Electronic Supplementary Information

Thermoresponsive Nanoparticles + Plasmonic Nanoparticles = Photoresponsive Heterodimers: Facile Synthesis and Sunlight-Induced Reversible Clustering

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Experimental

Synthesis of Fe_3O_4 magnetic nanoparticles: The magnetic nanoparticles were prepared based on the method reported by Park *et al.* (Ultra-Large-Scale Syntheses of Monodisperse Nanocrystals. *Nat. Mater*. **2004**, *3*, 891) First, iron oleate complex was synthesized as follows: 3.6 g of iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, ⩾98%, Sigma-Aldrich) was dissolved in 20 mL deionized water (DI water). 14.1 g of sodium oleate (⩾82%, Sigma) was dissolved in a mixed solvent containing 26.7 mL of ethanol (HPLC, Fisher) and 46.7 mL of hexane (AR, Fisher). The two resulting solutions were mixed and heated to 70 °C for 4 h. Afterwards, the upper organic layer was washed three times with 10 mL DI water in a separatory funnel. Hexane was then evaporated in a rotary evaporator at 65 ℃ for 2 h until a waxy solid form of iron oleate complex was obtained. Fe_3O_4 nanoparticles were synthesized by thermo-decomposition. Iron oleate complex (12 g) and oleic acid (1.9 g, 90 %, Aldrich) were dissolved in 1-octadecene (66.67 g, 90 %, Aldrich). The mixture was heated to 315 ℃ with a heating rate of ~3 $℃ \cdot min^{-1}$. The reaction was allowed to proceed at 315 ℃ for 30 min. The resulting Fe_3O_4 nanoparticles were washed with hexane and acetone and collected with centrifugation at 9000 rpm for 20 min. The washing and precipitating cycles were repeated for at least 3 times.

Synthesis of Ag-Fe_3O_4 heterodimers: 10 mg of the Fe_3O_4 nanoparticles, 10 mg of silver acetate (CH_3COOAg, 99 %, Sigma-Aldrich), and 0.2 g of PNIPAM (Mw = 20000 ~ 40000, Nibiner-Polymer) were well dissolved in a mixed solvent containing 8 mL of toluene (AR, Fisher) and 3 mL of ethanol. The solution was kept at 60 ℃ with stirring for 15 h under nitrogen to form Ag-Fe_3O_4 dimers. After reaction, the solvent was removed by rotary evaporation at 45 ℃ for 15 min. The resultant product can be readily dispersed in water. Fe_3O_4 nanoparticles capped with PNIPAM were also prepared with the same procedure but without adding CH_3COOAg.

Characterizations. The nanoparticles were characterized with Field Emission Transmission Electron Microscopy (FETEM, JEOL JEM-2100F, Japan) operated at 200 kV and Transmission Electron Microscopy (TEM, JEOL JEM-3010, Japan) operated at 300 kV. The photoresponse of the dimers was tested with a 150-W solar simulator (Newport 96000 with an AM 1.5 D filter, US). In order to remove UV and infrared light, a filter with cut-off wavelengths of 400 and 700 nm was attached. 1 mL aqueous dispersion of the Ag-Fe_3O_4 heterodimers or Fe_3O_4 nanoparticles with a concentration of 100 μg per mL was loaded into an open vial with 1 cm diameter. The vial was then placed under the solar simulator with stirring for 1 h. The distance between the vial to light source was about 10 cm. The ambient temperature surrounding the vial was 25 ℃. The size of the nanoparticles was obtained using dynamic laser scattering on a ZetaSizer Nano system (Malvern, UK) immediately upon removal of the sample from the solar illumination. Afterwards, the sample was allowed to stay at ambient conditions for 30 min before it was vortexed for 30 seconds and tested with the ZetaSizer again. For the preparation of TEM samples, 10 μL of the sample under illumination was dropped on a copper grid followed by drying. For comparison, TEM samples were also prepared using Ag-Fe_3O_4 dimers without solar illumination. Thermogravimetric analysis (TGA) was conducted under nitrogen protection. M-H curve was obtained with a vibrating sample magnetometer (VSM) at room temperature. The applied magnetic field was from 10000 to -10000 G and back to 10000 G again with a depth of 500 G. Background testing was also conducted with the same procedure. Before TGA and VSM tests, the Fe_3O_4 nanoparticles and Ag-Fe_3O_4 heterodimers were dried in oven at 75 ^{o}C overnight. Inductively coupled plasma mass spectrometry (ICP-MS) measurements were conducted to obtain the mass ratio of Fe3O4 to Ag in the heterodimers by dissolving the sample in 5% nitric acid.

Calculation of heat absorbed by Ag nanoparticles illuminated with solar simulator

The average diameter of Ag particle in dimer was 6.28 nm according to TEM measurement. The density of silver is 10.49 g·cm^{-3}. Therefore, the mass of Ag particle in one Ag-Fe_3O_4 dimer was:

$$10.49(g \cdot \mathrm{cm}^{-3}) \times \frac{4}{3}\pi R^3 = 10.49(g \cdot \mathrm{cm}^{-3}) \times \frac{4}{3}\pi \times 3.14^3(nm^3) = 1.36 \times 10^{-18} g$$

According to the results of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Thermogravimetric Analysis (TGA), the mass ratio of Ag particles in dried Ag-Fe_3O_4 dimers was 12.72%. The concentration of dimers for photoresponsive test was 100 μg/mL. The average volume of solvent surrounding each dimer is:

$$\frac{1.36\times10^{-18}(g)}{12.72\%\times100(\frac{\mu g}{mL})}=1.07\times10^{-13}mL$$

The intensity of visible light (400~700 nm) from the solar simulator (AM 1.5 direct) is ~1 W·m^{-2}·nm^{-1}. The visible light absorption of Ag-Fe_3O_4 dimers is shown in Fig. S5. The diameter of the sample vial was 1 cm. 1 mL of the dimer dispersion was illuminated with solar simulator. Therefore, the total heat absorbed by the Ag nanoparticle of a dimer in 1 h is:

$$Q=\frac{\sum_{i=400}^{i=700}I_i\times t\times S}{N}$$

$$=\frac{\sum_{i=400}^{i=700}I_0\times(1-10^{-A_i})\times t\times S}{N}$$

$$=1.6\times10^{-12}J$$

Where Q is the absorbed heat, I_i is the intensity of absorbed light, I_0 is the incident light intensity (approximately 1 W·m^{-2}·nm^{-1}), A_i is the absorbance from UV-vis measurement (Figure S5), t is the illumination time, S is the illuminated area (1cm^2), and N is the number of Ag particles in the sample.

The specific heat of Ag is 0.233 J·K^{-1}·g^{-1}. If there was no dissipation of heat to the surrounding materials, the temperature of Ag nanoparticle can increase by:

$$\frac{1.6\times10^{-12}(J)}{0.233(J\cdot K^{-1}\cdot g^{-1})\times1.36\times10^{-18}(g)}=5\times10^{6}K$$

The specific heat of water is 4.186 J·K^{-1}·g^{-1}. If all the heat absorbed by Ag nanoparticles is transferred to the solvent, it will cause the fluid temperature to increase by:

$$\frac{1.6\times10^{-12}(J)}{4.186(J\cdot K^{-1}\cdot g^{-1})\times1.07\times10^{-13}(g)}=3.6K$$

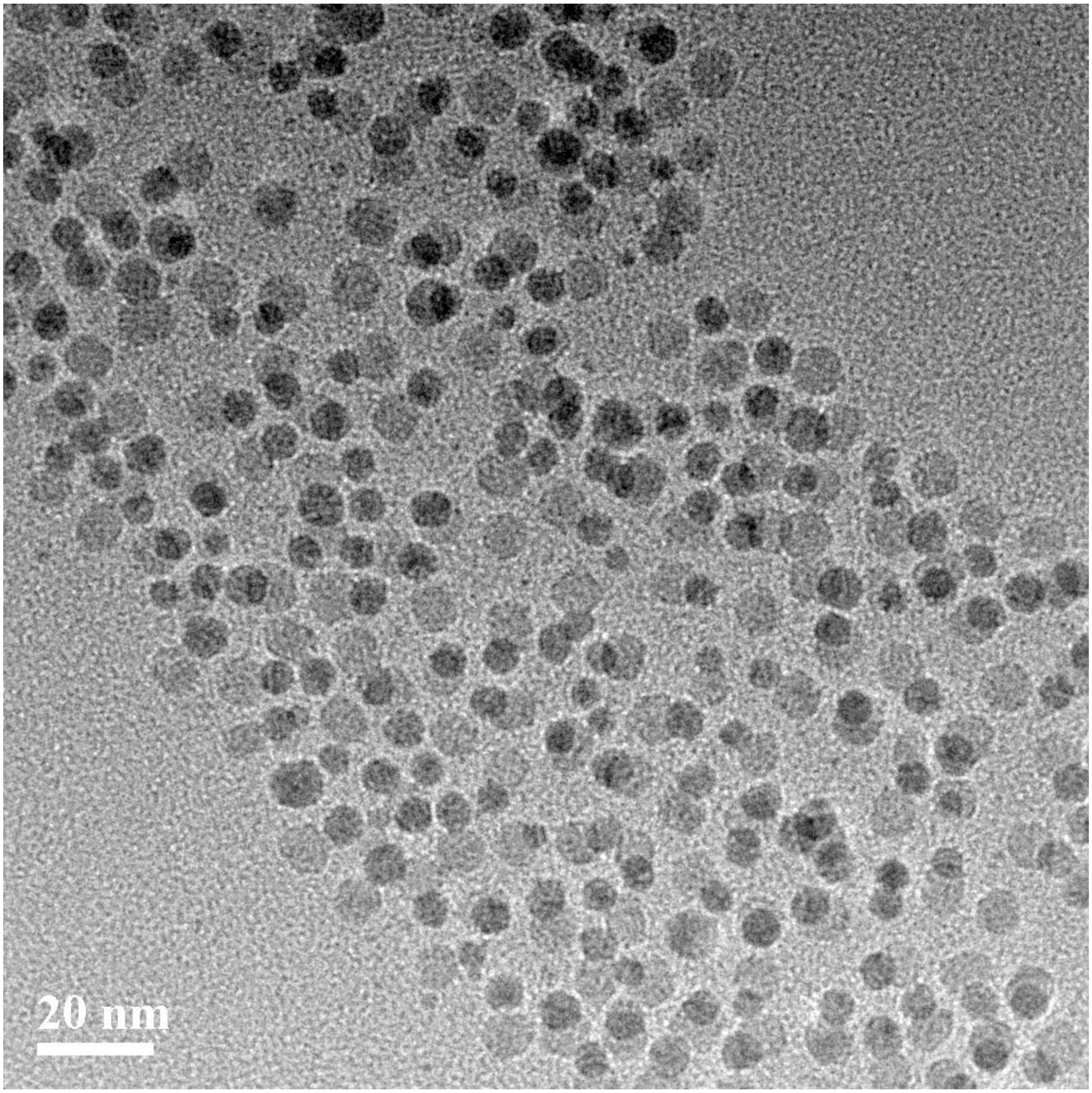

Figure S1. TEM image of Ag-F_3O_4 heterodimers before illuminated with solar simulator.

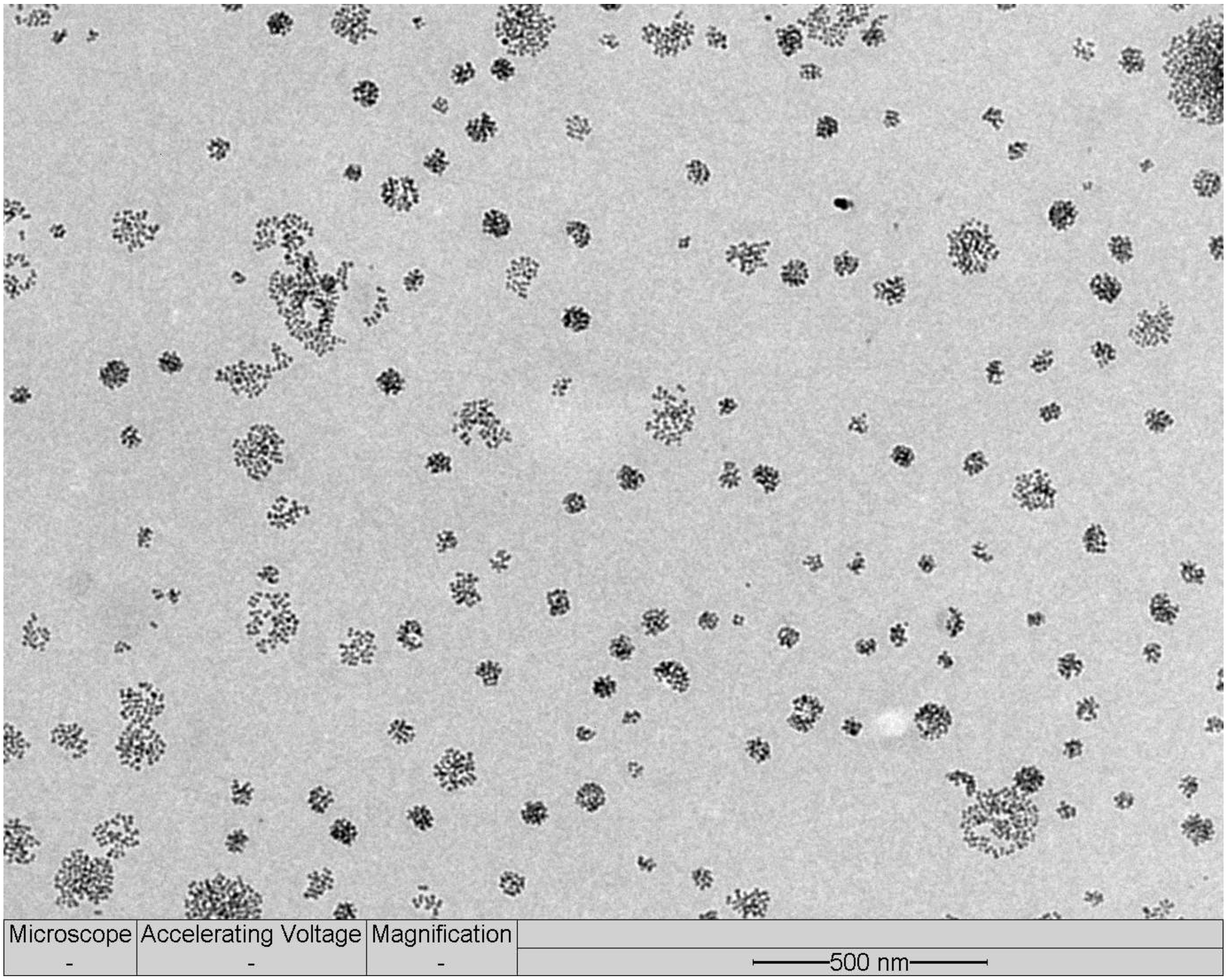

Figure S2. TEM image of Ag-F_3O_4 heterodimers illuminated with solar simulator.

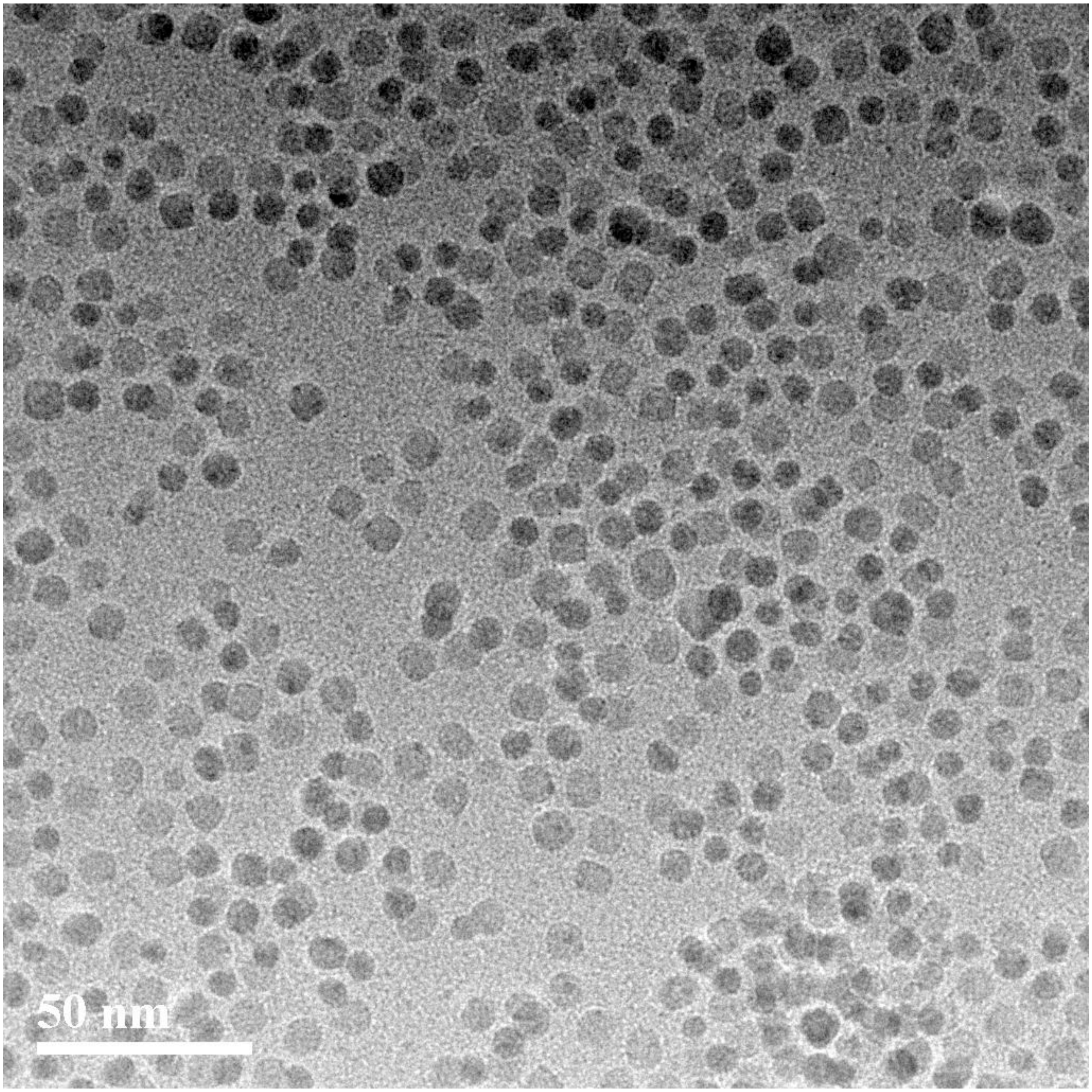

Figure S3. TEM image of re-dispersed Ag-F_3O_4 heterodimers. The sample was prepared after 30 minutes upon removal from solar illumination and vortexed for 30 seconds.

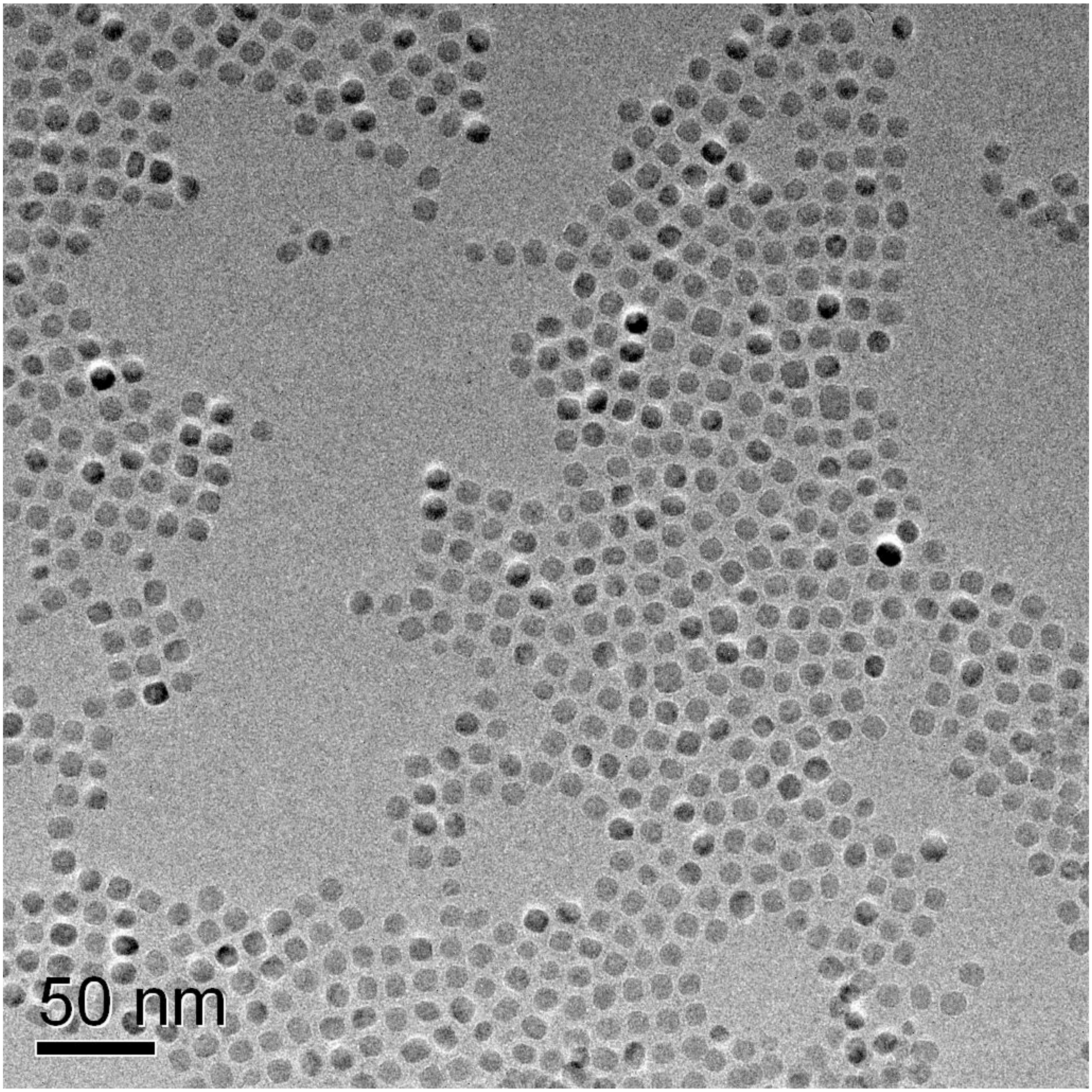

Fig. S4 TEM image of PNIPAM-capped Fe_3O_4 nanoparticles after illuminated with solar simulator.

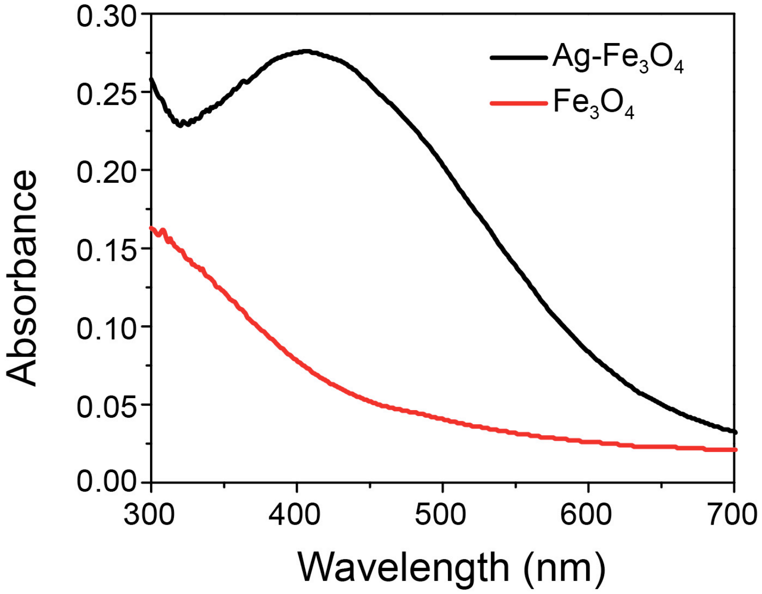

Figure S5. UV-vis spectra of Ag-Fe_3O_4 heterodimers and Fe_3O_4 nanoparticles.

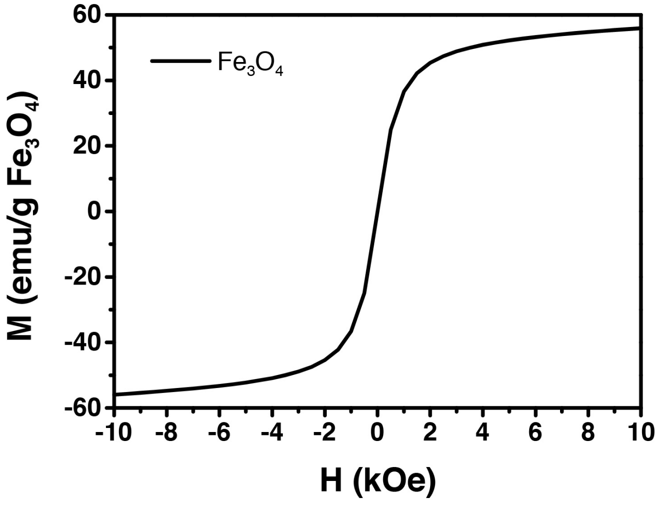

Fig. S6. Room temperature hysteresis loop of Fe_3O_4 nanoparticles.

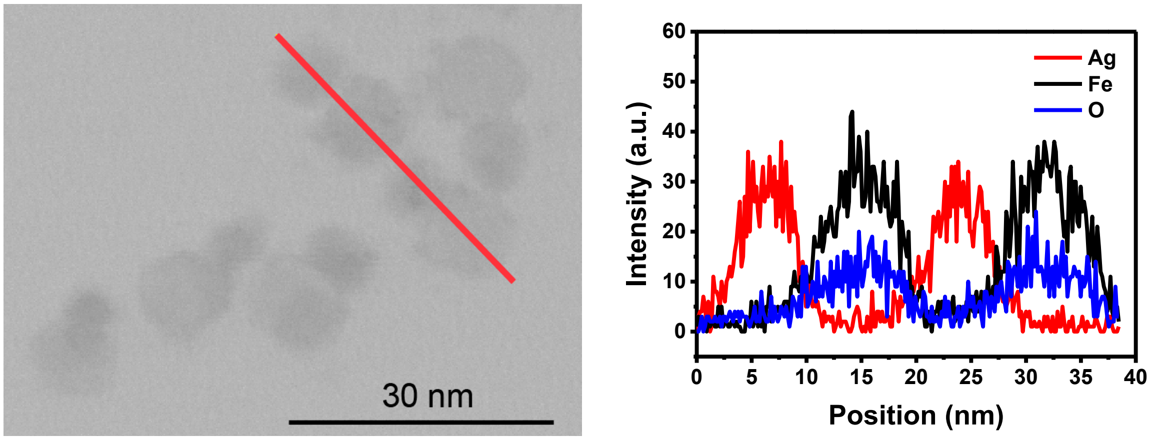

Fig. S7. EDX line scan of dispersed Ag-Fe_3O_4 dimers showing the elemental distribution of Ag, Fe and O.

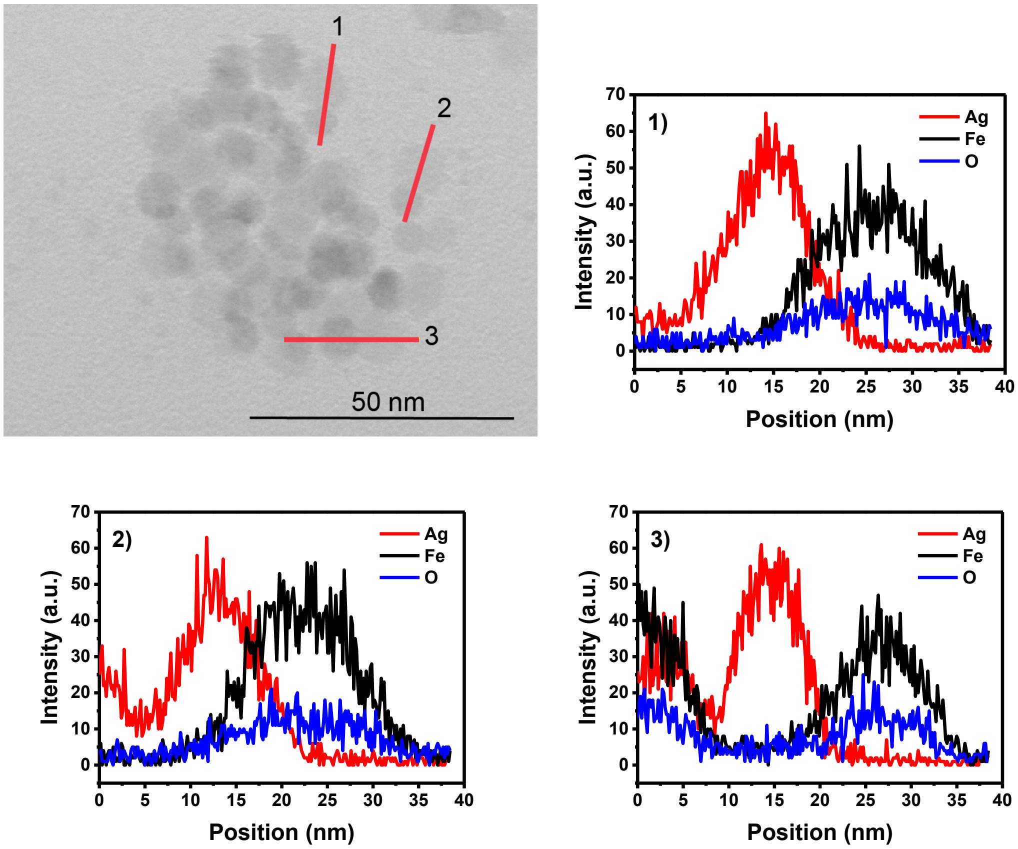

Fig. S8. EDX line scans of aggregated Ag-Fe_3O_4 dimers showing the elemental distribution of Ag, Fe and O.