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Supporting Information

# **Controlled Formation of Nanoparticle Clusters Mediated by Electrostatic Interaction**

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## 1. Experimental Section.

#### **1.1 Materials**

Hydrogentetrachloroaurate(III) hydrate, (99.9%, metal basis Au 49%), 3aminopropyltriethoxysilane (98%), and 4-aminothiophenol (97%) were purchased from Alfa Aesar. The 4-mercaptobenzoic acid (99%) was purchased from Sigma-Aldrich. Amphiphilic diblock copolymer polystyrene-*block*-poly (acrylic acid) (PSPAA) was purchased from Polymer Source. All chemical reagents were used without further purification.

#### 1.2 Synthesis of Au nanoparticles (AuNPs) and Au@PSPAA core-shell NPs.

AuNPs with diameter of 15 nm were synthesized using the reported citrate reduction method (G. Frens, *Nat. Phys. Sci.* **1973**, 241, 20). Briefly, 10 mg of hydrogen tetrachloroaurate(III) hydrate was first dissolved in 100 mL of water in a round bottom flask, then heated in oil bath at reflux for 10 min with vigorous stirring, followed by adding sodium citrate dihydrate (3 mL, 1% w/w) into the solution. The mixture was heated for 30 min more before cooling to room temperature. AuNPs with diameter at 40 nm were synthesized by a seed mediated approach, in which the 15 nm NPs were used as seeds. In detail, HAuCl<sub>4</sub> solution (10 mg in 90 mL DI water) was heated at reflux for 10 min with vigorous stirring, followed by adding seeds (15 nm, 15 mL) and sodium citrate dihydrate (1 % w/w, 400  $\mu$ L). The mixture was heated for another 30 min before cooling down to room temperature.

Au@PSPAA core-shell NPs were synthesized using the method developed by Chen group (T. Chen, et. al., *J. Am. Chem. Soc.* **2008**, 130, 11858). The concentration of core-shell Au@PSPAA NPs ( $d_{Au} = 15 \text{ nm}$ ,  $d_{overall} = 30 \text{ nm}$ ) used in our experiments was about 5×10<sup>11</sup> particles/mL, which was estimated from that of 15 nm AuNPs used.

### **1.3 Formation of NP Clusters on Substrate**

First, 3-aminopropyltriethoxysilane (APTES) was used to functionalize the substrate. Specifically, a silicon wafer (~5 mm×5 mm) was immersed in a fresh prepared APTES aqueous solution (1  $\mu$ L APTES in 1mL DI water) for 15 minutes. Then take the silicon wafer out, and rinse it with large amount of water. To deposit the citrate-stabilized Au NPs onto APTES-functionalized substrate, we immerse the substrate into a solution of 15-nm Au NPs (0.45 mL, ~ 2.9×10<sup>12</sup> particles/mL) for

1 minute and then rinse it with large amount of water. The distribution density of Au NPs on substrate can easily be controlled by changing the immersion time and the concentration of Au NPs. Then air plasma etching (Plasma Cleaner: Harrick, PDC-002) was used to remove the APTES and citrate, leaving bare Au NPs on substrate. Then we put the substrate into a solution of 4-aminothiophenol (4-ATP, 10 mM, in EtOH) for 30 min to modify the bare Au NPs with 4-ATP. After that, we immerse the substrate into a solution of citrate-stabilized Au NPs (0.45 mL, in water) with addition of 50  $\mu$ L 4-mercaptobenzoic acid solution (4-MBA, 10 mM, in EtOH). The 4-MBA molecules can replace the citrate ions covering the Au NP surfaces due to the strong interaction between thiol groups and Au, which gradually makes the Au NPs unstable in solution. After 40 minutes, the substrate was taken out and washed with water. The yield of NP dimers depends on the immersion time as discussed in the text.

## 2. Theoretical Analysis of the Yield of NP Dimers.

Put a substrate with individual positive-charged NPs on its surface into a solution containing negative-charged NPs. The number of individual NPs on substrate, denoted by  $N_1(t)$ , satisfies the following equation,

$$N_1(t) = N_0 - \int_0^t k N_1(t) dt , \qquad (1)$$

where the k is the rate of a NP in solution attaching to an individual NP on substrate and  $N_0$  is the initial number of individual NPs. The solution of Equation (1) is

$$N_1(t) = N_0 e^{-kt} (2)$$

which indicates that the  $N_1(t)$  decreases exponentially with time. If the electrostatic repulsion between negative-charged NPs is negligible, the rates of attaching a negative NP in solution to an individual NP and to a NP dimer (containing a negative-charged NP and a positive-charged NP) on substrate can be taken the same. Thus the number of dimers on substrate, denoted by  $N_d(t)$ satisfies the following equation,

$$N_{d}(t) = \int_{0}^{t} k N_{1}(t) dt - \int_{0}^{t} k N_{d}(t) dt .$$
 (3)

The solution of Equation (3) is

$$N_d(t) = N_0 k t e^{-kt}.$$
 (4)

To obtain the maximal value of  $N_d(t)$ , we differentiate  $N_d(t)$ , and let  $dN_d(t)/dt$  equal to zero.

$$\frac{dN_d(t)}{dt} = N_0 k e^{-kt} - N_0 k^2 t e^{-kt} = 0$$
(5)

So the  $N_d(t)$  reaches its maximal value  $N_0/e$  when t is equal to 1/k. As a result, the maximal yield of dimers is

$$\eta^{max} = \frac{N_d^{max}}{N_0} = e^{-1} \approx 36.8\%.$$
 (6)

This is to say, if there is no mechanism to effectively decrease the rate of attaching NPs to the dimers formed on substrate, the yield of dimers should be much lower than the value (~80%) observed in our experiments. Taking the electrostatic repulsion between the negative-charged NPs into account, we use  $k_1$  and  $k_2$  to denote the rates of a NP in solution attaching to an individual NP and to a dimer, respectively. In this case, Equation (3) will be modified to

$$N_d(t) = \int_0^t k_1 N_1(t) dt - \int_0^t k_2 N_d(t) dt \,.$$
(7)

where the number of individual NPs on substrate,  $N_1(t)$ , still take the form of Equation (2) with k substituted by  $k_1$ . The solution of Equation (7) is

$$N_d(t) = k_1 N_0 \frac{e^{-k_1 t} - e^{-k_2 t}}{k_2 - k_1}$$
(8)

Let  $dN_d(t)/dt = 0$ , and we can obtain that when  $t = In(k_1/k_2) / (k_1-k_2)$ , the  $N_d(t)$  reaches its maximal value,

$$N_{d}^{max} = \frac{k_1 N_0}{k_1 - k_2} \times \left( e^{-\frac{k_1}{k_1 - k_2} ln \frac{k_1}{k_2}} - e^{-\frac{k_2}{k_1 - k_2} ln \frac{k_1}{k_2}} \right) = \frac{m N_0}{m - 1} \times \left( \frac{1}{m^{\frac{1}{m - 1}}} - \frac{1}{m^{\frac{m}{m - 1}}} \right), \quad (9)$$

where  $m = k_1/k_2$ . Thus, the maximal yield of NP dimers is

$$\eta^{max} = \frac{N_d^{max}}{N_0} = \frac{m}{m-1} \left( \frac{1}{m^{\frac{1}{m-1}}} - \frac{1}{m^{\frac{m}{m-1}}} \right).$$
(10)

Some typical values of  $\eta^{\text{max}}$  obtained at different values of *m* are listed in Table S1. When *m* tends to 1, the  $\eta^{\text{max}}$  tends to 36.8% as expected. To increase the  $\eta^{\text{max}}$  to about 80%, the value of *m* should be as large as 12. Thus in our experiments, the rate of attaching a NP to an individual NPs is much larger than that of attaching a NP to a dimer, which can be attributed to the electrostatic repulsion between the same charged NPs.

m	1.01	1.1	1.5	2	4	6	8	10	12	16	32
η <sup>max</sup> (%)	36.97	38.55	44.44	50.00	63.00	69.88	74.30	77.43	79.78	83.12	89.40

**Table S1.** Some typical values of  $\eta^{max}$  obtained at different values of *m*.



Figure S1. SEM image of Au NP dimers with 15-nm gap. The inset shows a TEM image of the Au@PSPAA core-shell NPs with shell thickness about 15nm.



Figure S2. SEM image of dimers made up of Au NPs and Fe<sub>2</sub>O<sub>3</sub>@PSPAA core@shell NPs. The inset shows a TEM image of the Fe<sub>2</sub>O<sub>3</sub>@PSPAA core@shell NPs.