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

Supporting information of

Gold Mesoflowers (AuMFs) with High Density of Multilevel Long Sharp Tips: Synthesis and Characterization

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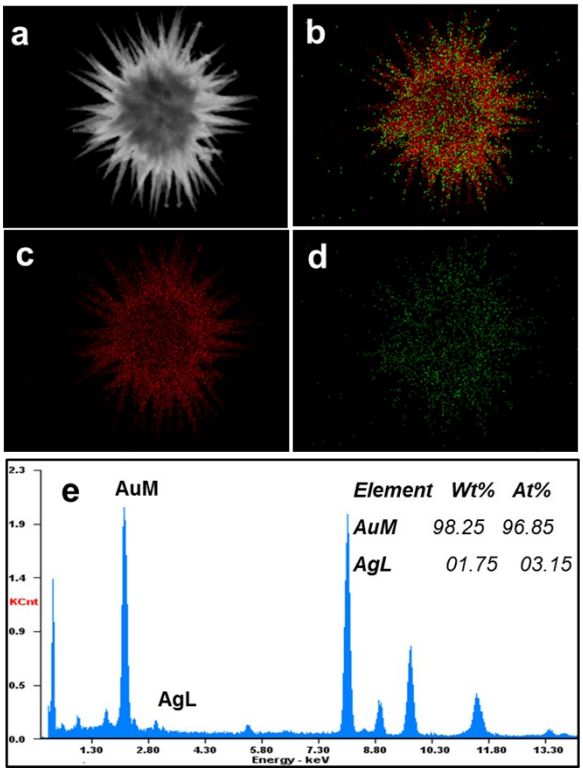

Figure S1. (a) STEM image, (b) over lapping elements, (c) gold element, (d) silver element, and (e) EDX–spectrum of branched AuMFs synthesized at typical condition: 30 µL HCl (1.0 M), 180 µL $HAuCl_4$ (10 mM), 20 µL $AgNO_3$ (10 mM), and 150 µL ascorbic acid (10 mg/mL).

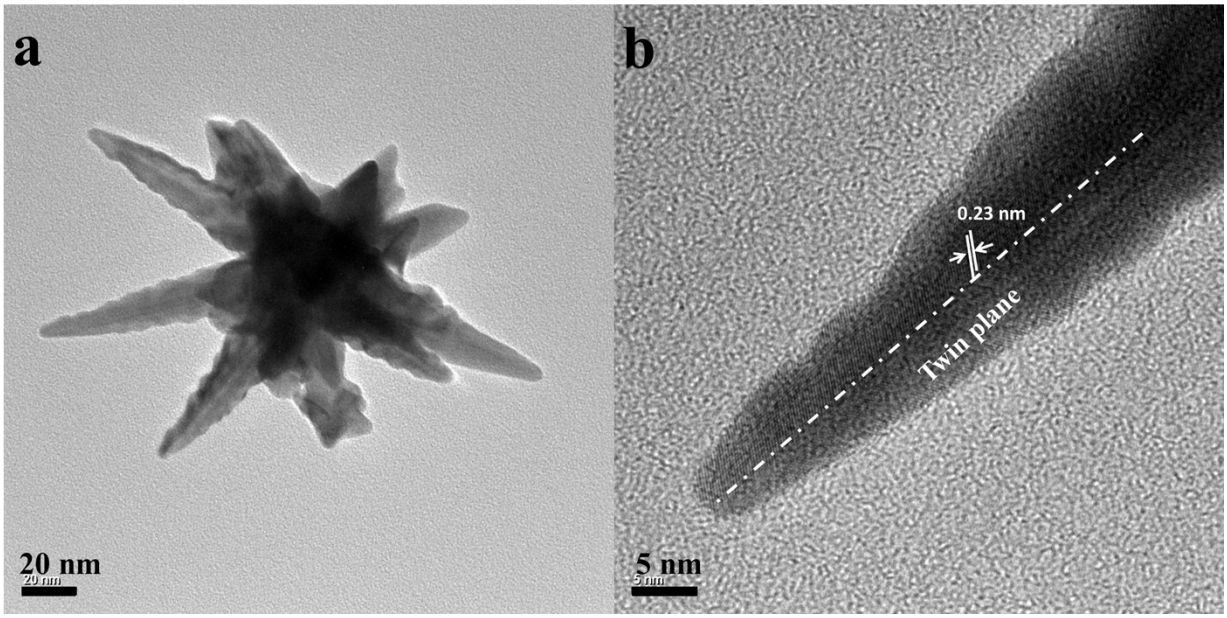

Figure S2. (a) TEM image of gold nanostars in Figure 2a synthesized upon replacing 30 µL of HCl (1.0 M) by 15 µL H_2SO_4 (1.0 M) and (b) HRTEM image of a single tip.

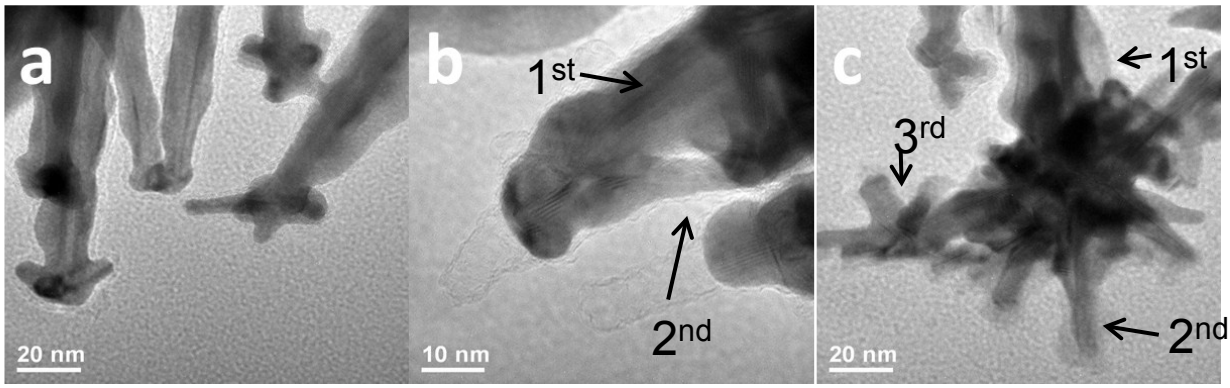

Figure S3. Additional TEM images of multilevel tips with different branching levels corresponding to branched AuMFs shown in Figure 3c and 3f, respectively: (a) tip heads, (b) 2nd tip and (c) 3rd tip.

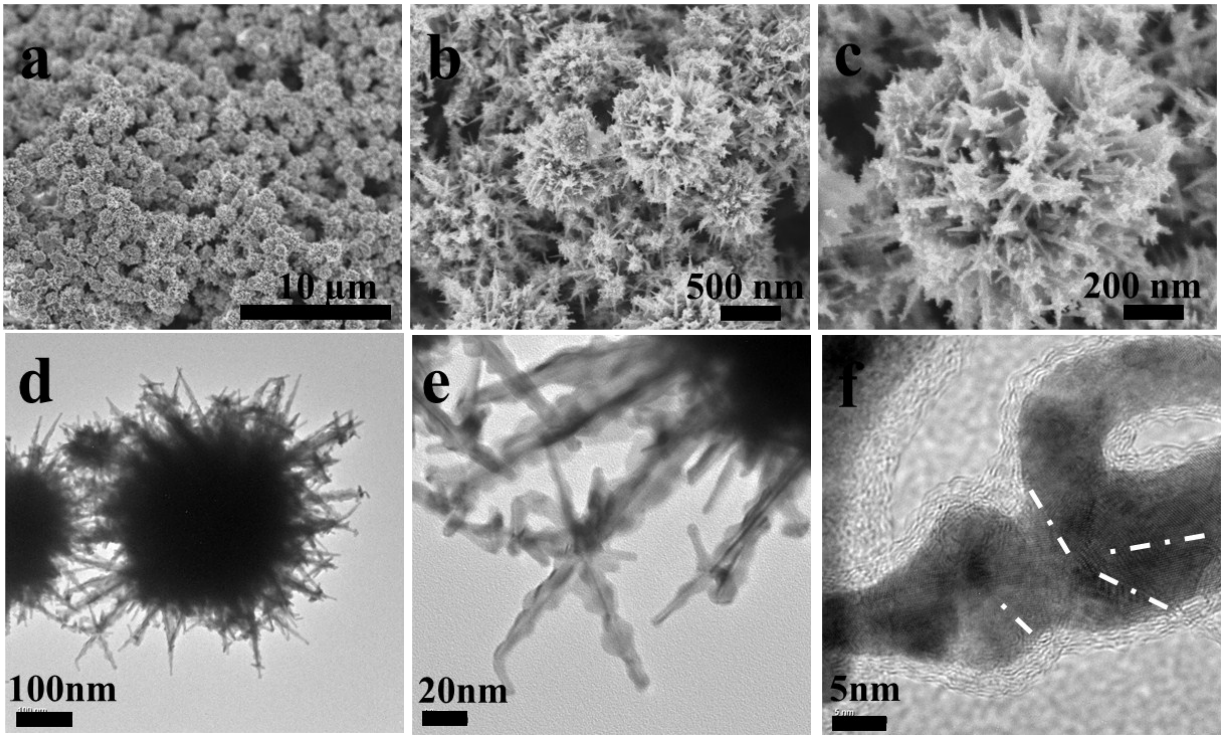

Figure S4. SEM and TEM images at different magnifications of supra-structure of AuMFs containing of hyper-branched tips synthesized by adding 120 µL NaCl (1.0) into the growth solution from a NaCl stock solution (1.0 M). The white dash-lines indicate the twin planes.

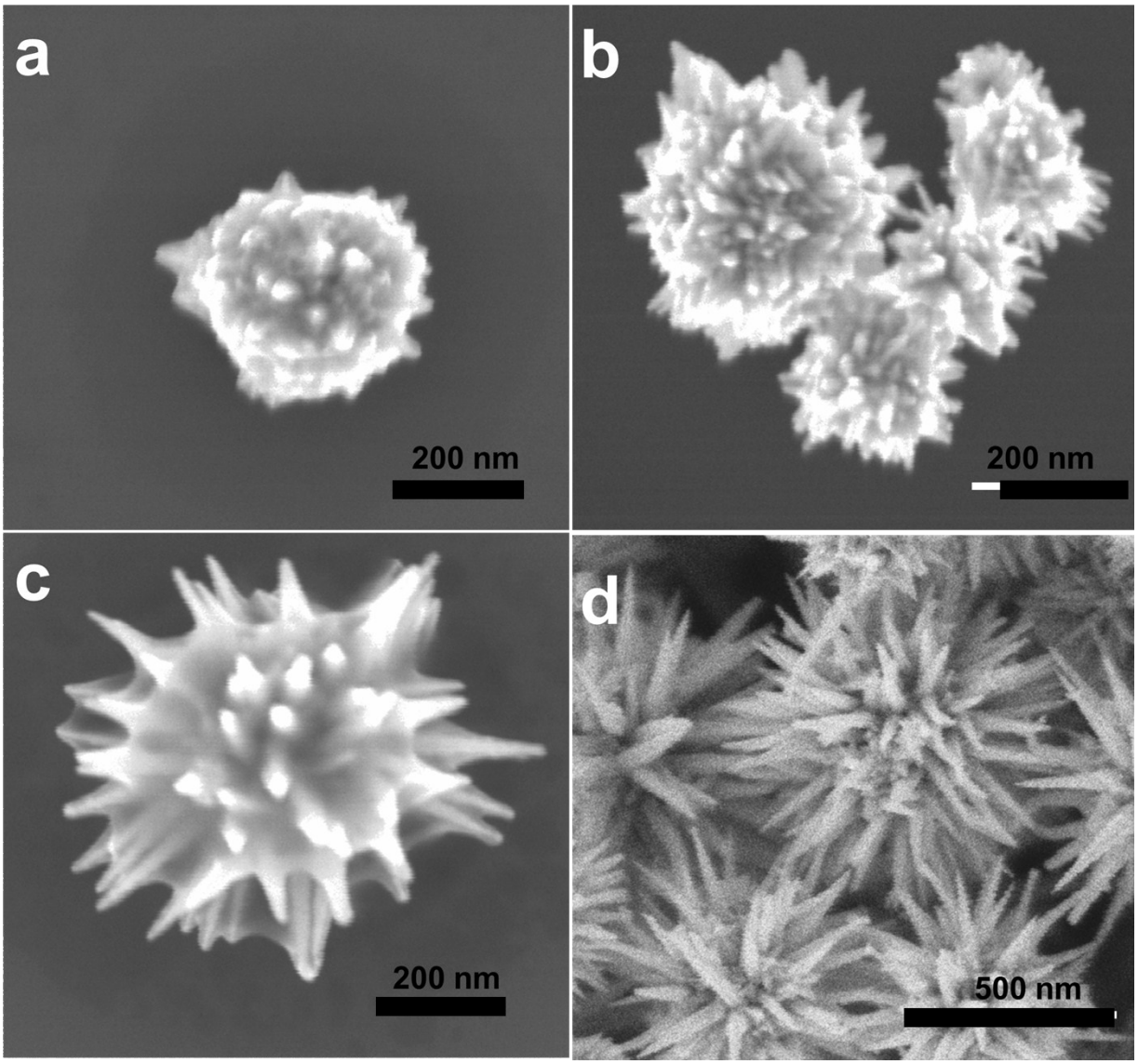

Figure S5. Time-dependent SEM images of typical branched AuMFs at different growth stages: (a) 15 s, (b) 30s, (c) 90s, (d) 240s. The interval particles were taken at different reaction time, diluted by 20 times in the aqueous solution containing 1.0 mM 4-aminothiophenol to block the further growth of the particles. The obtained particles were followed by centrifugation at 5000 rpm in 2 minutes to remove all excess amount of 4-aminothiophenol before taking SEM. Small protrudes were observed in the early stage of branched AuMFs and followed by further elongation to form long and sharp tip when the reaction proceeded

The electromagnetic field enhancement plays a dominant role in surface-enhanced spectroscopy. To demonstrate the great potential applications of the AuMFs in surface-enhanced spectroscopies, the maximum electromagnetic field enhancement and hot spots volume in AuMFs in the MIR and NIR regions are further calculated. For comprehensive comparison, three criterions are used to define the hot spot, i.e., regions with electric field enhancement larger than $1x10^3$, $1x10^4$, and $1x10^5$.[1] And "hot spots volume" is defined as the whole volumes of all the regions with electric field enhancement larger than the defined criterion.[1] The simulated EM field distributions for the three models in the MIR and NIR regions are shown in Figure 8c, and the calculated maximum electric field enhancement and hot spots volume are summarized in Table S1.

Table S1. Summary of the simulation results for three models of branched gold mesoflowers. The hot-spots volume is defined as the regions where the EM field enhancement (E^2) larger than 10^3, 10^4, and 10^5 accordingly

Models			1 (Low aspect ratio tip)	2 (High aspect ratio tip)	3 (Hyper-Branched tip) The angle among the main and small tip is 45º	
					Main tip	Small tip
Core size diameter (nm)			400	400	400	
Tip length (nm)			250	250	250	25
Tip bottom diameter (nm)			45	25	25	10
Tip head diameter (nm)			10	7	7	7
First SPR peak 1000~1500 nm	Maximum EM enhancement		5.9×10^3	7×10^4	2.1×10^4	
	Hot- spot volume (nm^3)	|E|^2>10^3	4680	57788	58658	
		|E|^2>10^4	0	2106	884	
		|E|^2>10^5	0	0	0	
Second SPR peak 1500~3000 nm	Maximum EM enhancement		$1.45x10^5$	3.82×10^5	2.62×10^5	
	Hot-spot volume (nm^3)	|E|^2>10^3	268482	751062	597622	
		|E|^2>10^4	13902	73766	56174	
		|E|^2>10^5	128	2626	1268	

Reference:

(1) Li, A.; Li, S. *Nanoscale* **2014**, *6*, 12921-12928.