Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting Information

Self-assembly of Au@Ag core-shell nanocubes embedded with internal standard for reliable quantitative SERS measurements

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Experimental section

Materials

Cetyltrime-thylammonium bromide (CTAB) and polyvinyl pyrrolidone (PVP) were purchased from Sigma-Aldrich Co., Ltd., sodium borohydride ($NaBH_4$) and ascorbic acid (AA) were purchased from Acros Organics Co., Ltd., cetyltrime-thylammonium chloride (CTAC, 97%) was purchased from Aladdin Chemical Co., Ltd., silver nitrate ($AgNO_3$) and chloroauric acid ($HAuCl_4$) were purchased from Sinopharm Chemical reagent Co. Ltd., 4-MBA was purchased from Tokyo Chemical Industry Co., Ltd., dichloromethane (CH_2Cl_2) and n-hexane were obtained from Tianjin Bodi Chemical Co., Ltd., CV was purchased from Adamas Reagent Co., Ltd., APM was purchased from Aladdin Industrial Corporation. All the reagents were used as received. Deionized water (>18.0 MΩ) was used in all the experiments.

Synthesis of 40 nm Au NCs

At first, 3 nm Au nanoclusters and 10 nm Au nanospheres seed were synthesized according to the method proposed by Xia Younan group [1]. Then, CTAC solution (25 mL, 100 mM) was mixed with AA solution (1.625 mL, 10 mM) at temperature of 30 °C. And 10 nm Au seed solution (125 μL) was added to the mixed solution and gently stirred for 2 min. $HAuCl_4$ solution (25 mL, 0.5 mM) was added to the reaction system in a rapid stirring condition. The reaction system was changed from light red to bright red for half a minute and the mixture was stirred for 15 min and centrifuged (8000 rpm, 15 min). Finally, the product was dispersed CTAC solution (50 mL, 20 mM).

Synthesis of Au@Ag NCs with different edge length

Firstly, $AgNO_3$ solution (50 mM) of 0.125 mL, 0.25 mL, 0.5 mL and 0.75 mL were mixed with Au NCs seed solution (50 mL) respectively and stirred at 60 °C for 20 min. Subsequently, AA solution (500 mM) of 0.125 mL, 0.25 mL, 0.5 mL and 0.75 mL was added and the mixture was gently stirred for 3 hours under a water bath at 60 °C. After completion of the reaction, the reaction was stopped by an ice-water bath and the solution was centrifuged and the product was dispersed in CTAC solution (20 mM).

4-MBA modification

4-MBA solution (1 mL, 5×10^{-5} M) was added to 40 nm Au NCs solution (50 mL) at 30℃ and the mixture was stirred for 2 min. Then the reaction was standing for 30 min. Finally, the solution was centrifuged (8000 rpm, 15 min) and the product was dispersed in CTAC solution (50 mL, 20 mM), which was the seed of the next step of growing Au@4-MBA@Ag NCs.

Synthesis of Au@4-MBA@Ag NCs

$AgNO_3$ solution (50 mM) of 0.25 mL were mixed with Au NCs@4-MBA seed (50 mL) respectively and stirred at 60 °C for 20 min. Subsequently, AA solution (500 mM) of 0.25 mL was added and the mixture was gently stirred for 3 hours under a water bath at 60 °C. After completion of the reaction, the reaction was stopped by an ice-water bath and the solution was centrifuged and the product was dispersed in CTAC solution (20 mM).

Self-assembly of Au@Ag NCs monolayer film

The self-assembled process of monolayer film is modified from previous works [2, 3]. At first, 10 mL of the Au@Ag NCs solution were centrifuged and re-dispersed into CTAC solution (1 mM, 10 mL), then again centrifuged and re-dispersed into PVP ethanol solution (1 mL, 1% (mass ratio)), and finally centrifuged and re-dispersed into ethanol solution (1 mL).Then a certain amount of water and n-hexane are added into a container to form a water-oil interface. Subsequently, the Au@Ag NCs dispersed in ethanol of 200 μL were added to the interface slowly until a dense monolayer was formed. At last, the monolayer film was transferred onto silicon wafer with hydrophilic treatment.

Preparation of CV samples and APM spiked drink samples

To prepare the CV sample standard solution, 0.01 g CV powder was weighed and then dissolved it into 100 mL water. Aqueous solutions of CV (0.3 ppm, 0.25 ppm, 0.2 ppm, 0.15 ppm, 0.1 ppm, 0.05 ppm) were prepared by diluting CV standard solution with different proportions.

To prepare APM standard solution, 0.01 g APM powder was weighed and then dissolved it into 100 mL water. Aqueous solutions of APM (1500 ppm, 1300 ppm, 1100 ppm, 900 ppm, 700 ppm, 500 ppm) were prepared by diluting APM standard solution with different proportions. To prepare spiked drink samples, the drinks obtained from local market was firstly stirred and boiled to take out carbon dioxide from drink. Then, 0.1 mL APM solution with different concentrations was added to the 0.9 mL drink sample. Thus APM spiked drink samples (150 ppm, 130 ppm, 110 ppm, 90 ppm, 70 ppm, 50 ppm) were obtained.

Characterization and SERS measurement

UV-Vis spectroscopy was carried out by a spectrophotometer (Model Lambda 750, Perkin Elmer, USA) and the spectra were collected between 400 nm and 800 nm. Scanning electron microscopy (SEM) images were taken using a microscopy (model

S-4800, Hitachi, Japan) with an acceleration voltage of 5.0 kV. The Transmission electron microscope (TEM) images of the particles were obtained using a JEM-2100 TEM instrument (JEOL, Japan).

Raman spectra were recorded using a portable compact laser Raman Spectrometer (BWS415-785H B&W Tek, Inc.). The excitation wavelength of the laser is 785 nm. The spot size of focus laser beam is 10 μm in diameter. The typical laser power and accumulation time was 150 mW and 10 s respectively unless otherwise stated. The spectrum range of the spectrometer is 175 to 2700 cm^{-1} with a spectral resolution of better than 3 cm^{-1}. Boxcar averaging was used to smooth the raw spectrum and a baseline correction routine was performed to obtain the final spectrum with the background subtracted.

FDTD simulations

The FDTD calculations were performed using FDTD Solutions 8.0 software developed by Lumerical Solutions Inc. For all simulations, the dielectric function of gold was represented with the fitting from Johnson and Christy's data and that of sliver were taken from Palik (0~2μm). And the size of the nanostructure were set according to the statistical results of the average size measured from the experimental results. For all the array calculation, the gap of the Au@Ag NCs were set to 2 nm and the background refractive index was set to 1 (the refractive index of air). The periodic boundary condition was applied to x, y and z axis directions. When we calculate the extinction spectra of Au@Ag NCs array, a plane wave source with a wavelength range of 400 to 800nm was selected and the mesh size was set as 0.1 nm for all the samples. While calculating the EM near-field distribution of the periodic and randomly distributed Au@Ag NCs array, the light source was a plane wave source with a wavelength of 785 nm. Meanwhile, the mesh size was set at 0.05 nm for Au@Ag NCs array with smaller edge length (46 nm and 56 nm), 0.1 nm for Au@Ag NCs array with larger edge length (68 nm and 82 nm).

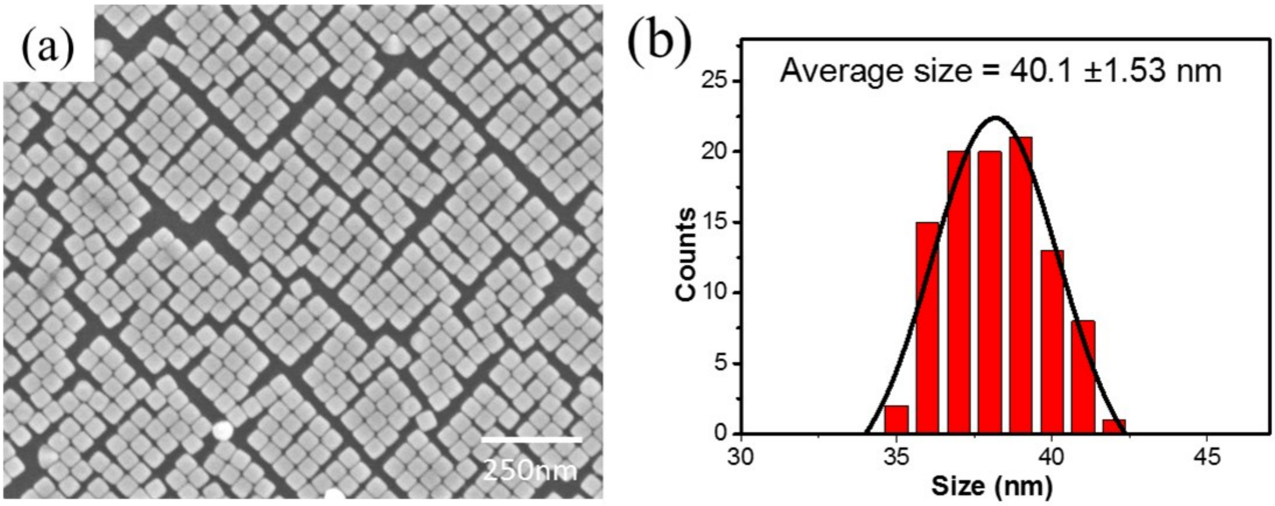

Fig. S1 (a) SEM image of core Au NCs; (b) corresponding particle size distribution of core Au NC colliod with fitted Gaussian distribution (dark line).

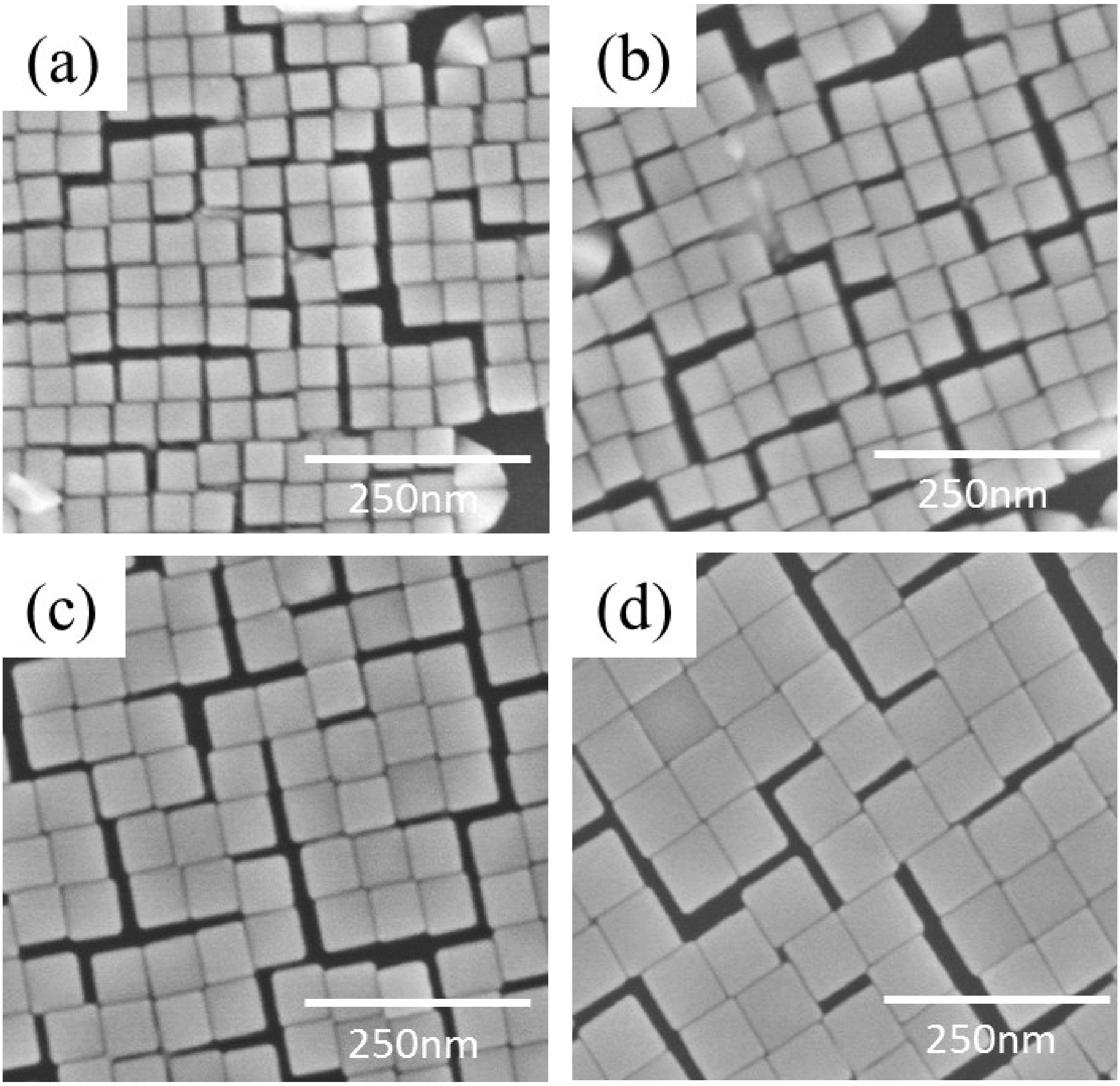

Fig. S2 SEM images of the Au@Ag NC colliods with different edge length of (a) 46 nm, (b) 56 nm, (c) 68 nm, (d) 82 nm.

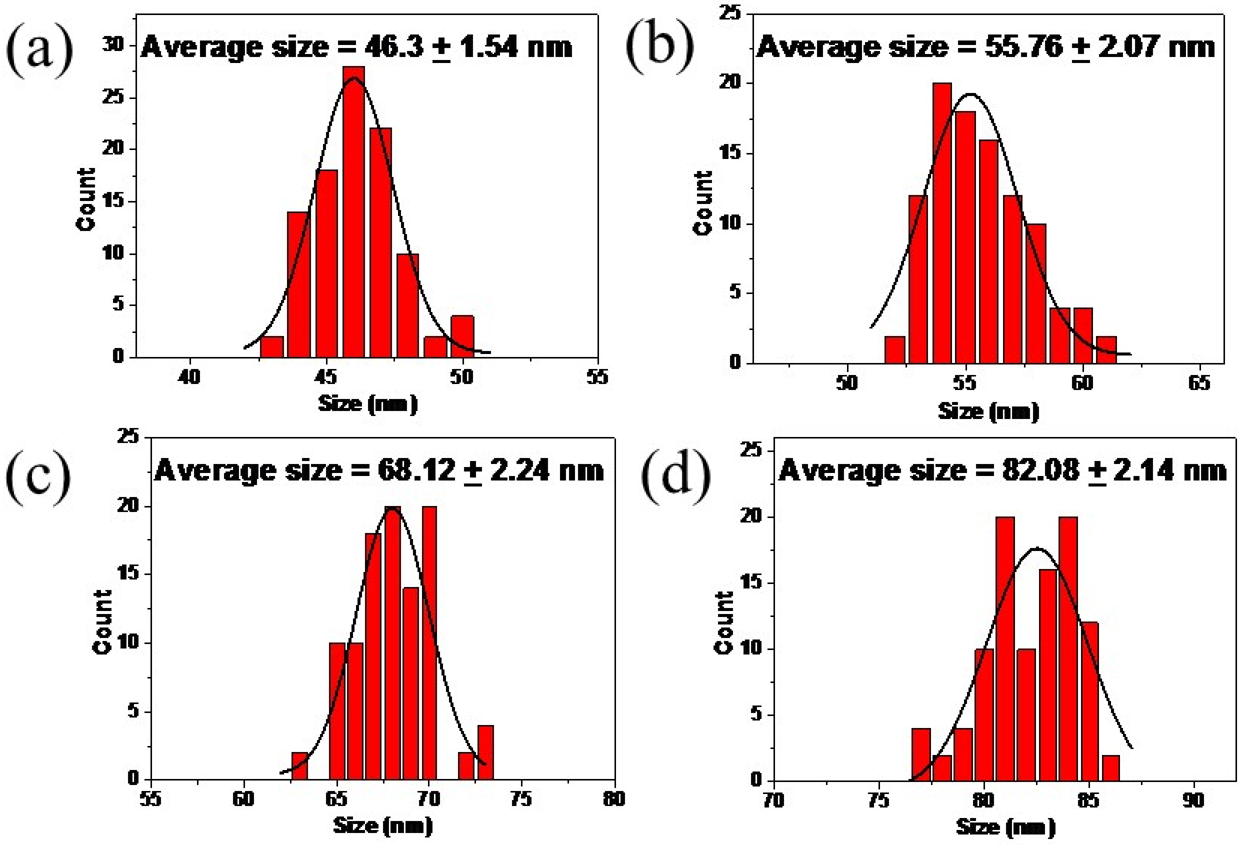

Fig. S3 The particle size distribution of Au@Ag NC colliods of four different edge lengths with corresponding fitted Gaussian distribution (dark line).

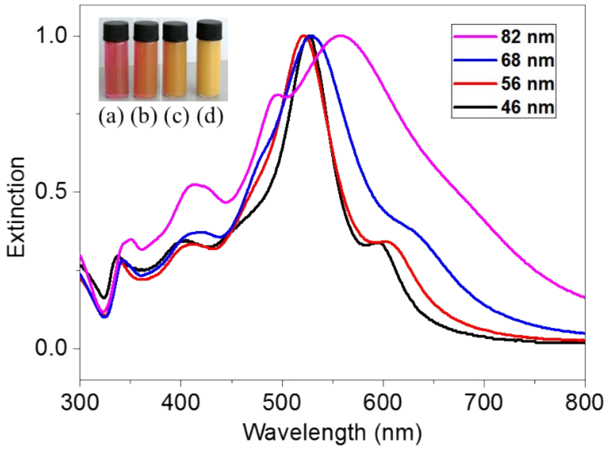

Fig. S4 Extinction spectra of Au@Ag NCs (focused core size 40 nm) with four edge lengths: (a) 46 nm, (b) 56 nm, (c) 68 nm, (d) 82 nm, respectively; inset figure: corresponding photograph of Au@Ag NCs colloids with different edge length.

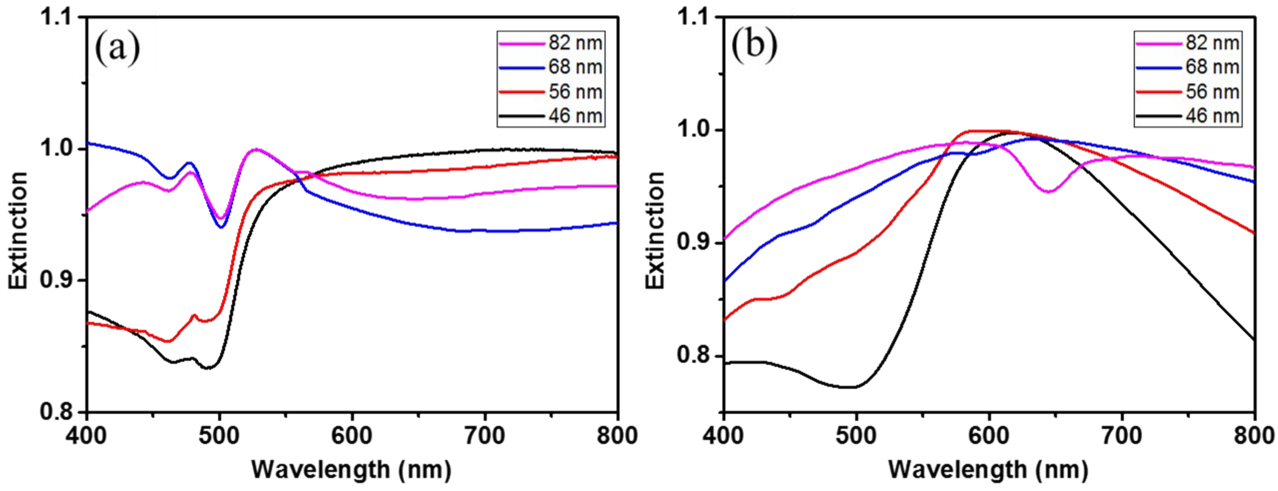

Fig. S5 Extinction spectra of each Au@Ag NC monolayer film with four different edge lengths (a) experimental results; (b) FDTD caculated results.

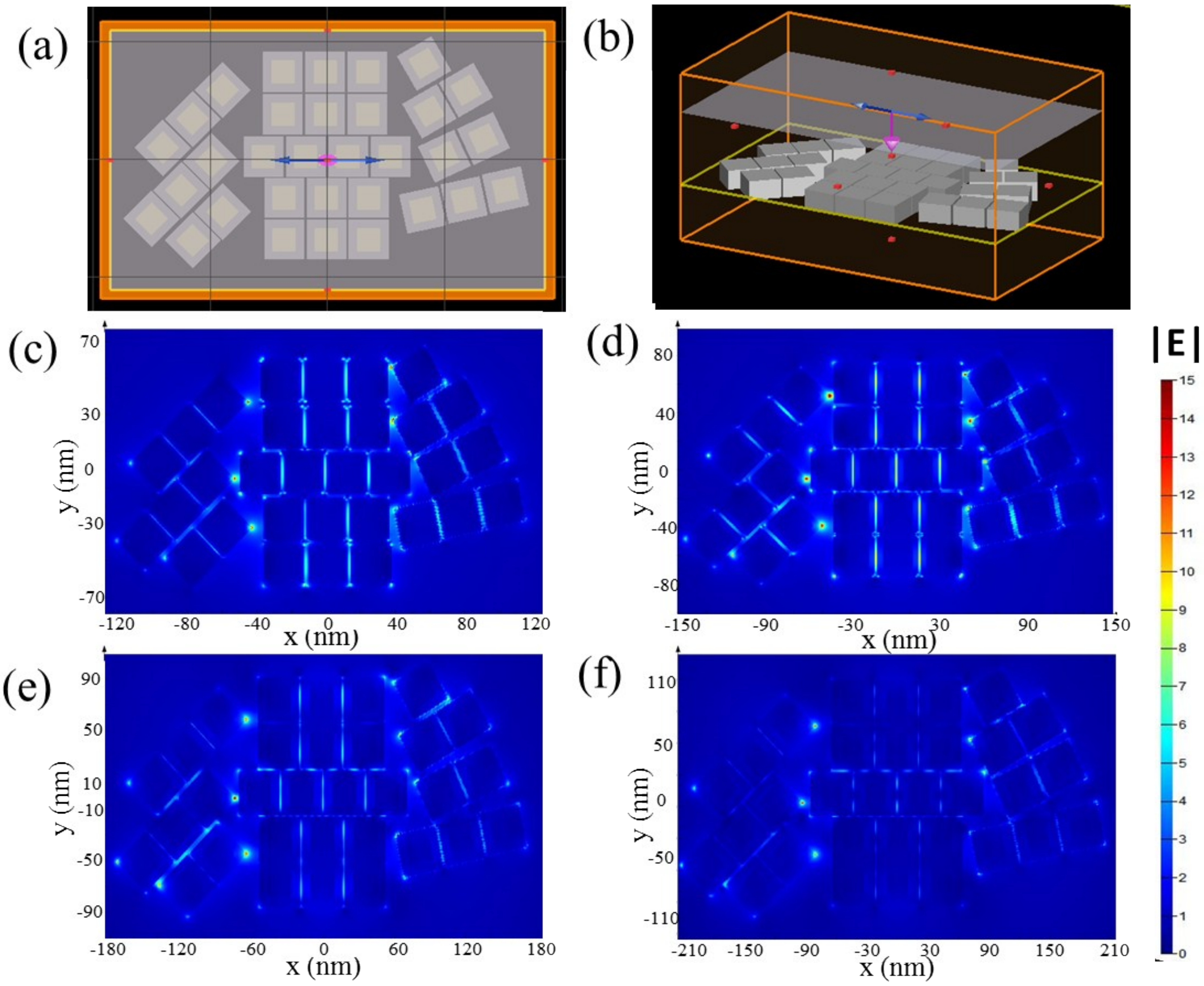

Fig. S6 EM near-filed distribution simulation model of randomly distributed Au@Ag NCs from XY view (a) and prerspective view (b) The simulation results of monolayer film based on Au@Ag NCs with different edge length (c) 46 nm; (d) 56 nm; (e) 68 nm; (f) 82 nm.

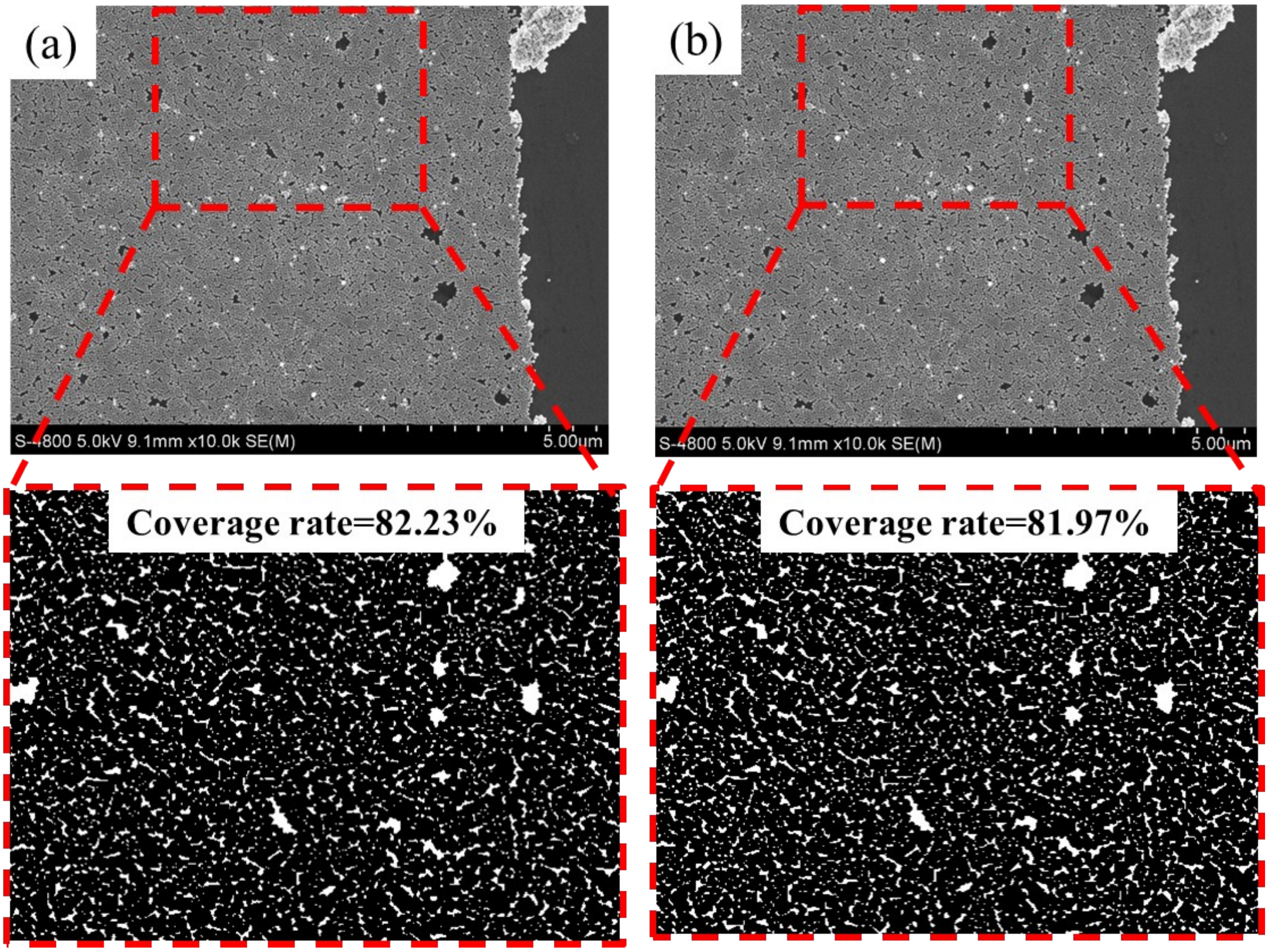

Fig. S7 The SEM image of Au@Ag NCs monolayer film at the same position with low magnification times before (a) and after (b) immersing into the CV aqueous solution. Lower pitcure: the local magnification pitcures calculated by Image J software.

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[2] Y. H. Lee, C. K. Lee, B. Tan, J. M. Rui Tan, I. Y. Phang and X. Y. Ling, Nanoscale, 2013, **5**, 6404-6412.

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