Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Electronic Supplementary Information

Large Area Controllable Hexagonal Close-packed Single-crystalline Metal Nanocrystal Arrays and Localized Surface Plasmon Resonance Response

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A. The influence of metal deposition methods on Au nanocrystal morphology

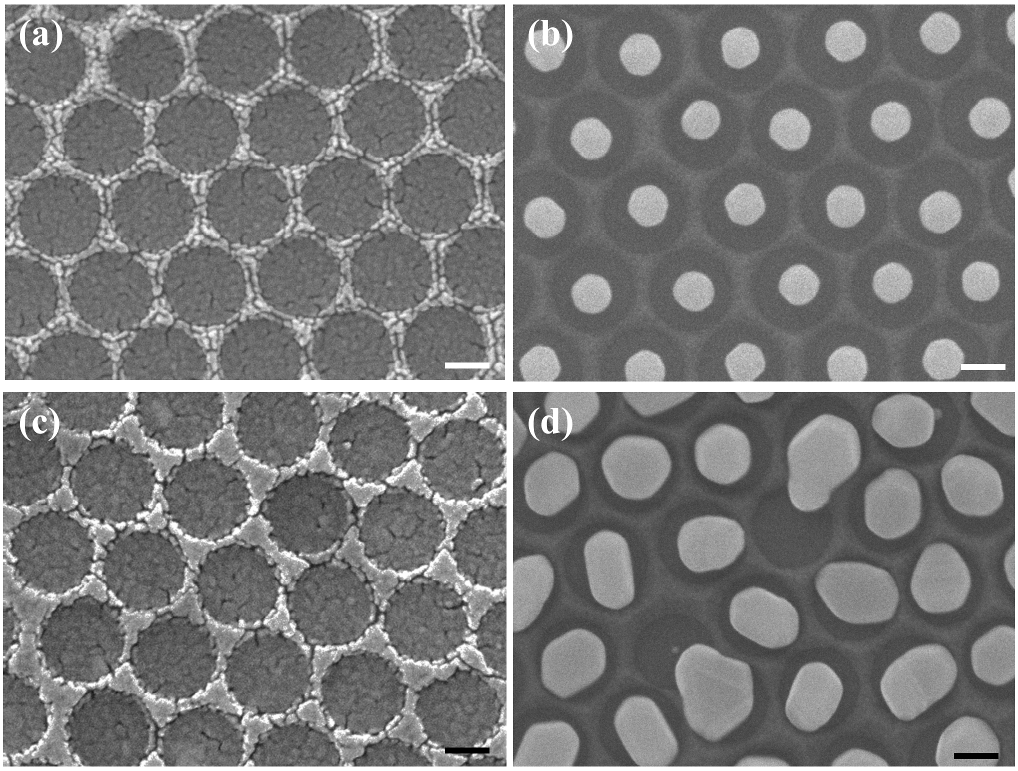

Fig. S1 SEM images of (a) 8 nm Au thin film deposited onto SiO_2 cells with an e-gun system, (b) the Au nanocrystal array formed by dewetting of Au thin film in (a) under annealing. (c) 8 nm Au thin film deposited onto SiO_2 cells with a plasma sputtering system, (d) the Au nanocrystal array formed by dewetting of Au thin film in (c) under the same annealing condition. All the scale bars represent 100 nm.

B. The influence of pretreatments on the continuity and uniformity of metal thin films and morphologies of metal nanocrystal arrays

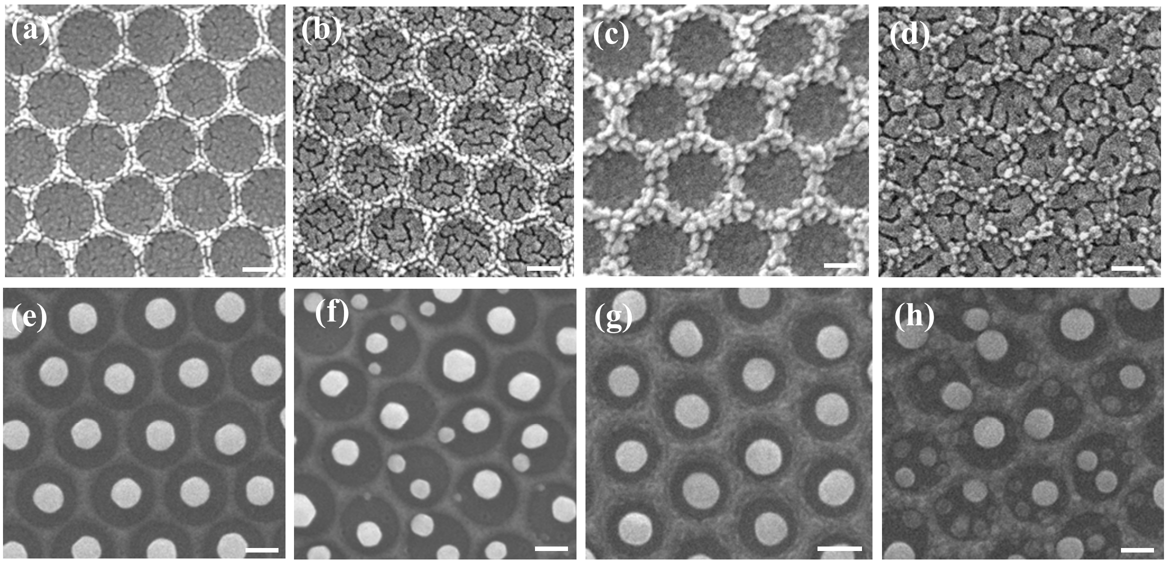

Fig. S2 SEM images of 8 nm Au thin film deposited onto SiO_2 cells (a) with and (b) without dipping HF before Au deposition. SEM images of 10 nm Ag thin films (c) with and (d) without Ge nucleation layer beneath Ag thin films. (e, f) The corresponding Au nanocrystal array formed by dewetting of Au thin film in (a, b) with the same annealing conditions. (g, h) The corresponding Ag nanocrystal array formed by dewetting of Ag thin film in (c, d) with the same annealing conditions. All the scale bars represent 100 nm.

C. The effects of surface energy on uniformity and continuity of metal layers

For the fabrication of Au nanocrystals, the samples (Si substrates with SiO_2 honeycomb cells as shown in Fig. 1b of main text) were dipped with HF to remove the native oxide on Si surface and loaded into deposition chamber immediately for following evacuation and metal deposition. Although native oxide is expected to be present on Si surface by this process, after HF treatment it is weak $SiO_{x\ (x < 2)}$, which has the property and surface energy different from the SiO_2 honeycomb cells. The surface energy difference between native oxide on Si surface after HF treatment and SiO_2 honeycomb cells can be verified by further experiment as described in the following paragraph as well as shown in the supplementary information (Fig. S3a and S3c). For the fabrication of Ag nanocrystals, the Ge layer was coated onto Si substrate *before* the formation of SiO_2 cells and therefore the Ge coated Si surface is present at the bottom of SiO_2 cell. In both cases, two different materials (bare Si or weak $SiO_{x\ (x < 2)}$ vs. SiO_2; Ge coated Si vs. SiO_2) with different surface energies are present. The corresponding surface energy values are provided in reference 26 of the main text.

The uniformity and continuity of metal layer are shown to be dominated by surface energy instead of terrain barrier. To highlight the effects of surface energy on uniformity and continuity of metal layers, we deposited metal layers onto substrates without SiO_2 cells and discussed for both Au and Ag cases. In the case of Au, we deposited Au onto three different substrates without SiO_2 cells: (a) Si with HF-treatment, (b) Si without HF-treatment and (c) SiO_2 under the same condition described in the experimental section. A uniform and continuous Au layer on Si with HF-treatment is shown in Fig. S3a. Uneven and discontinuous Au layers on Si without HF-treatment and SiO_2 shown in Fig. S3b and S3c indicate the unfavorable conditions for wetting of Au layers. The benefit of HF-treatment on the wetting of Au layer on Si surface can be highlighted and distinguished from Fig. S3a and S3b. In addition, the results shown in Fig. S3b and S3c can also support our explanation about the surface energy difference between native oxide on Si surface after HF treatment and SiO_2 honeycomb cells as mentioned in the first paragraph. In the case of Ag, we deposited Ag onto two substrates without SiO_2 cells: (d) Ge coated Si and (e) SiO_2 under the same condition described in the experimental section. A uniform and continuous Ag layer on Ge coated Si is seen in Fig. S3d. and uneven and discontinuous Ag layers on SiO_2 is evident in Fig. S3e. According to these experimental results, we can clarify that the surface energy dominates the uniformity and continuity of metal layer which necessitates surface treatments for obtaining uniform and continuous metal layer.

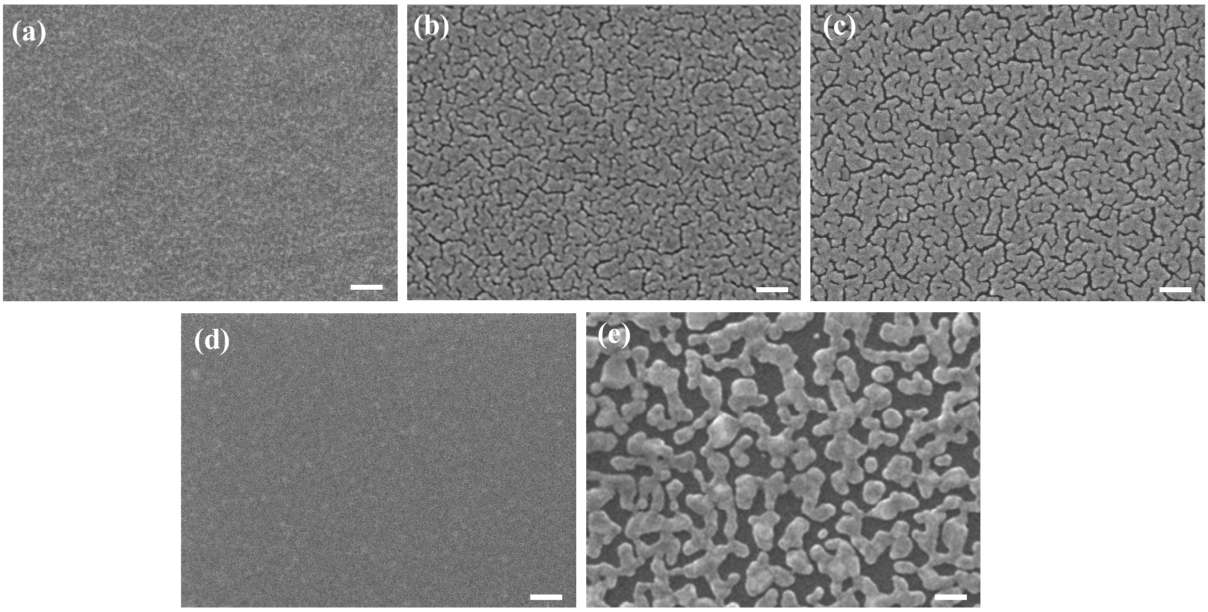

Fig. S3 SEM images of 8 nm Au thin film deposited onto (a) Si with HF-treatment, (b) Si without HF-treatment and (c) SiO_2; 8 nm Ag thin film deposited onto (d) Ge coated Si and (e) SiO_2 under same condition described in experimental section. All the scale bars represent 100 nm.

D. The measured and calculated scattering spectra of transferred Au nanocrystal arrays on flexible substrate(PU)

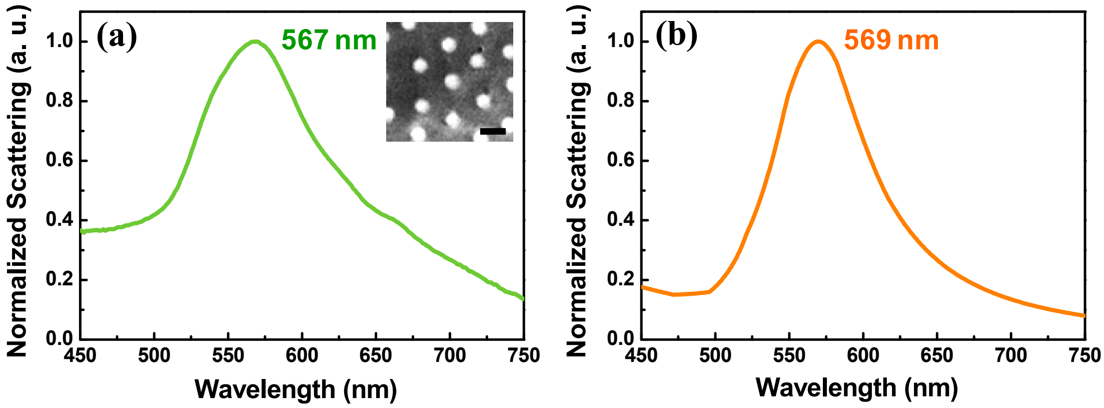

Fig. S4 The (a) measured and (b) calculated scattering spectra of transferred Au nanocrystal arrays on PU with crystal sizes of 72 nm and center-to-center distance of 190 nm. The corresponding SEM image is shown in the inset of (a) and the scale bar represents 100 nm.