Electronic Supplementary Information

Reversible Luminescence Switching of $NaYF_4$:Yb,Er Nanoparticles with Controlled Assembly of Gold Nanoparticles

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Experimental Section

Materials: Y_2O_3, Yb_2O_3, and Er_2O_3 were purchased from China Rare Earth Online Co., Ltd. Other chemicals were purchased from Beijing Chemical Reagent Company. All the chemicals were used as received. Deionized water (18.2 MΩ·cm) was used throughout the synthesis of Au NPs.

Synthesis of Au NPs: Au NPs were prepared by using a seed-mediated method.[Ref8] The resultant Au NPs were CTAB-stabilized and had an average diameter of 9.4 ± 1.1 nm.

Assembly and Disassembly of Au NPs: Generally, 10 μL of 1 mM L-cysteine solution was added into 3 mL of the as-synthesized gold colloidal solution. The pH was adjusted to 3 with concentrated HCl solution. After aging the gold solution for 10 min, the color of the solution changed from ruby red to blue, indicating the occurrence of the assembly of Au NPs. To disassemble the Au NPs, the pH of the solution was adjusted to 11 with 5 M NaOH aqueous solution. The color of the solution changed from blue to pink during the disassembly process.

Synthesis of $NaYF_4$:Yb,Er NPs: Rare earth nitrate solutions were obtained by dissolving rare earth oxides (Y_2O_3, Yb_2O_3, and Er_2O_3) with nitric acid. The concentrations were determined by EDTA titration. For the preparation of $NaYF_4$:Yb,Er NPs, 1.20 g of EDTA, 2.569 mM $Y(NO_3)_3$, 0.579 mM $Yb(NO_3)_3$, 0.064 mM $Er(NO_3)_3$, 0.14 g of sodium ethoxide, and 0.46 g of $(NH_4)HF_2$ were dissolved in 40 mL of water. The mixture was then diluted to 80 mL with ethanol. After stirring for 30 min, the solution was transferred to a Teflon-lined autoclave and heated at 220 °C for 24 h. The resultant NPs were EDTA-stabilized and had an average diameter of (120 ± 40) nm.

Coating $NaYF_4$:Yb,Er NPs with Silica Shell: Typically, 30 mg of $NaYF_4$:Yb,Er NPs were dispersed in the mixture of 1.5 mL of water and 20 mL of ethanol by sonication. After the addition of 400 μL of 25% ammonia and 1.2 mL of TEOS (tetraethyl orthosilicate), the mixture was stirred for 1 h. To remove excess TEOS, the NPs were centrifuged and redispersed in ethanol for three times. The thickness of the silica shell coating on $NaYF_4$:Yb,Er NPs is about 20 nm.

Instrumentation: Particle size and its dispersion were examined with a TEM (200CX, JEOL, Japan) operated at 160 kV. Fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer equipped with a 980 nm diode laser as the excitation source. UV-visible spectra were acquired on a Hitachi U-3010 spectrophotometer.

Effect of cysteine concentration on the reactivity

The amount of cysteine molecules loaded on the Au NPs is a crucial factor affecting the assembly activity of the Au NPs. To evaluate this factor, the effect of a series of cysteine concentrations is examined. Here the pH of the solution is adjusted to 3 to accelerate the assembly. Fig. S1 shows the extinction spectra of the Au NP assemblies obtained at varying cysteine concentrations. The extinction peak at 523 nm is weakened 5 min after the addition of cysteine and a new peak at a longer wavelength appears simultaneously. Within the same reaction time, higher cysteine concentrations lead to larger red-shift of the new peak. This indicates that the assembly process is accelerated or facilitated with increased cysteine concentrations. This is reasonable because the more cysteine is present in the solution, the greater probability there is for cysteine to bond on the surface of Au NPs, which subsequently leads to higher extent of assembly of Au NPs. However, more cysteine can cause excessive assembly and precipitation of Au NP aggregates. We therefore choose a concentration of 3–4 μM for cysteine in the following experiments to ensure a mild and stable assembly of Au NPs in a reasonable reaction time.

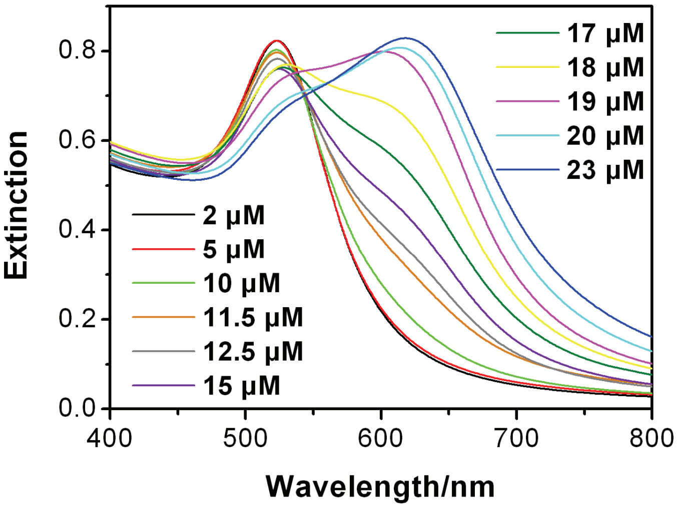

Fig. S1 Extinction spectra of the Au NP assemblies obtained at varying cysteine concentrations at pH of 3. The reaction time is 5 min.

Effect of temperature on the reactivity

Another important factor, the reaction temperature, is also examined. Au NP solutions with the same pH value (pH = 3) and cysteine concentration (3.0 μM) have been allowed to stand for 10 min under room temperature, 60, and 90 °C, respectively. The extinction spectra were compared (Fig. S2) to examine the extent of the spectra shift. A strong plasmon peak at 637 nm is observed for the reaction under 90 °C, but only a very weak plasmon peak at ca. 632 nm is observed for the reaction at 60 °C. A comparison of the intensity and position of the extinction peaks obtained at different reaction temperatures indicates that the extent of Au NP assembly is different, and that higher temperatures make the Au NPs more active towards assembly. It is also noticed that the reaction under room temperature does not induce a distinct spectral shift, namely, the assembly has not yet occurred within this short period of time. Nevertheless, after the reaction was allowed to proceed for a sufficient period of time, all these samples were assembled in the same degree as that occurred at 90 °C. Hence, it is reasonable to conclude that the assembly of Au NPs is promoted at higher temperatures. We attribute this phenomenon to the accelerated moving rate of cysteine molecules which speeds up the assembly process under higher temperatures. Even so, assembly at high temperatures is not recommended for the risk of oxidation of Au NPs to Au(I) ions.[7]

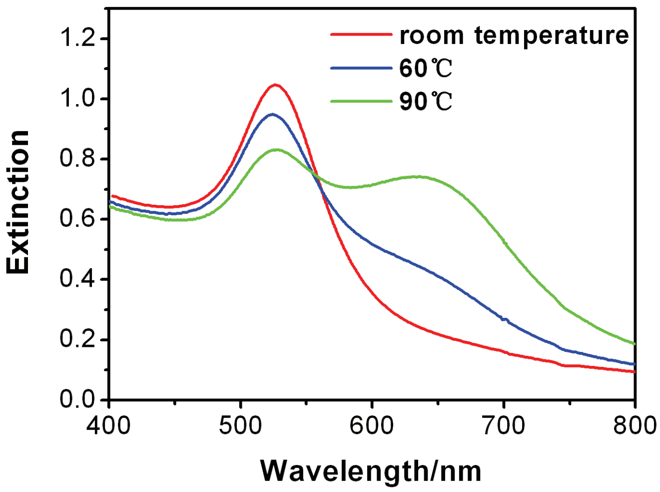

Fig. S2 Extinction spectra of the assemblies obtained at different reaction temperatures with the same pH of 3 and cysteine concentration of 3.3 μM. The reaction time is 10 min.

Effect of particle size on the reactivity

The assembly and disassembly behavior of differently sized Au NPs is also evaluated. Fig. S3a shows the extinction spectra corresponding to 9.4 and 12.7 nm Au NPs before and 15 min after the addition of cysteine. The original extinction peaks of the 9.4 and 12.7 nm Au NPs are positioned at 523 and 526 nm, respectively. After the introduction of cysteine, the extinction peaks greatly reduce in intensity, and new ones corresponding to the assembly appear. The extinction corresponding to the assembly of 12.7 nm Au NPs located at longer wavelength and appears more intense than that of 9.4 nm Au NPs. This suggests a higher assembly activity of larger NPs. These results can be ascribed to that larger particles have relative large surface areas to facilitate the attachment of cysteine and carry out more cysteine molecules, which makes them more active and exhibit fast response in cysteine-induced assembly.

The assembly realized through the electrostatic interaction between the zwitterionic groups is weakened and destroyed by tuning the pH to basic one, and the Au NPs is released from the assembly. It is important to examine the disassembly behavior for manipulating the SPB of Au NPs. To evaluate the optimum particle size for both assembly ability and reversibility, assemblies from 9.4 and 12.7 nm Au NPs were treated with NaOH solution to explore the disassembly activity. After tuning the pH from 3 to 11, the solution corresponds to assemblies of 9.4 nm Au NP changes from purple blue to pink immediately. But the solution which contained assemblies of 12.7 nm Au NPs does not show obvious color change. Extinction spectra were collected 10 min after the addition of NaOH solution (Fig. S3b). The extinction spectrum of 9.4 nm Au NPs shows a dramatic blue-shift and only one extinction peak located at 530 nm can be identified in the end, implying that the assemblies are broken up effectively. On the contrary, the extinction spectrum of 12.7 nm Au NPs still shows two extinction peaks corresponding to the assemblies and isolated particles. It is obvious that it is difficult to separate the assemblies of 12.7 nm Au NPs into isolated ones under the mild conditions because of the intense interaction introduced by much more cysteine molecules. To search for the conditions to untie the assemblies of 12.7 nm Au NPs, elevated temperatures from 30, 60, to 90 °C with a reaction time of 40 min were examined (Fig. S3c). The disassembly only takes place at 90 °C with the color of the solution changing from purple blue to pink accompanied with a little color fading due to the oxidation of Au(0) into Au(I) ions. Lower temperatures do not induce color change except subtle color fading at 60 °C. To sum up, assemblies from large particles are difficult to break not only for the stronger electrostatic interactions induced by more cysteine molecules attached on the larger surface of the NPs, but also for the lower surface curvature promoted much more limited space among the tight assembled NPs. It is inconvenient for OH^- ions to penetrate into these highly linked NPs to break down the electrostatic interaction between cysteine molecules. The difficulty in deprotonizing the surface of densely packed NPs has also been reported previously.[S1] Furthermore, the pH-dependent assembly of 9.4 nm Au NPs is capable of being cycled for several times by tuning the solution from acid to basic condition(Fig. S4).

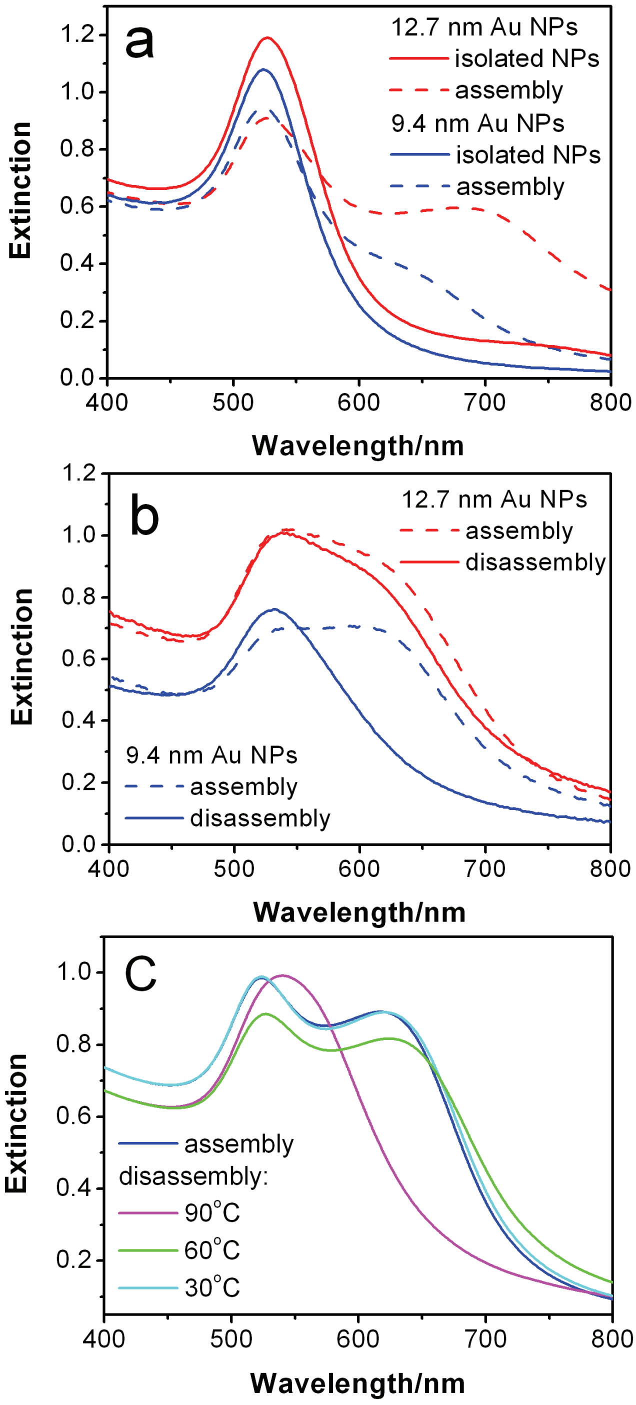

Fig. S3 (a) Extinction spectra showing the assembly of Au NPs of different sizes. The pH, cysteine concentration, and reaction time are 3, 3.3 μM, and 15 min, respectively. (b) Extinction spectra showing the disassembly of Au NPs of different sizes. The disassembly time for 9.4 and 12.7 nm Au NPs are 10 min and 2 h, respectively. The pH and cysteine concentration are 11.0 and 3.3 μM, respectively. (c) Extinction spectra showing the disassembly of 12.7 nm Au NPs under different temperatures for 40 min. The extinction spectrum of the assembled NPs is provided for reference.

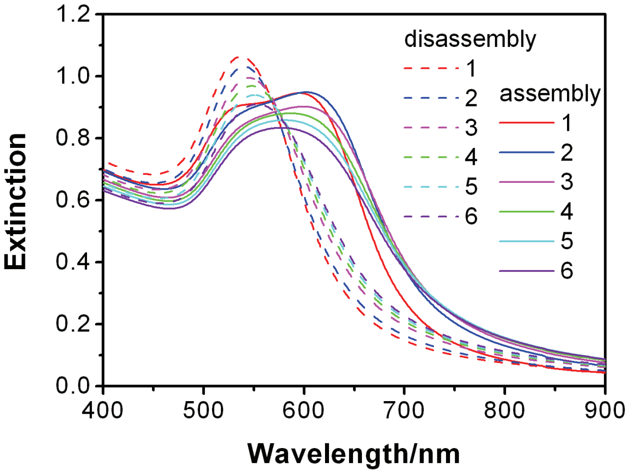

Fig. S4 Extinction spectra showing the reversible assembly and disassembly of 9.4 nm Au NPs at room temperature (6 cycles).

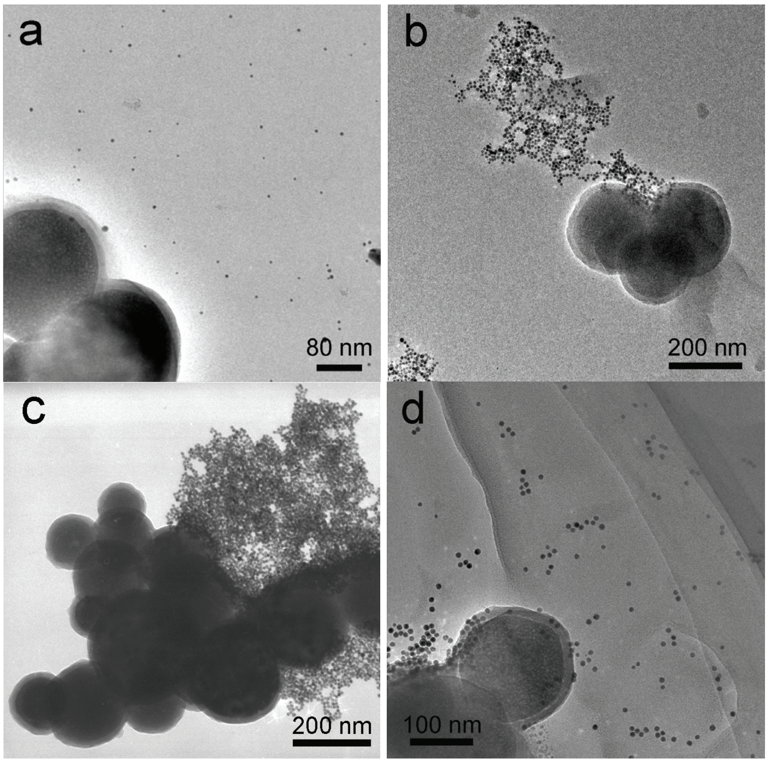

Fig. S5 TEM images of (a) $NaYF_4$:Yb,Er and isolated Au NPs, (b) Au NPs assembled into 2D structures and (c) 3D architectures, (d) disassembled Au NPs. The $NaYF_4$:Yb,Er NPs are coated with a ~20 nm thick silica shell.

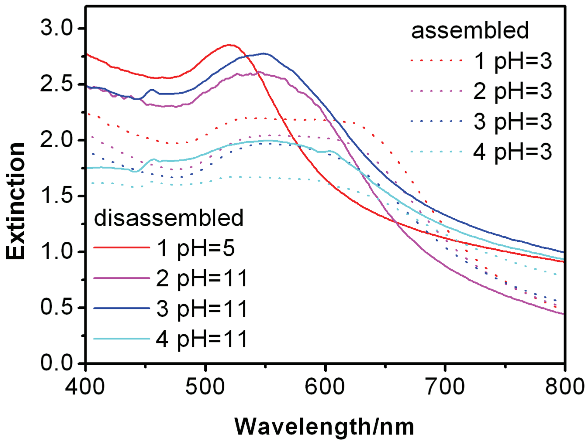

Fig. S6 The extinction spectra of Au NPs (9.4 nm) and $NaYF_4$:Yb,Er NPs mixed at pH = 5 without cysteine (red solid line), and reversible assembly (pH = 3) and disassembly (pH = 11) of Au NPs in the presence of $NaYF_4$:Yb,Er NPs at room temperature.

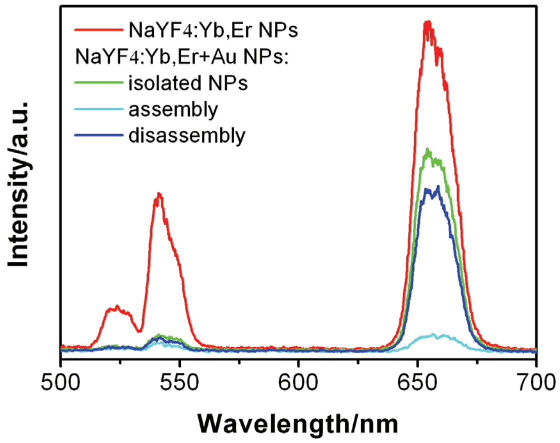

Fig. S7 Upconversion emission of $NaYF_4$:Yb,Er NPs without and with isolated, assembled, and disassembled Au NPs. As control experiments, $NaYF_4$:Yb,Er and Au NPs are poured into two separate quartz cells. The cell containing Au NPs is located between that of $NaYF_4$:Yb,Er NPs and the spectral signal detector.

Reference

[S1] I.-I. S. Lim, W. Ip, E. Crew, P. N. Njoki, D. Mott, C.-J. Zhong, Y. Pan and S. Zhou, *Langmuir*, 2007, **23**, 826.