Solvent-Induced Division of Plasmonic Clusters

Supporting Information

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Experimental Part

Synthesis of gold nanospheres (Au_{10}). Gold seeds (~1.5 nm) were prepared by borohydride (10 mM, 0.3 mL) reduction of $HAuCl_4$ (0.25 mM, 5 mL) in aqueous cetyltrimethylammonium bromide solution (CTAB, 100 mM). After 30 minutes, an aliquot of seed solution (0.6 mL) was added to a growth solution (100 mL) containing cetyltrimethylammonium chloride (CTAC, 100 mM), $HAuCl_4$ (0.18 mM) and ascorbic acid (0.36 mM). The mixture was left undisturbed for 12h at 25 °C. Upon synthesis, the solution was centrifuged (9000 rpm, 2h) to remove excess CTAC and ascorbic acid, and redispersed in water to a final gold concentration of 2.5 mM.

Synthesis of gold nanospheres (Au_{40}). Gold nanoparticles with diameter of 40 nm were obtained by seeded growth of 10 nm gold nanoparticles. To grow 10 nm gold nanospheres up to 40 nm diameter, a volume of 2.5 mM 10 nm gold colloid (0.08 mL) was added under magnetic stirring to a growth solution (25 mL) containing benzyldimethylammonium chloride (BDAC, 100 mM), $HAuCl_4$ (0.5 mM), and ascorbic acid (1 mM). The mixture was left undisturbed for 30 min at 30 °C, and then washed twice by centrifugation. The particles were finally dispersed in water to a final gold concentration of 5 mM.

Ligand exchange. To replace surfactant with hydrophobic polymer, thiolated polystyrene (PS-SH) (Polymer Source, Inc) with molecular weight of 53 kg/mol was used. THF solution (10 mL)

of PS-SH (1 molecule of PS-SH per nm^2 of gold surface) was added dropwise under sonication to the dispersion of gold nanoparticles (5 mM, 1mL). The solution was left for 15 min in an ultrasonic bath. To ensure ligand exchange, the resulting mixture was left undisturbed for 12 h, and then centrifuged twice (12000 rpm for Au_{10} and 7000 rpm for Au_{40}, 60 min). The particles were finally dispersed in THF.

Synthesis of unary clusters. In a typical self-assembly experiment, water (0.4 mL) was added to the Au_{40}@PS_{509} colloid (1.6 mL, THF) under magnetic stirring. In the final mixture the concentration of gold was set to be between 10^{-11} M and 12.5×10^{-11} M (in terms of NPs). The solution was left undisturbed for 10 min under ambient condition. To quench further aggregation, a solution of PS_{403}-*b*- PAA_{62} (Polymer Source, Inc) in THF (6 mg/mL, 0.2 mL) was added. Subsequently, the water content was increased up to 35 wt%, followed by increasing the temperature up to 70 ºC, which was maintained for one hour. The final solution was centrifuged twice (3500 rpm, 20 min) and dispersed in pure water.

Synthesis of binary clusters. In a typical experiment, water (0.4 mL) was added to the mixture (1.6 mL THF) containing Au_{10} and Au_{40} at different ratios, under magnetic stirring. The solution was left undisturbed for 10 min under ambient condition. To quench further aggregation, a solution of PS_{403}-*b*-PAA_{62} in THF (6 mg/mL, 0.2 mL) was added. Subsequently, the water content was increased up to 35 wt%, followed by increasing the temperature to 70 ºC, which was maintained for one hour. The final solution was centrifuged twice (2500 rpm, 20 min) and dispersed in pure water.

Solvent-induced size decrease of binary clusters. To the mixture of binary clusters Au_{10}/Au_{40}=50, stabilized with copolymer (2.8 mL, 35 wt% H_2O in THF) different amounts of dioxane (0.5, 1, 1.5 mL) were added under magnetic stirring. The solution was left undisturbed for 10 min under ambient condition, followed by increasing the temperature up to 70 ºC, which was maintained for one hour. The final solution was centrifuged twice (2500 rpm, 20 min) and dispersed in pure water.

TEM characterization. The aqueous colloids containing the clusters (7 µL) were drop-casted on a carbon coated copper TEM grid by evaporation for 2 hours. TEM images were obtained in a JEOL JEM 2010F field emission gun transmission electron microscope, operating at 200 kV.

DLS characterization. Dynamic Light scattering experiments were performed on a Zetasizer, Nano-SZ (Malvern). Aqueous solutions containing kinetically locked plasmonic clusters (20 µL) were diluted in Milli-Q water (2 mL) that was previously filtered through a membrane filter with nominal pore size of 0.45 µm. The measurements were performed at room temperature.

$$E = \frac{200RL^2kT}{\pi s^3}e^{-\pi D/L} - \frac{R}{6}\left(\frac{A_{232}}{D-2L} - \frac{2A_{123}}{D-L} + \frac{A_{121}}{D}\right) - 4\pi RD_0\gamma(1-f)e^{-(D-2L)/D_0}$$

Eq 1. Energy interaction potential for two gold nanoparticles stabilised with polystyrene.[1] The first two components correspond to polymer brush and van der Waals interactions, where R is the radius of the nanoparticles, L is the length of the polymer chain, s is the footprint diameter of a single polymer chain, and A is the Hamaker constant. The third term accounts for hydrophobic interactions, where γ is the interfacial energy of the polystyrene in a specific solvent composition, and D_0 is the hydrophobic decay length. The hydrophobic term is effectively zero in the pure solvent case, when f = 1, and contributes an increasingly attractive hydrophobic interaction as f progressively decreases from 1 to 0.

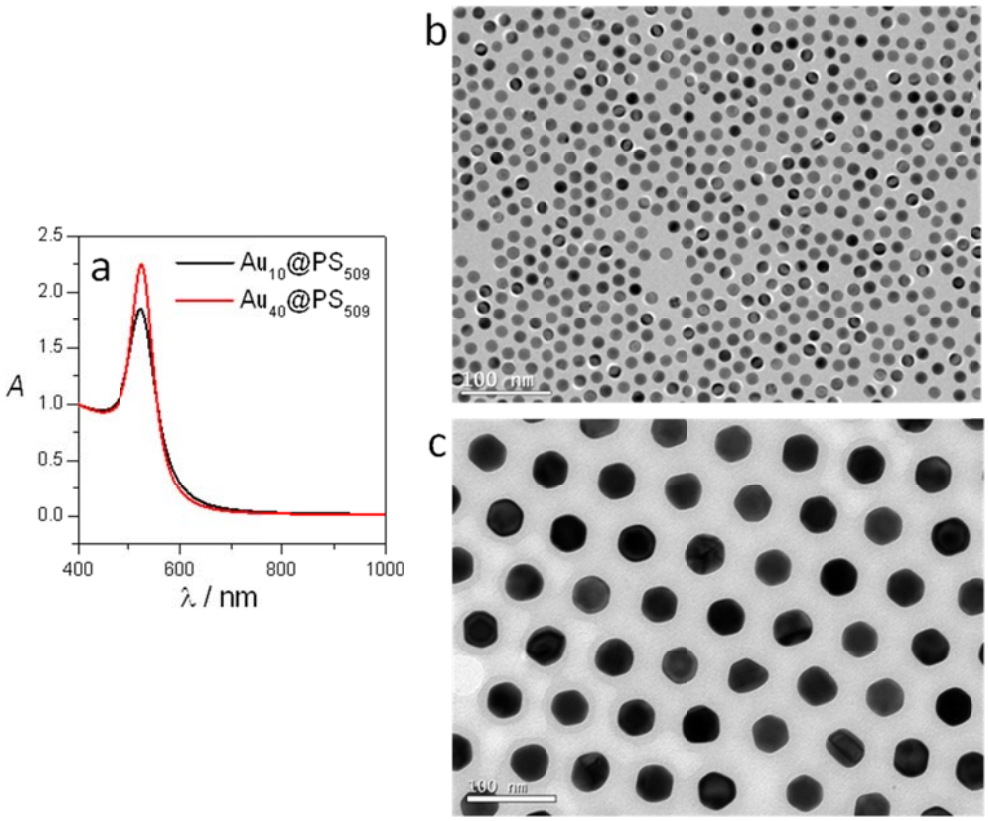

Figure S1. Nanoparticle building blocks. (a) UV-vis spectra of Au_{10} and Au_{40} dispersed in THF. (b,c) TEM images of Au_{10} and Au_{40}.

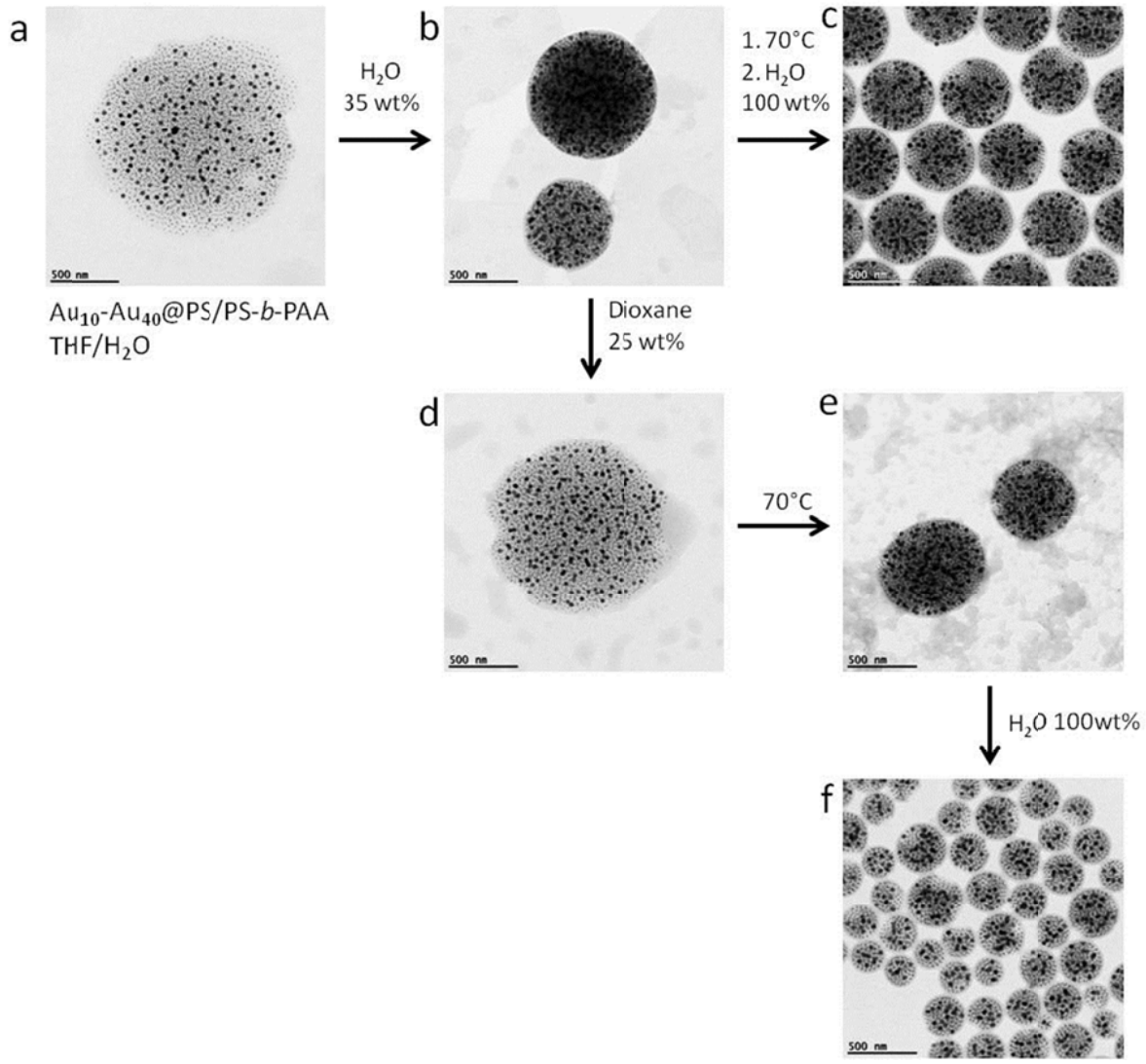

Figure S2. Schematic presentation of the synthetic pathway. (a-c) standard preparation of the binary mixture. (d-f) additional steps for treatment with dioxane.

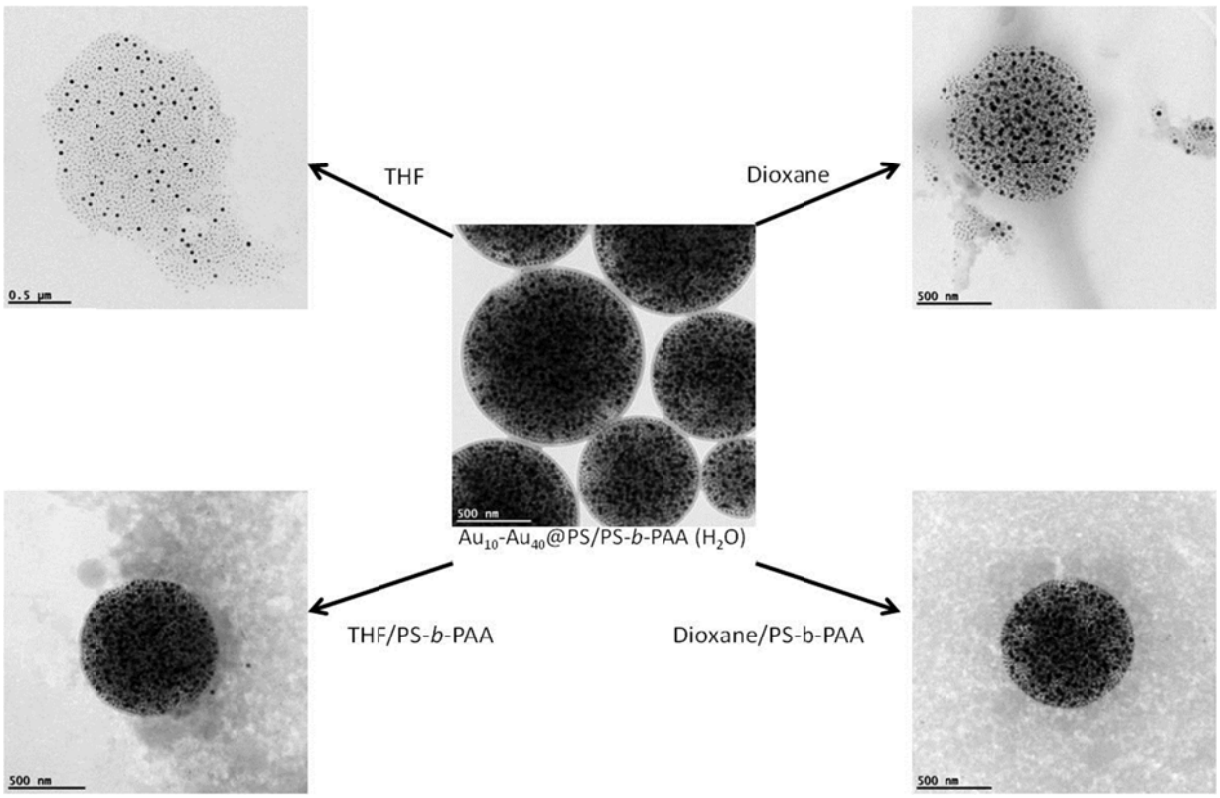

Figure S3. Treatment of binary clusters in pure water with THF and dioxane. The addition of good solvent without the copolymer leads to disintegration of the clusters at a certain time window of (5 min). The clusters maintain their size when THF or dioxane are added together with copolymer.

REFERENCES

1. A. Sánchez-Iglesias, M. Grzelczak, T. Altantzis, B. Goris, J. Pérez-Juste, S. Bals, G. Van Tendeloo, S. H. Donaldson, B. F. Chmelka, J. N. Israelachvili, and L. M. Liz-Marzán, *ACS Nano*, 2012, **6**, 11059–11065.