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Supplementary Information

Light-induced reversible hydrophobization of cationic gold nanoparticles via electrostatic adsorption of photoacid

Hang Zhang,* Muhammad Junaid, Kai Liu, Robin H. A. Ras, Olli Ikkala*

Department of Applied Physics, Aalto University, P.O. Box 15100, FI 02150 Espoo, Finland.

E-mail: hang.zhang@aalto.fi, olli.Ikkala@aalto.fi

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Materials

The following chemicals were purchased from Sigma-Aldrich: gold(III) chloride trihydrate ($HAuCl_4 \cdot 3H2O$, >99.9% trace metals basis), sodium citrate tribasic dihydrate (BioUltra, 99.5%), tannic acid (TA, ACS reagent), potassium carbonate (K_2CO_3, 99.995% trace metals basis), 1,3-propanesultone (>99%), 2,3,3-trimethylindolenine (98%), salicylaldehyde (>99.0%), octadecylamine (>99.0%), (11-mercaptoundecyl)-*N,N,N*-trimethylammonium bromide (MUTAB, >90%), 6-Amino-1-hexanethiol hydrochloride (AHT), toluene (puriss, >99.7%).

Hydrochloric acid (HCl) solution 1M (NIST standard solution) was purchased from Fisher Scientific. Ethanol (99.5%) was purchased from ALTIA Oyj (Finland). MilliQ water (18.2 MΩ, DirectQ 3 UV, Millipore) was used in all experiments.

Methods

Gold nanoparticles

To synthesize gold nanoparticles with an average diameter of 10 nm, a seeded growth method in the presence of tannic acid was used.[1] All solutions were freshly prepared before the reaction. Briefly, 150 mL of 2.2 mM aqueous solution of trisodium citrate dihydrate was mixed with 0.1 mL of 2.5 mM tannic acid and 1 mL of 150 mM potassium carbonate in a 250 mL three-neck flask. The solution was heated to 70 °C in an oil bath. Subsequently, 1 mL of 25 mM $HAuCl_4 \cdot 3H_2O$ solution was quickly injected under vigorous stirring, and the solution was kept at 70 °C for another 5 min. In this way, gold seeds with an average diameter of 3.5 nm were formed. Directly after the formation of gold seeds, 55 mL of this solution was extracted, and 55 mL of 2.2 mM citrate solution was added. After the temperature of the solution reached again 70 °C, 0.5 mL of 25 mM $HAuCl_4 \cdot 3H_2O$ solution was injected to initiate the growth of the seed. After 10 min, an identical injection was carried out. This growth procedure including extraction, addition of citrate and two injections of gold precursor was carried out for 4 times in total for 10 nm AuNPs and 1 time for the 5 nm AuNPs.

For the cationization of the citrate protected AuNPs, a two-step phase-transfer method was used.[2] First, the AuNPs were transferred to toluene by vigorously shaking 30 mL of AuNPs solution with 6 mL of toluene containing 5 µmol octadecylamine. The toluene phase was then separated and washed with 30 mL of water to remove the citrate. Afterwards, 3 mL of water and 300 μL of 4 mM MUTAB in EtOH were added to the toluene solution. The two-phase mixture were vigorously shaken for the cationized AuNPs to be transferred to the water phase. 200 microliters of 0.1 M HCl solution was added to complete the transfer process. The aqueous phase was collected and washed extensively with toluene to remove the excess of ODA and MUTAB. The aqueous phase containing AuNPs was finally diluted to 20 mL and centrifuged at 25 000 g for 40 min (10 nm) and 34 000 g for 45 min (5 nm) and collected as 1.5 mL stock solution. For amine functionalization, AHT was used instead of MUTAB following the same protocol.

Characterization of the AuNPs was carried out by transmission electron microscope (TEM, Tecnai 12). The TEM grids were plasma-treated for 30 s ($H_2 + O_2$, Gatan 950 Advanced Plasma System), and a droplet of AuNP solution was casted on the grid with excess of the liquid removed by a filter paper. The size of the particles was analysed using the "Analyse Particle" function of ImageJ (version 1.52i). The diameter was calculated from the area of the particles assuming spherical geometry. More than 1000 particles were analyzed. The average diameter is 10.9 ± 1.2 nm and 5.1 ± 0.4 nm for the two batches respectively.

Photoacid

The photoacid was synthesized according to literature. 2,3,3-Trimethylindolenine (3.18 g, 20 mmol) was mixed with 1,3-propanesultone (2.44 g, 20 mmol) and then heated to 90 °C for 6 h under nitrogen protection. The solid purple product was collected by filtration and washed thoroughly with diethyl ether. 600 mg (2.14 mmol) of the dried product and 292 mg of 2-hydroxybenzaldehyde (2.4 mmol) were then added to 12.0 mL of anhydrous ethanol, and the solution was refluxed overnight. The resulting orange solid was collected by filtration and rinsed thoroughly with ethanol (5 × 10 mL). The final product was dried in vacuum and stored in freezer (-20 °C) under nitrogen protection. The pH measurement was carried out by a Mettler Toledo SevenExcellence pH meter.

The 0.2 mM photoacid solution was prepared by adding 1 mg of photoacid to 13 mL of water and sonication until full dissolution. In a typical experiment, 20 μL of 0.1M HCl solution were mixed with 1.95 mL of photoacid to adjust the pH to 2.70. Then 30 μL of AuNP solution was mixed thoroughly with the photoacid solution. Self-assembly of the AuNPs was triggered by irradiation using a table lamp at room temperature and below, or a 455 nm LED (25 mW cm^{-2}, M455L3-C2, Thorlab) at higher temperatures, as stronger irradiation is needed for full activation of the photoacid at high temperatures.

UV-Vis characterization

The spectra were measured on an Agilent Cary 5000 UV-Vis spectrometer equipped with a temperature-controlled liquid cell holder. The temperature of the cuvette was controlled with an accuracy of ± 0.2°C.

Zetapotential

The zetapotential of the AuNPs was measured on a Zetasizer Nano ZS90 (Malvern) using disposable folded capillary cells (DTS1070, Malvern). For each measurement, at least 10 runs were carried out to obtain the average value. For all samples, the solution was equilibrated at 10°C for 10 min beforehand. For the irradiation experiment, the sample was kept at 10°C and irradiation was carried out for 5 min by a table lamp. Afterwards the sample was measured immediately at 10°C, which took less than 2 min. The low temperature was chosen to minimize the recovery of the photoacid after irradiation, and used for all solutions to ensure consistent results.

Light-induced phase transfer of the AuNPs

1 mL of 0.2 mM photoacid solution containing 100 μL of AuNPs was adjusted to pH 2.70 by 0.1 M HCl solution. The solution was then added to a 15 mL centrifuge tube containing 2 mL of toluene. The aqueous phase was irradiated by a 455 nm LED (25 mW cm^{-2}) for 5 minutes at room temperature and then vigorously shaken until the phase-transfer is complete. Since the shaking results in an emulsion-like and slightly turbid aqueous phase, the solution was further irradiated for 1 h at room temperature until both phases became clear for the UV-Vis measurement. For the recovery process, the mixture was left in darkness for 1 h at room temperature or 10 min at 50°C in a water bath. Afterwards the solution was shaken again for the AuNPs to migrate into the aqueous phase. UV-Vis spectra were taken after both phases became clear. The same phase transfer procedure has been carried out for 5.1 nm AuNPs as shown in Supporting Information Figure S10.

For the demonstration of purification process, the 10.9 nm AuNPs were first transferred into toluene phase by irradiation. The toluene phase with the AuNPs were then transferred in a new centrifuge tube, which contained pure water. After overnight storage in darkness, the AuNPs migrated into the pure water phase with the help of gentle shaking, thus completing the purification process as shown in Supporting Information Figure S12.

Contact angle measurement on flat gold substrate

Gold substrates were prepared on 2 cm × 2 cm silicon wafers by an electron-beam evaporator (MASA IM-9912, Micronova, Finland) in a clean room. Firstly, silicon wafers were cleaned by ultrasonication in acetone for 15 minutes and then washed with isopropyl alcohol and deionized water respectively, and lastly dried under N_2-flux. Afterwards, cleaned silicon wafers were mounted in the e-beam evaporator and 10 nm Titanium adhesion layer was evaporated at a rate of 0.2 Å/sec under high vacuum (10^{-8} mbar). Finally, a 150 nm Au film was evaporated on the same silicon wafers at a rate of 1.5 Å/sec. The surface of the substrate was characterized by atomic force microscopy (Dimension Icon, Bruker) in tapping mode (Supporting Information Figure S13), which shows a surface roughness of 2.3 nm using Root Mean Square method.

To prepare the cationized gold substrate, the substrate was first cleaned by oxygen plasma (Diener Pico, 100W) for 5 min and then immediately immersed in a 1 mM ethanolic solution of MUTAB. After overnight incubation, the substrate was rinsed with copious amount of ethanol and deionized water and then blow-dried with nitrogen. For the control experiment, a freshly plasma-treated gold substrate was used instead of the cationized substrate.

The contact angle measurement was done on freshly prepared substrate (within 20 minutes) using a 0.2 mM photoacid solution (pH 2.70). The droplet volume was 3 μL, and contact angles were measured using an Attension Theta contact angle goniometer from Biolin Scientific, following the protocol from Huhtamäki et al.[3] The contact angle evolution was recorded using the goniometer software (OneAttension Version 3.2) and analyzed using the Young-Laplace method. The mean value of the left and right contact angles was used. A home-built humidity chamber was used to minimize the evaporation of the liquid.

Calculation of the photoacid to ligands ratio

The total amount of ligands were estimated by assuming each ligand (MUTAB) occupies 0.214 nm^2 on the surface of gold nanoparticles. Therefore, on average there are roughly 1744 ligand molecules on each AuNP, assuming the AuNPs are spherical. The concentration of citrate-protected AuNPs in the as-prepared solution is estimated to be 1.2×10^{13} NPs/mL.[1] Based on this, the concentration of AuNPs in the final photoacid solution is estimated to be 7.2×10^{12} NPs/mL, assuming that no loss of AuNPs took place during the modification process. This translates into 1.25×10^{16} ligand molecules per milliliter, while each milliliter of the solution contains 0.2 mM photoacid (1.20×10^{17} molecules/mL). Therefore, the ratio of photoacid to ligand is 10 in the standard solution. The other ratios (1.5 - 15) are calculated correspondingly.

Fitting of the half-life of photoacid recovery

Half-life ($t_{1/2}$) of a first order decay reaction depends on the rate constant as shown in Equation S1,

$$t_{1/2} = \frac{ln2}{k} \quad \text{(S1)}$$

where *k* is the rate constant of the reaction. Equation S2 shows the Arrhenius equation,

$$k = Ae^{\frac{-E_a}{RT}} \quad \text{(S2)}$$

where *k* is the rate constant of the reaction, *A* the pre-exponential factor, E_a is the activation energy, *R* is the gas constant, and *T* is the absolute temperature. Combining Equations S1 and S2, the temperature-dependence of half-life can be written in Equation S3.

$$t_{1/2} = Be^{\frac{C}{T}} \quad \text{(S3)}$$

where *B* and *C* are constants to be fitted, and *T* is the absolute temperature.

To determine the half-life of the recovery processes shown in Figure 3a, the starting value of the absorbance at 420 nm was measured to be 0.148 and the equilibrium value to be 2.377. Therefore, the mean value 1.263 was used as the absorbance value corresponding to the half-life. Fitting of the half-life using Equation S3 was carried out with OriginPro (2019). The fitting results in $B = 1.16 \times 10^{-21}$ min, and $C = 1.47 \times 10^{4}$ K.

Supporting Figures

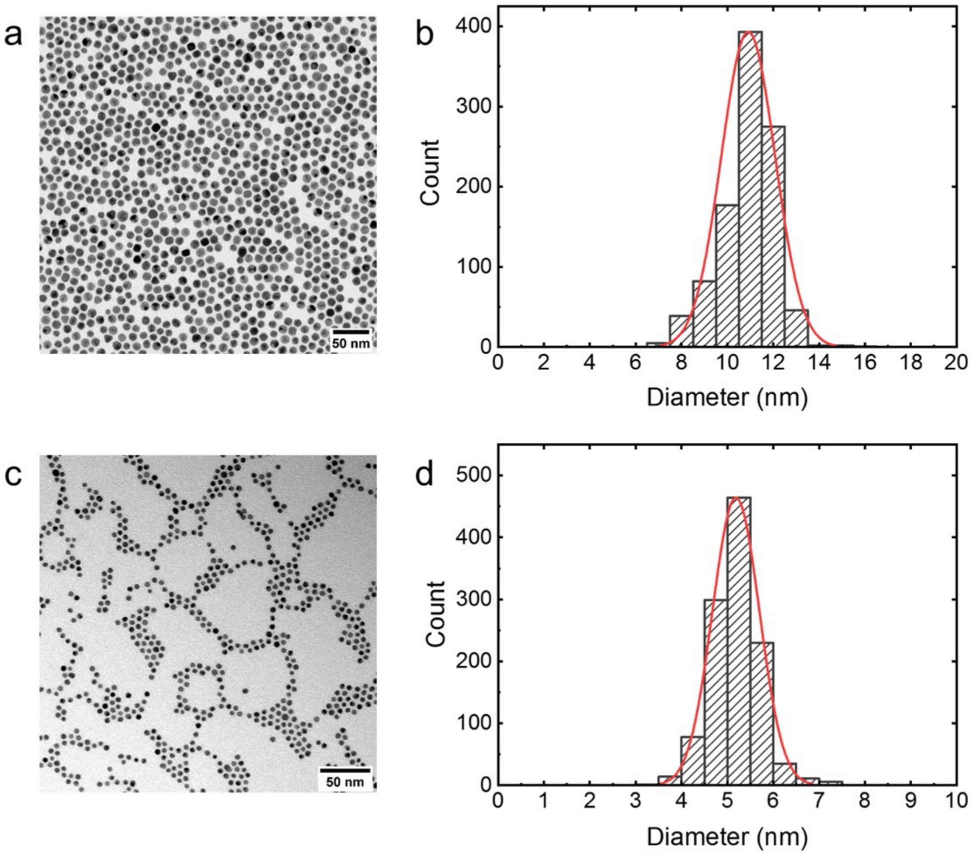

Figure S1. TEM images and size distributions of cationic AuNPs. (a) Representative TEM image of 10.9 nm AuNPs. (b) Size distribution of the 10.9 nm AuNPs. Red curve: normal distribution fitting. (c) Representative TEM image of 5.1 nm AuNPs. (d) Size distribution of 5.1 nm AuNPs.

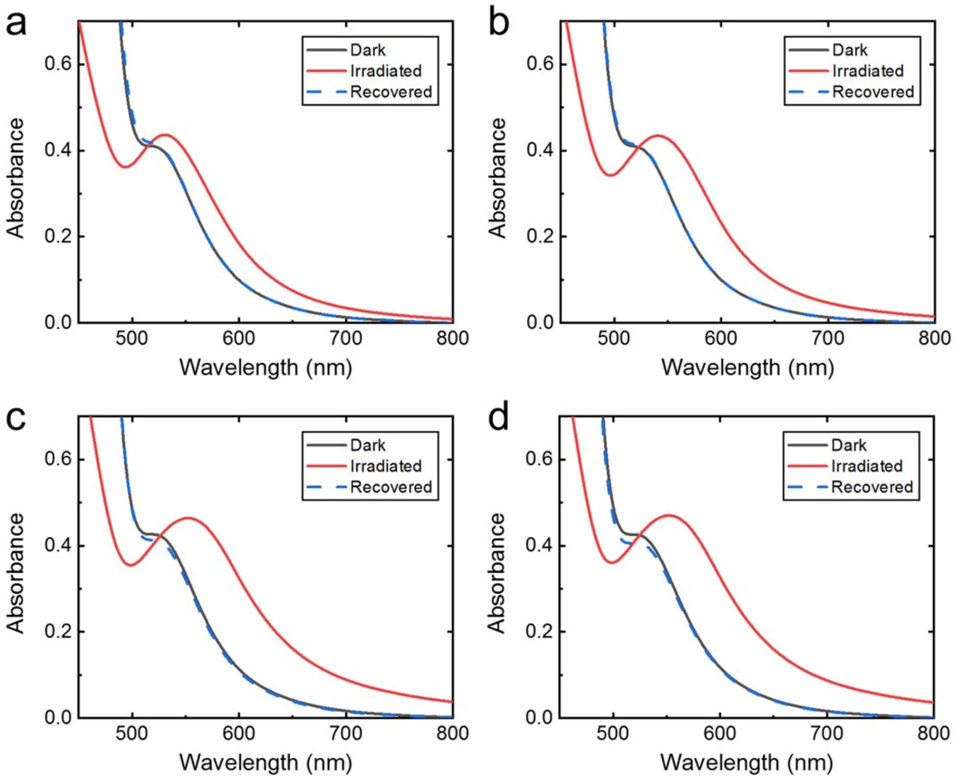

Figure S2. UV-Vis spectra of AuNP/photoacid at different pH. (a) pH 2.3, (b) pH 2.5, (c) pH 3.0, and (d) pH 3.2.

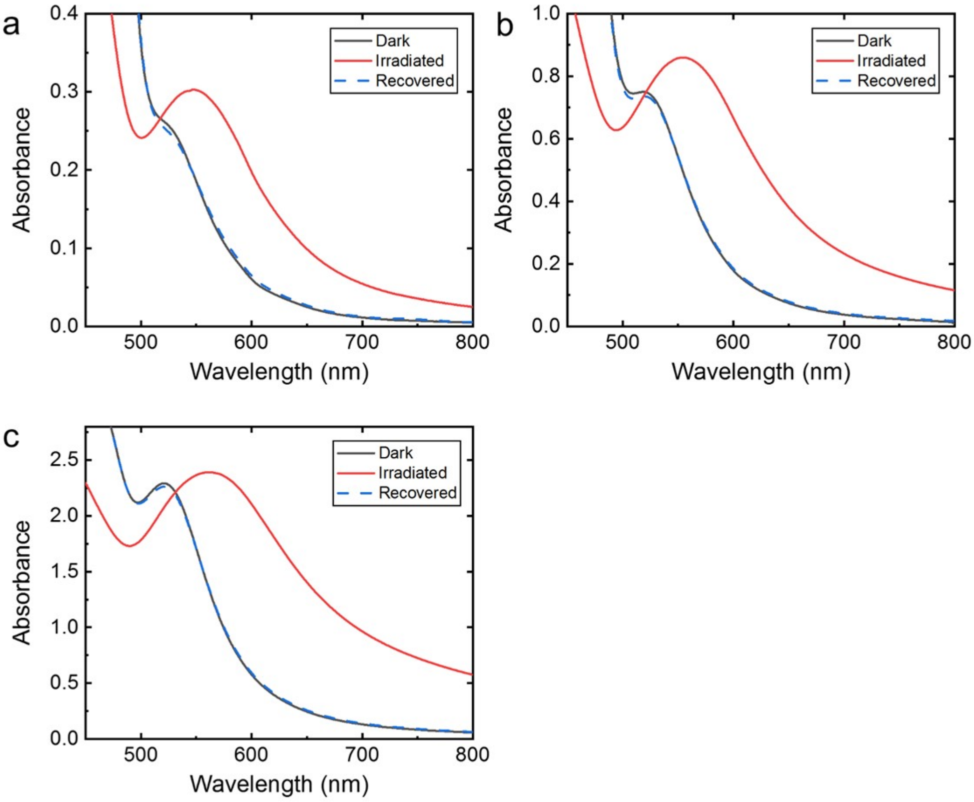

Figure S3. UV-Vis spectra of AuNPs/photoacid with different photoacid/ligand ratio. (a) 15, (b) 5, (c) 1.5. Photoacid concentration of 0.18 mM was used for all samples to compensate for the diluting effect at high AuNP concentrations. pH: 2.7.

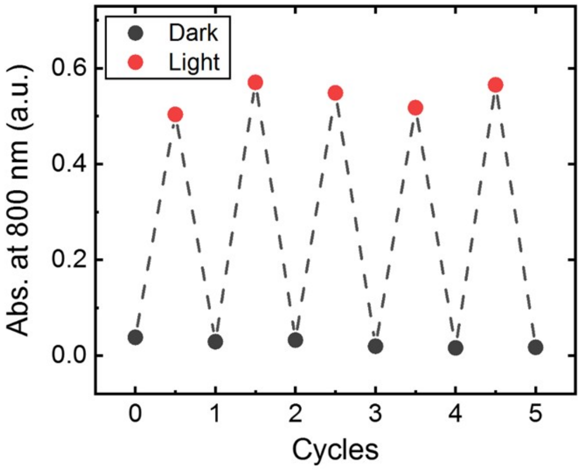

Figure S4. Absorbance change at 800 nm of the AuNPs/Photoacid solution upon repeated irradiation/darkness cycles.

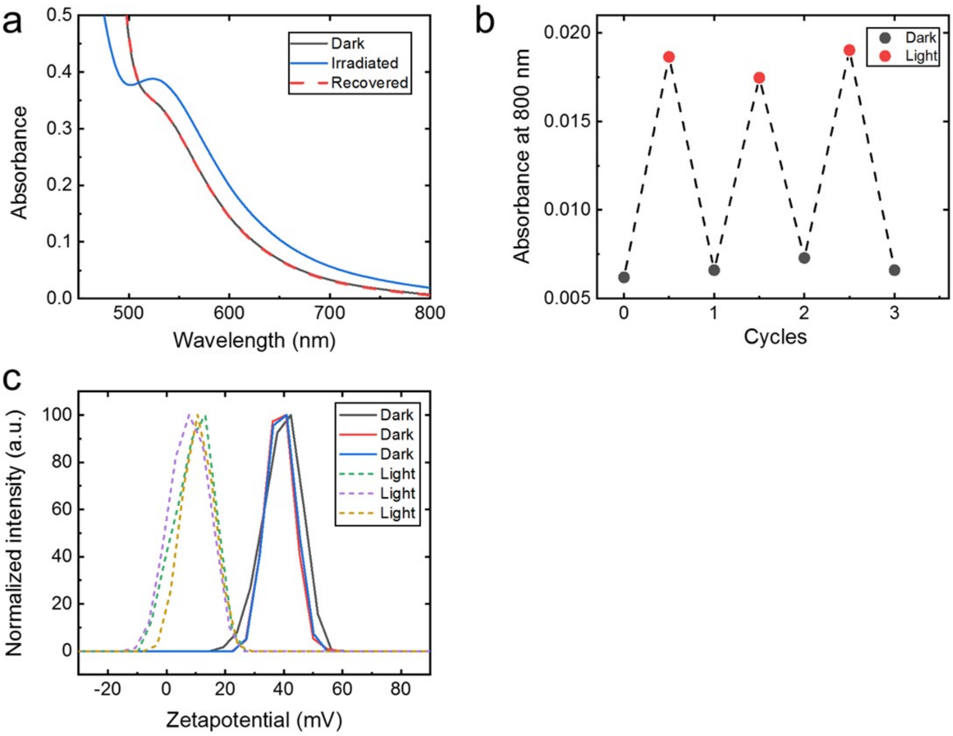

Figure S5. Light-induced reversible aggregation of cationic 5.1 nm AuNPs. (a) UV-Vis spectra of the AuNP/photoacid solution before and after irradiation. (b) Absorbance change at 800 nm upon three cycles of irradiation. (c) Zeta potential change of AuNPs upon three cycles of irradiation. Irradiation: 5 min white light (table lamp).

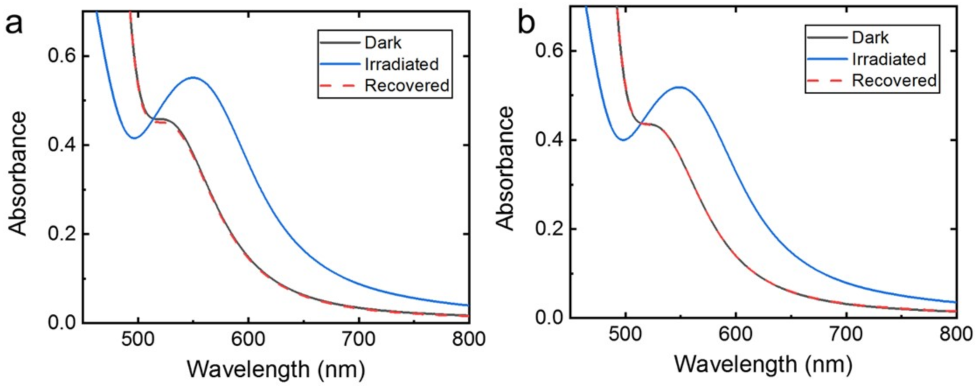

Figure S6. AuNP/Photoacid solution after storage at room temperature. (a) UV-Vis spectra of the solution after storage for 3 days. (b) UV-Vis spectra of the solution after storage for 7 days. pH: 2.70. Irradiation: table lamp for 5 min.

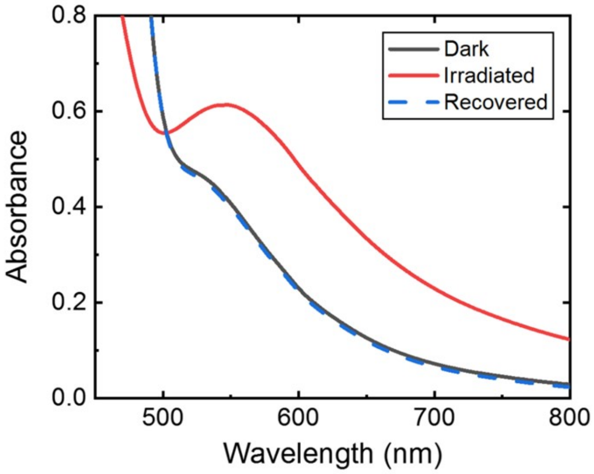

Figure S7. AuNPs (5.1 nm) modified by 6-amino-1-hexanethiol showing reversible assembly/disassembly in a 0.2 mM photoacid solution upon irradiation. pH: 2.70. Irradiation: table lamp for 5 min.

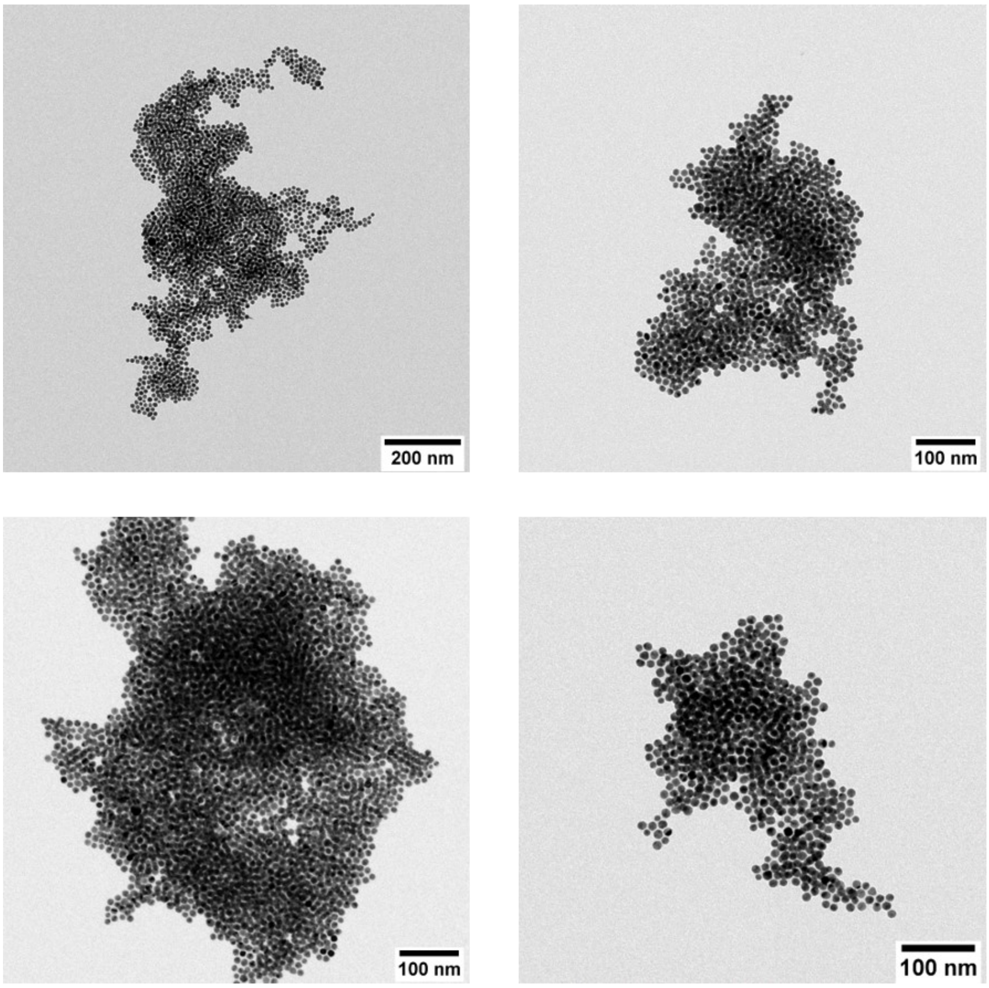

Figure S8. TEM images of the light-induced AuNP aggregates.

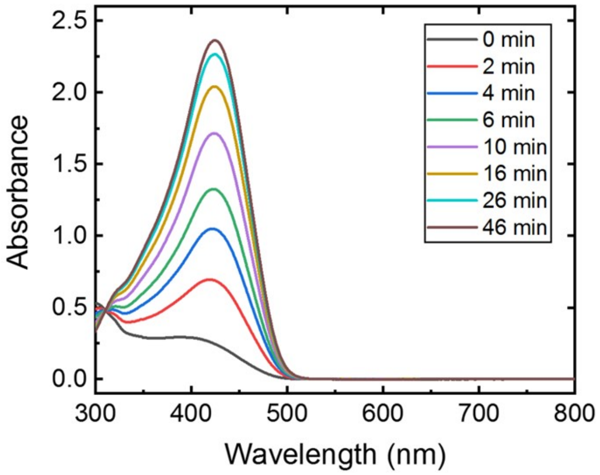

Figure S9. Recovery of UV-Vis spectra of the photoacid solution at room temperature after irradiation for 5 min by a table lamp.

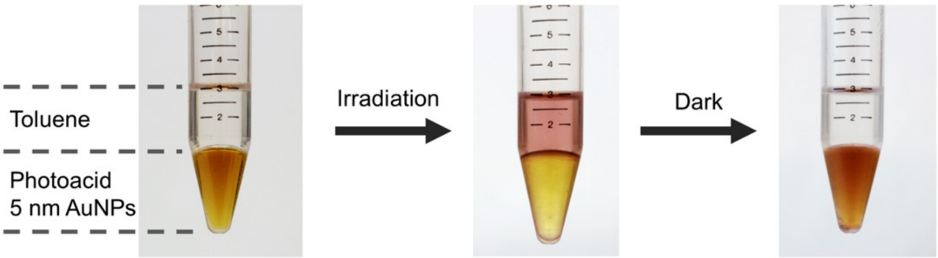

Figure S10. Light-induced reversible phase transfer of 5.1 nm AuNPs between water and toluene phases.

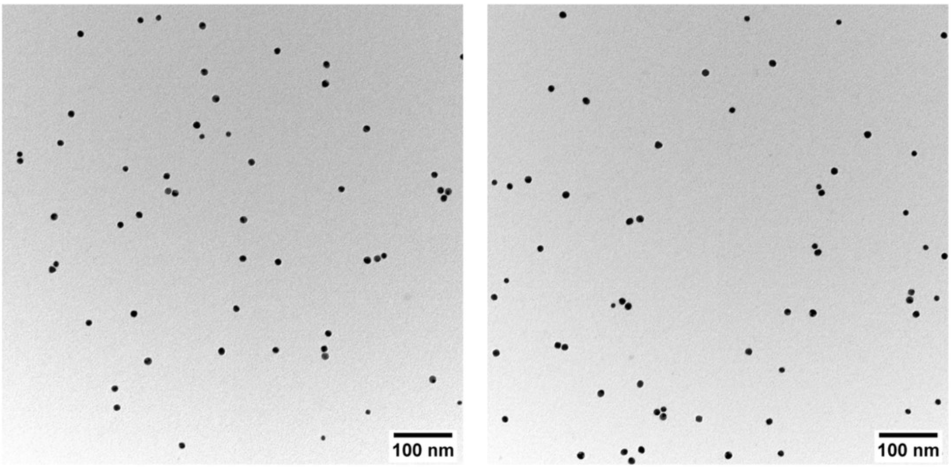

Figure S11. TEM images of the AuNPs in the toluene phase after light-induced phase transfer.

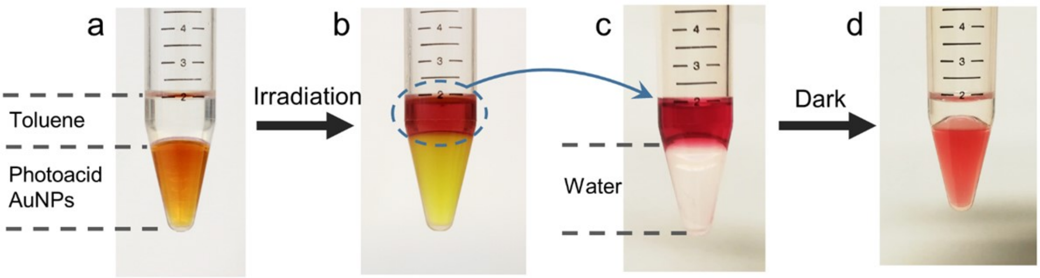

Figure S12. Light-induced phase transfer of 10.9 nm AuNPs into pure water phase. (a) Toluene phase and aqueous phase containing photoacid and 10.9 nm AuNPs. (b) Migration of AuNPs into the toluene phase upon irradiation. (c) The toluene phase containing AuNPs was transferred into a new centrifuge tube containing pure water. (d) After storage in darkness, the AuNPs in the toluene phase migrate into the water phase.

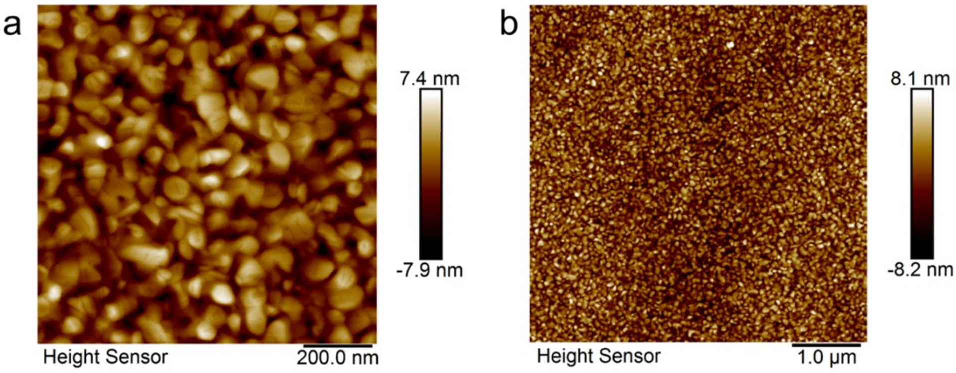

Figure S13. AFM characterization of the surface topography of the gold substrate. (a) 1 × 1 µm^2. (b) 5 × 5 µm^2.

Caption for Supporting Movie S1

Video showing the contact angle change of the photoacid solution on a cationic gold surface upon irradiation (Figure 4). Irradiation starts at $t = 0$ s. Video accelerated by 4 times.

References

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