorption peak of gold itself[6], the absorption peak at 570 nm belongs to the LSPR absorption peak of the coupling between Au nanobowl.[7] The hot area of Au nanobowl mainly comes from the coupling mode. Therefore, we chose red light to excite the LSPR of Au nanobowl. The reason why we don't use green light is because some of the energy is absorbed by the gold material itself and the coupling energy will be weakening, the relatively low resonance coupling could not regulate the site-selective growth of Ag nanoparticles. And it has been proved in experiments. (The Figure S1(a-c) shows the result irradiated by green light)

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