Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Synthesis of gold nanodisk-molecular layer-gold film vertical structure: Molecular layer as the spacer for SERS hot spots investigation

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Enhancement factors (EFs) are calculated using the equation EF = $(I_{sers}/N_{ads})/(I_{bulk}/N_{bulk})$ by assuming the benzenethiol packing density of 6.8 * 10^{14} molecules cm^{-2} and 4MBA molecules adsorbed only on the sidewall of an Au nanodisk with the diameter of 350 or 700 nm. The laser beam was focused on a spot size of 1 μm^2 in diameter.

I_{sers}: the SERS intensity of each sample.

N_{ads}: the number of 4MBA molecules adsorbed on the sidewall of an Au nanodisk.

I_{bulk}: the SERS intensity of 4MBA molecules adsorbed on a bare gold film.

N_{bulk}: the number of 4MBA molecules adsorbed on a gold film within the area of 1 μm^2.

Figure S1. I-V measurements were acquired in ambient conditions and the resistances were measured by recording the I-V characteristic between -1 and +1 μA. For bridging the samples with gold wire electrodes, bigger gold disks with the diameter of 1 μm were synthesized. I-V curves of four Au disk-SAMs-Au film molecular junctions were shown in the figure and the brown line represents the average value. We calculate the resistances of 4.28 × 10^{13} Ω (red), 7.50 × 10^{13} Ω (black), 1.16 × 10^{14} Ω (green) and 1.92 × 10^{14} Ω (blue). These values are in line with the data reported for molecular junctions with high resistance (ref. 28).

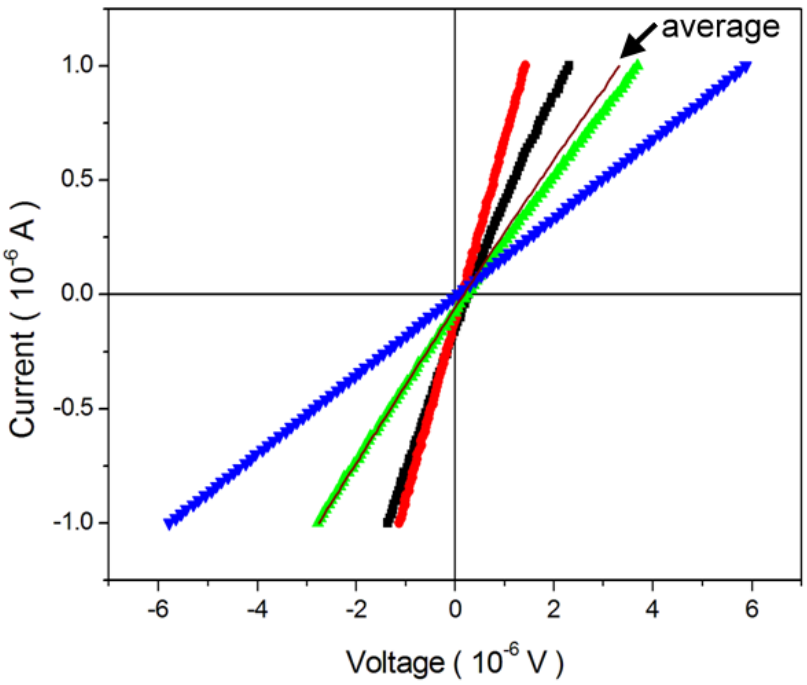
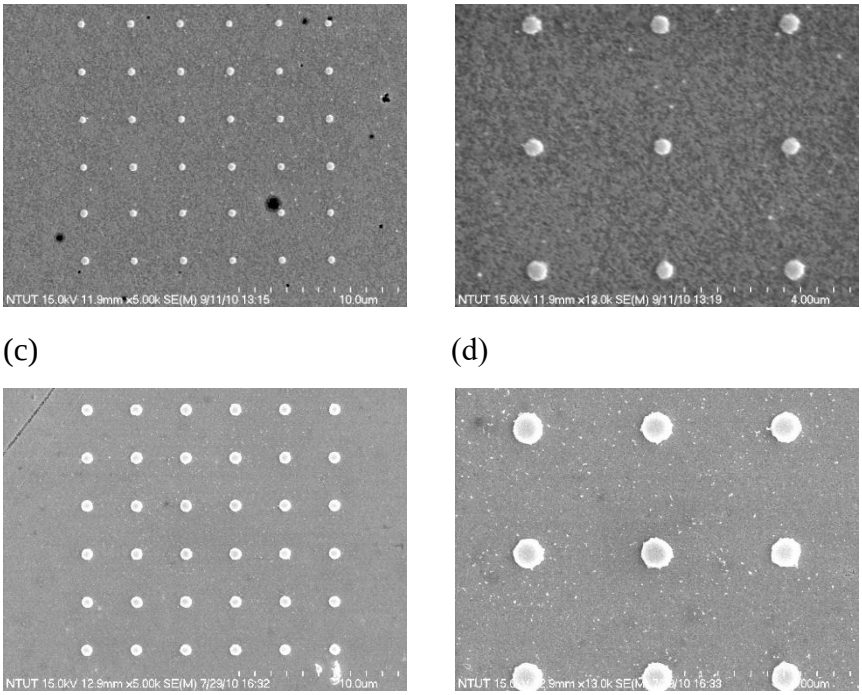


Figure S2. SEM images of (a) a 6*6 $Au_{disk/poly/SAM}$ array with a diameter of 350 nm for each nanodisk; (b) the high magnification image of (a); (c) a 6*6 $Au_{disk/poly/SAM}$ array with a diameter of 700 nm for each nanodisk; (d) the high magnification image of (c). The gap of these two sample is 2.4 nm.

(a) (b)



(c) (d)

Figure S3. The AFM (a) height profile and (b) width profile of the $Au_{disk/poly/SAM}$ array in Fig. 2c.

(a) (b)

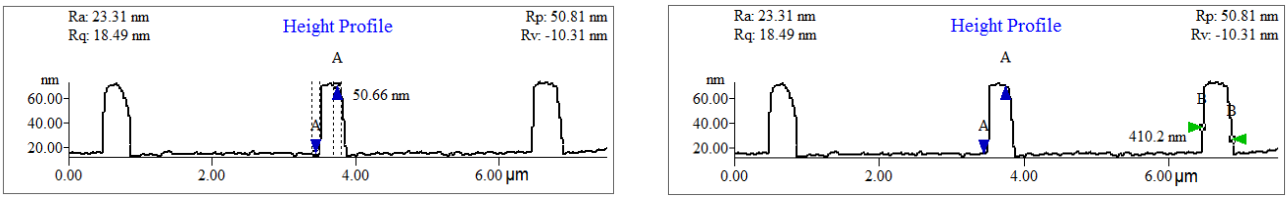


Figure S4. The AFM (a) height profile and (b) width profile of the $Au_{disk/poly/SAM}$ array in Fig. 4b.

(a) (b)

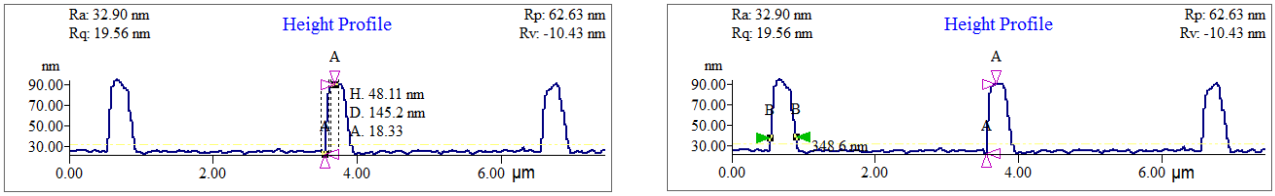
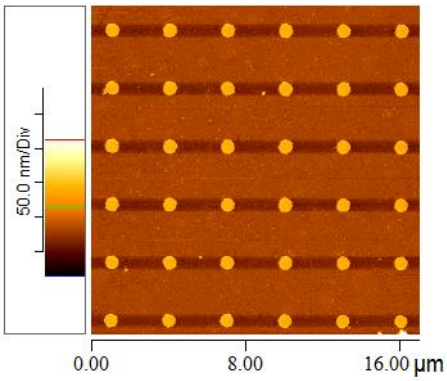
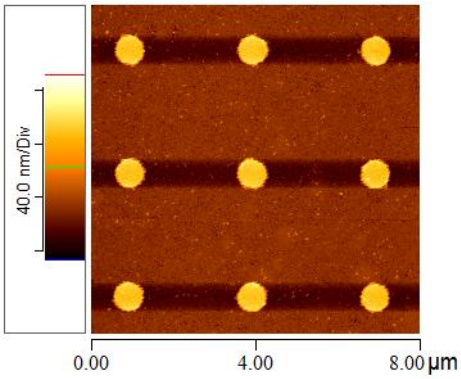


Figure S5. AFM (a), (b) topographies, (c) height profile and (d) width profile of an $Au_{disk/poly/SAM}$ array with a diameter of 700 nm for each nanodisk. The gap of this sample is 7.9 nm.

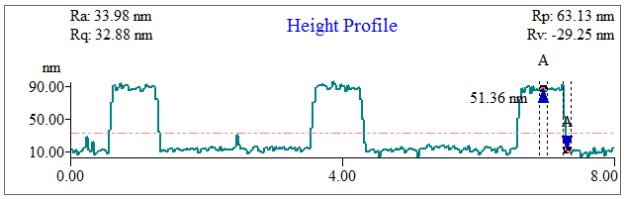
(a)



(b)



(c)



(d)