Dynamic Adsorption Self-assembly of Au nanocubes for opposite charge Au nanoparticles in real time

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S1. Experimental Section

Materials: Gold(III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$, Sigma-Aldrich Co., St Louis, MO, USA), sodium borohydride ($NaBH_4$, Shanghai Lingfeng Chemical Reagent CO., LTD), cetyltrimethylammonium bromide (CTAB, Shanghai Lingfeng Chemical Reagent CO., LTD), copper sulfate ($CuSO_4$, Shanghai Lingfeng Chemical Reagent Co., Ltd), and l-ascorbic acid (AA, Sinopharm Chemical Reagent Co., Ltd), Citrate gold nanoparticles (solvent: citrate buffer, diameter: ~15 nm, volume: 25 ml, Sigma-Aldrich Co., St Louis, MO, USA) were used as received without further purification.

CTAB-Au NC preparation: In a typical synthesis experiment,[1] a $HAuCl_4$ solution (6.25 mL, 1 mM) was mixed with 18.75 mL of 0.1 M CTAB, followed by adding 150 μL of ice-cold NaBH4. The final mixture solution appeared as a brownish-yellow color named as seed solution. The seed solution was kept at 25°C for 4 hours for extra $NaBH_4$ decomposing. A HAuCl4 solution (5.00 mL, 2 mM) was mixed with 20.00 mL of 0.02 M CTAB at 25 °C, into which 50.0 μL of 0.010 M $CuSO_4$ was added. Then, 3.00 mL of a 0.10 M freshly prepared ascorbic acid (AA) solution was added. The

solution turned from orange to colorless (Growth solution). Then, 30 μL of the seed solution was added into the growth solution at 25 °C. The color of the solution gradually changed to violet-red within 10–30 min. After being centrifuged at 12000 rpm for 15 min and washed with deionized water once, the final concentration of the CTAB is 10 mM.

Ex situ experiment: 30 μL,50 μL,70 μL and 90 μL of Au nanocube solution was added in 150 μL of citrate Au NPs solution, respectively. The UV-vis (lambda950, Perkin Elmer Co., Ltd) was used to measure the self-assembly situation in solution. The TEM and HRTEM images of dry samples were collected by JEOL JEM-2200FS operating at 200 kV.

In situ experiment: ~0.6 μL of mixture solution (the volume ratio of Au NC and Au NPs is 2:1) was loaded into homemade liquid cell with two ~20-nm thick SiN_x membranes separated by ~200-nm thick spacer that sandwich the specimen solution. The liquid cell was sealed inside the Liquid Flow TEM holder (Hummingbird Scientific, Lacey, WA, USA) and inserted into a JEOL 2200FS TEM (JEOL Ltd, Akishima, Tokyo, Japan) operated at 200 kV. The TEM images were recorded at a rate of 10 frames per second using Gatan Orius CMOS camera at the resolution of 890*882 pixels. Electron beam doses can be calculated using Gatan Microscopy Suite software (GMS) version 3.0.

S2. Au nanocube (NC) surface being modified by cetyltrimethylammonium bromide (CTAB)

The thickness of CTAB coating on the Au NC surface arranged in two layers around is ~2 nm (Figure S1A). Amino groups of CTA^+ causes positive charge on the NC surface. The interplanar spacing of 0.235 nm corresponds the (111) plane of Au colloid shown in the HRTEM image in Figure S1B.

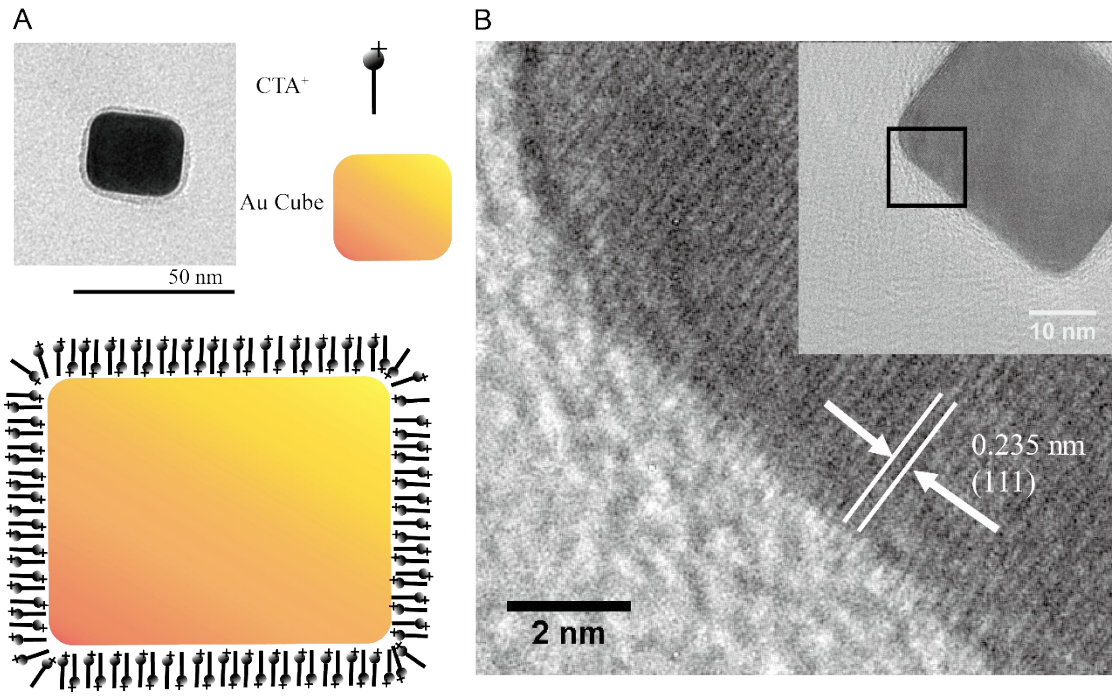

Figure S1. The TEM images of Au NC. (A) TEM image of the CTAB layer coating the Au NC surface. (B) The HRTEM image of Au NC with the (111) plane.

S3. The mean squared displacement (MSD)

In statistical mechanics, the mean squared displacement (MSD)[2,3] is defined as

$$MSD \equiv MSD < r^2 \geq \frac{1}{N}\sum_{n=1}^{N}\{[x_n(t) - x_n(0)]^2 + [y_n(t) - y_n(0)]^2\} \quad (1)$$

Where N is the number of particles to be averaged, $x_n(0)=x_0$, $y_n(0)=y_0$, are the reference positions of each particle at time 0, $x_n(t)$, $y_n(t)$ are the positions of each particle at time t.

S4. Comparative experiments of particle motions under different chemical environment.

The pure CTAB-gold NC solution (~0.6 μL) with ~10 mM CTAB is loaded on the liquid cell hold to be observed using TEM as shown in Fig. S2A. Compared with the 20 nm NC rotating and jumping rapidly (Fig. SA upper, Supporting Movie 6), the 30 nm NC moved almost imperceptibly (Fig. SA bottom , Supporting Movie 7) which indicated that the bigger size NC is not easy to move under this electron radiation condition (5.2 $e^-/(Å^2 \cdot s)$). The edge length of the NC using in the self-

assembly experiment in the main text is 35 nm which will be even more stable than the 30 nm NC. So the bigger size of NC make it stuck on the substrate firmly in such a low electron dose condition (< 6 $e^-/(Å^2 \cdot s)$).

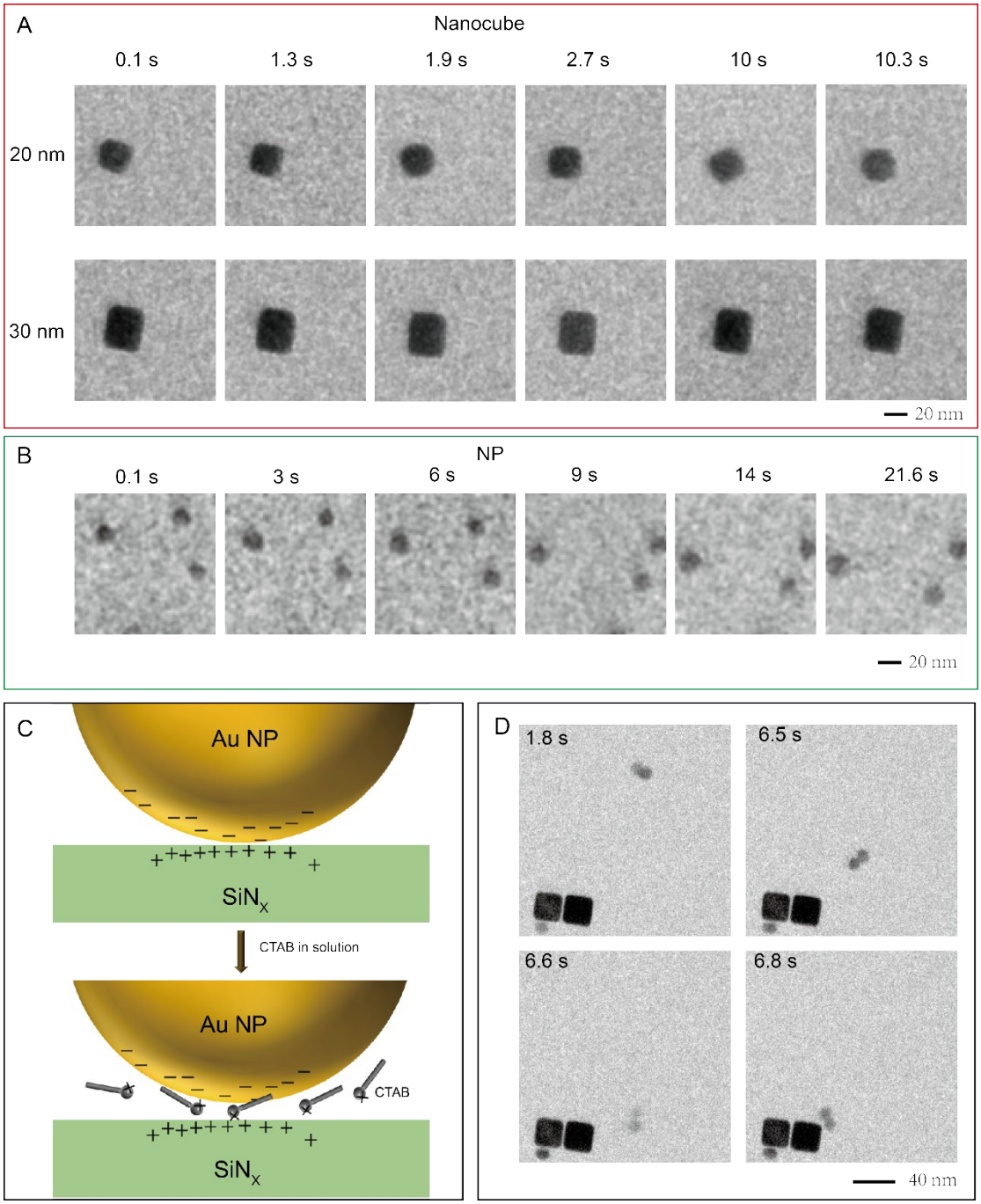

Figure S2 The comparative experiments of particle motions. (A) A time series of TEM images showing the dynamic motion of 20 nm and 30 nm NC. Electron beam dose: 5.2 $e^-/(Å^2 \cdot s)$. Images with Gaussian blur filter, σ=1 pix. (B) A time series of TEM images showing pure citrate Au NPs attaching on the SiNx substrate. Electron beam dose: 5.5 $e^-/(Å^2 \cdot s)$. Images with Gaussian blur filter,

σ=1.5 pixs. (C) The schematic diagram of CTA^+ inserted into the gap of citrate Au and the positive charge substrate to shield their electrostatic attraction. (D) A time series of TEM images showing the CTAB NC and citrate NP self-assembly motions in high CTAB concentration (~40 mM). Notes that the citrate Au twins formation indicating the repulsion force among citrate Au NPs decreasing. Electron beam dose: 6.0 $e^-/(Å^2 \cdot s)$.

Meanwhile, the pure citrate NPs are also adsorbed on the substrate firmly (Fig. S2B, Supporting Movie 8) without adding the CTAB Au NC. The citrate Au NPs just moved slightly (at 9 s) in the vicinity. However, when the positive molecular fragment (CTA+) was added in solution, they will shield or reduce the charge attraction between citrate NP and the positive SiN_x substrate (Fig. S2C) which make citrate NPs move randomly. in Fig. S2D (Supporting Movie 9).

S5. Non-attachment dynamic behavior of NP which passed away near the NC.

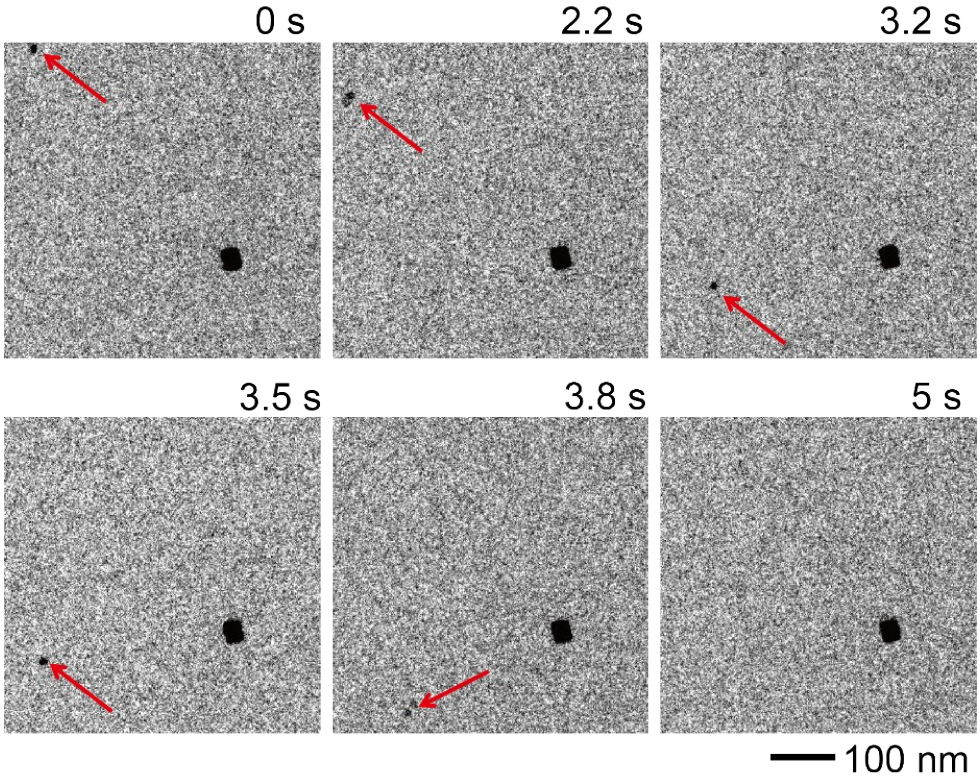

Figure S3 A time series of TME images show the NP keeps jumping and moves away from the Au NC without attachment. Electron beam dose: 4.1 $e^-/(Å^2 \cdot s)$.

Supporting Movie Captions

Supporting Movie 1: Dimer formation dynamic process of NP and NC attachment at the corner.

Supporting Movie 2: Dimer formation dynamic process of NP and NC attachment at the edge.

Supporting Movie 3: Trimer formation dynamic process of a secondary NP and a dimer attachment at the cube corner.

Supporting Movie 4: Trimer formation dynamic process of a secondary NP and a dimer attachment at the NP.

Supporting Movie 5: A NP moves away from A NC without being captured by the NC electrostatic force.

Supporting Movie 6: The 20 nm NC rotate and jump rapidly at the substrate.

Supporting Movie 7: The 30 nm NC was stuck on the substrate without vigorous activities.

Supporting Movie 8: The pure citrate Au NPs are stuck on the substrate.

Supporting Movie 9: The self-assembly process of NC and NPs in higher CTAB concentration (40 mM).

Supporting Information Reference

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