

## Supporting Information

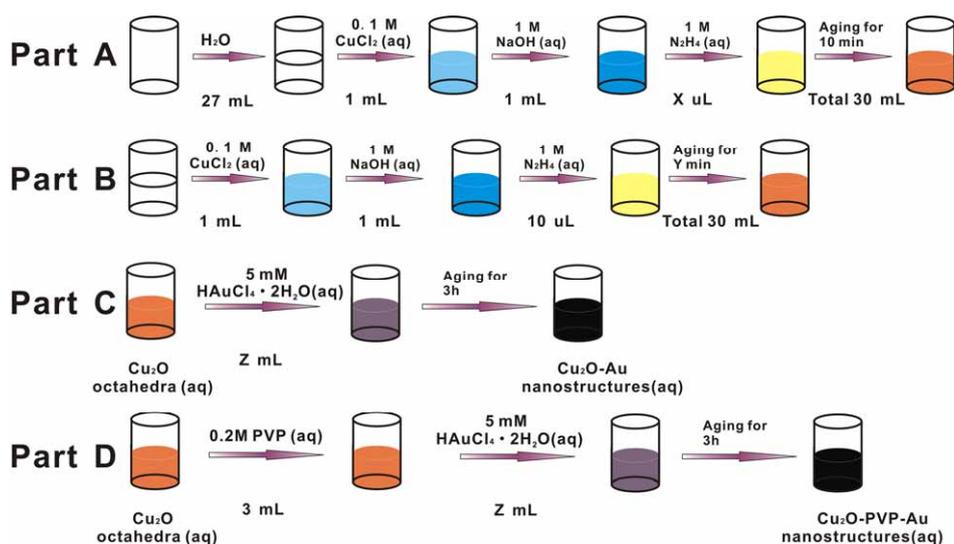
### **A new strategy for the surface-free-energy-distribution induced selective growth and controlled formation of Cu<sub>2</sub>O-Au hierarchical heterostructures with a series of morphological evolutions.**

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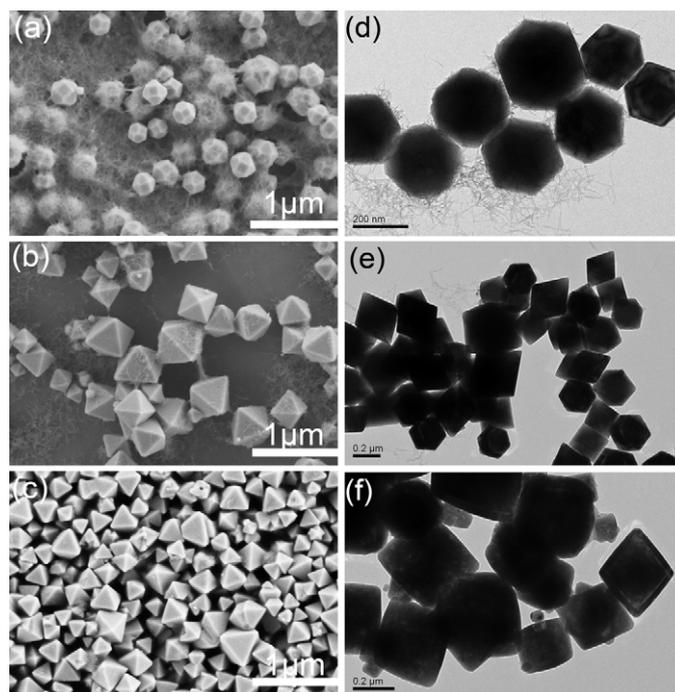
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**Scheme S1** Schematic illustration of the procedure used to synthesize (part A and B)  $\text{Cu}_2\text{O}$  crystals, (part C)  $\text{Cu}_2\text{O}$ -Au hierarchical heterostructures and (part D)  $\text{Cu}_2\text{O}$ -PVP-Au heterostructures.

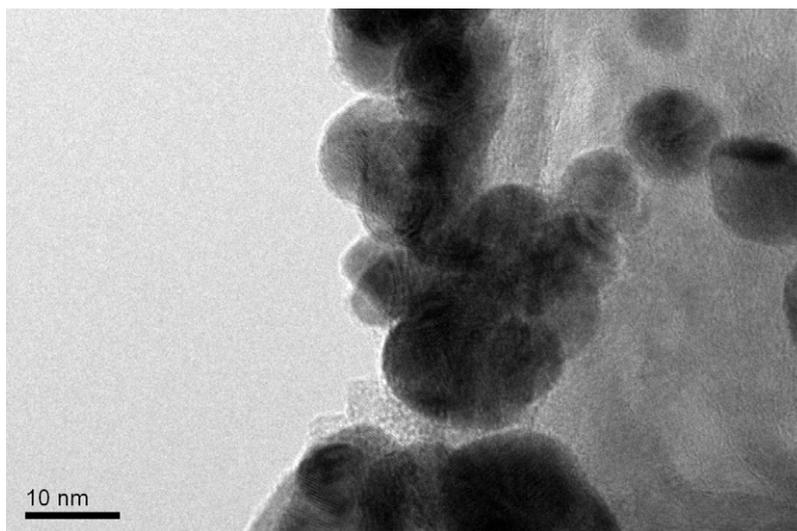
<i>Products</i>	<i>0.1 M CuCl<sub>2</sub> (mL)</i>	<i>1.0 M NaOH (mL)</i>	<i>1 M N<sub>2</sub>H<sub>4</sub> (<math>\mu</math>L)</i>	<i>0.2 M PVP</i>	<i>H<sub>2</sub>O (mL)</i>	<i>5 mM HAu Cl<sub>4</sub> (aq)</i>	<i>Aging time (min)</i>
<i>a. cubic octahedral octahedron</i>			10				
<i>b. octahedron</i>			40				
<i>d. octahedron</i>			80				10
<i>e. corrosive-octahedron</i>			120				
<i>f. face-holed octahedron</i>			200				
<i>g. cubic octahedral octahedron</i>			300				10
<i>h. octahedron</i>			10		27		30
<i>i. octahedron</i>	1	1					60
<i>j. Au nanoclusters growth along the crystal edges of octahedron</i>			120			0.25	
<i>k. Au nanoclusters growth on the crystal faces of octahedron</i>			120			0.5	
<i>l. Cu<sub>2</sub>O-Au nanostructures</i>			120			0.75	180
<i>m. Au nanowhiskers</i>						1	
<i>n. Cu<sub>2</sub>O-Au heterostructures</i>			120			0.25	
<i>o. Cu<sub>2</sub>O-Au heterostructures</i>			120	3		0.5	
<i>p. Cu<sub>2</sub>O-Au heterostructures</i>			120			0.75	
<i>q. Cu<sub>2</sub>O-Au heterostructures</i>			120			1	

**Table S1** Different products and their amount of all chemicals.

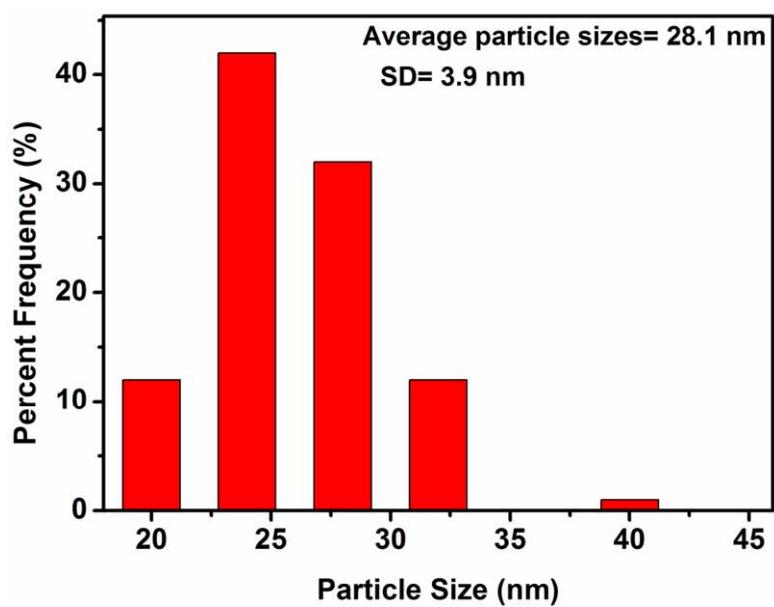


**Fig. S1** FE-SEM and TEM images of  $\text{Cu}_2\text{O}$  nanocrystal evolution from cubo octahedral to octahedron with  $10 \mu\text{L}$  of hydrazine hydrate. The reaction times of each sample are 5 min (a), 20 min (b) and 60 min (c), respectively.

Three main reasons can account for these phenomena. 1. The cubo-octahedral and octahedral  $\text{Cu}_2\text{O}$  bound by  $\{111\}$  and  $\{100\}$  facets were formed owing to the different growth rates along  $\langle 100 \rangle$  versus  $\langle 111 \rangle$  directions. A strong reductant such as  $\text{N}_2\text{H}_4 \cdot 2\text{H}_2\text{O}$  is helpful to the growth of  $\text{Cu}_2\text{O}$   $\{111\}$  planes, while the weaker reductant such as sodium ascorbate is adopted, the  $\text{Cu}_2\text{O}$  become cubes with six  $\{100\}$  facets. 2. At the same reaction time, the more  $\text{N}_2\text{H}_4 \cdot 2\text{H}_2\text{O}$  adopted, the more growth rates of  $\{111\}$  facet acquired, resulting the evolution from cubo-octahedron to octahedron. 3. As the reaction progresses, the  $\text{N}_2\text{H}_4$  can adsorb on  $\{100\}$  planes of cubo-octahedrons and suppress the growth of  $\{100\}$  planes, resulting the formation of octahedrons.

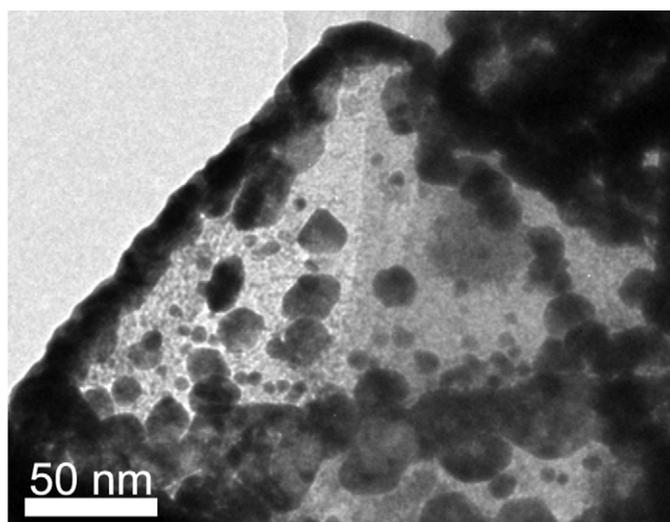


**Fig. S2** TEM image of the AuNGs comprised by several small Au nanoparticles.

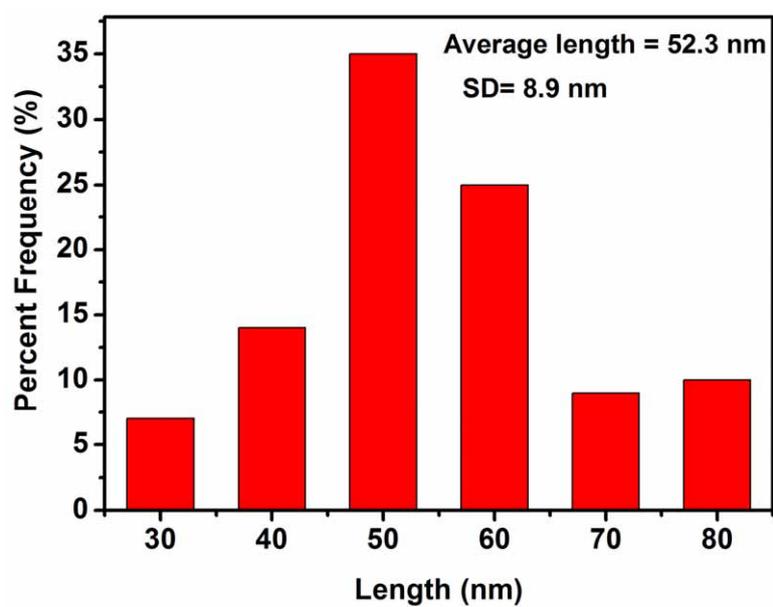


**Figure S3.** The average particle size of the AuNGs.

Image-Pro Plus 6.2 software was used to obtain the size distributions diagrams of AuNGs and the number of AuNGs is 400.



**Fig. S4** TEM image of the Cu<sub>2</sub>O-Au heterostructures with pores and splits.



**Fig. S5** The average length of the AuNWs.

Image-Pro Plus 6.2 software was used to obtain the size distributions diagrams of AuNWs and the number of AuNWs is 400.

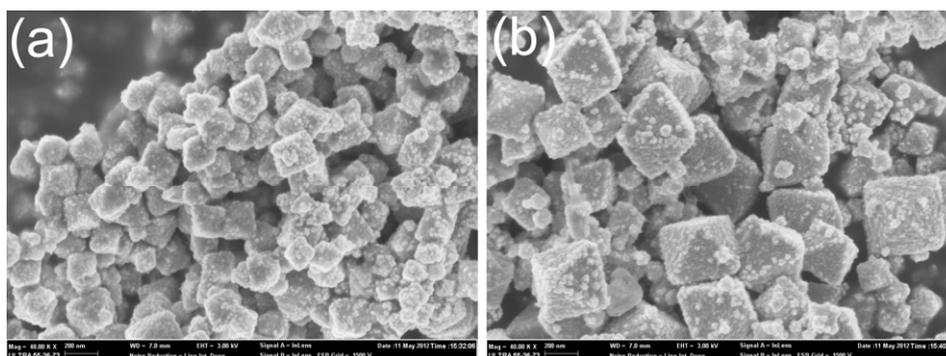
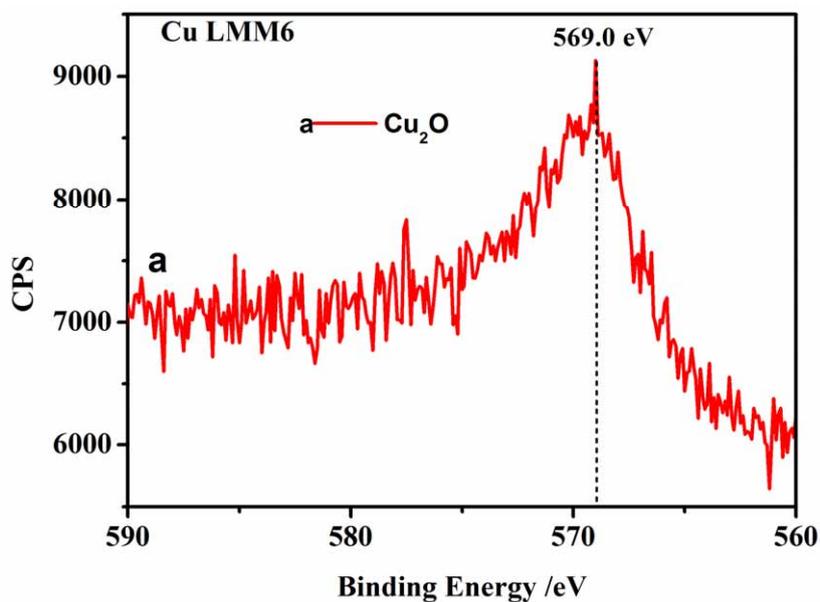


Fig. S6 FE-SEM images Cu<sub>2</sub>O-PVP-Au heterostructures. (0.5 mL HAuCl<sub>4</sub>)

Due to the decreasing of diversity of the surface energy distribution between {111} facets and crystal edges with the introduction of PVP, the trend of the selective growth on the crystal edges is significantly drop down.



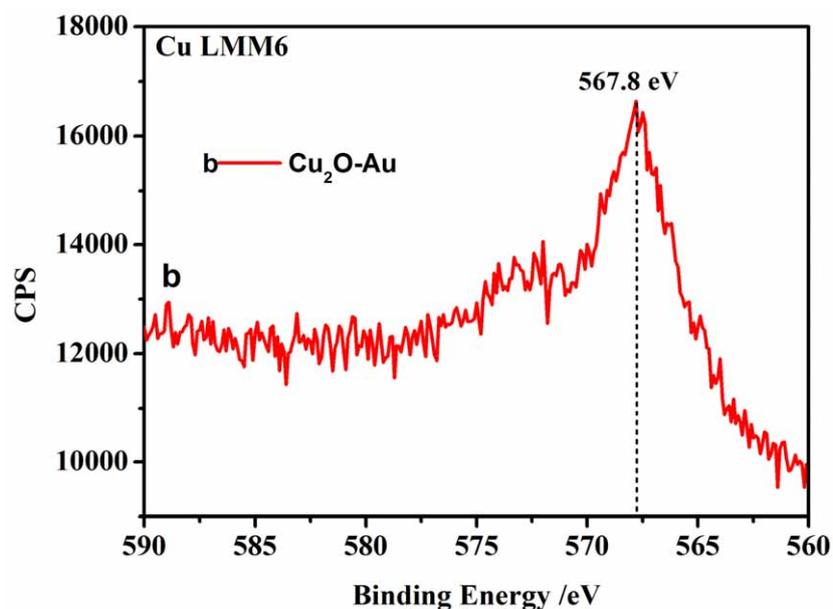
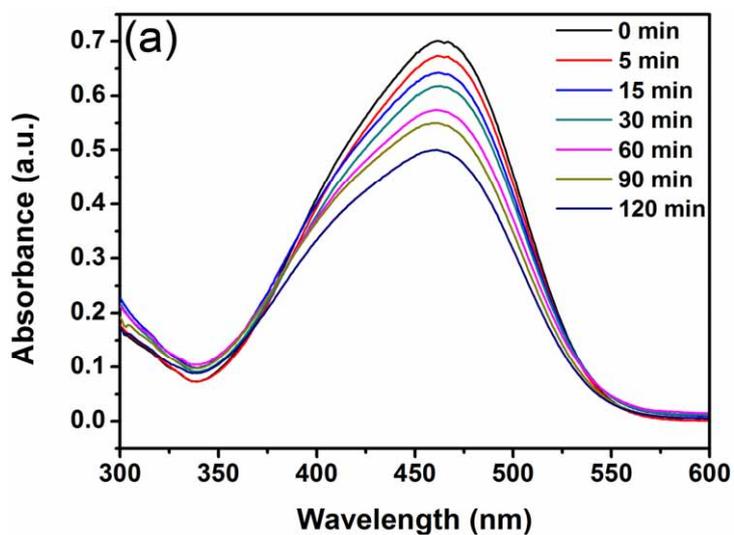
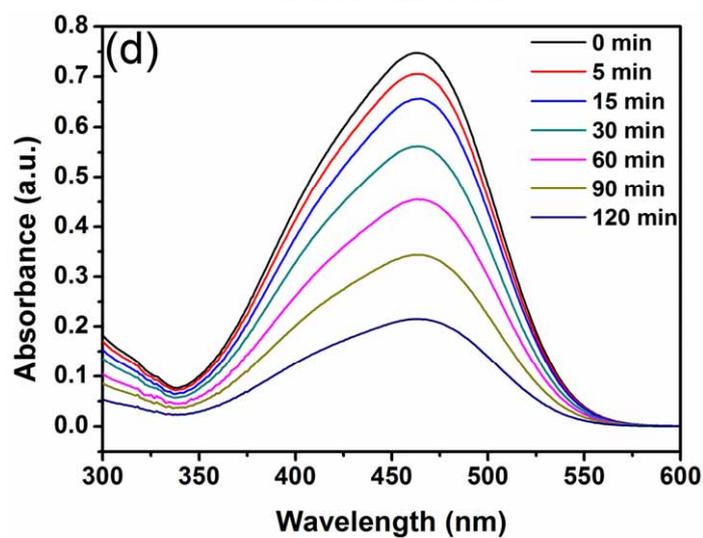
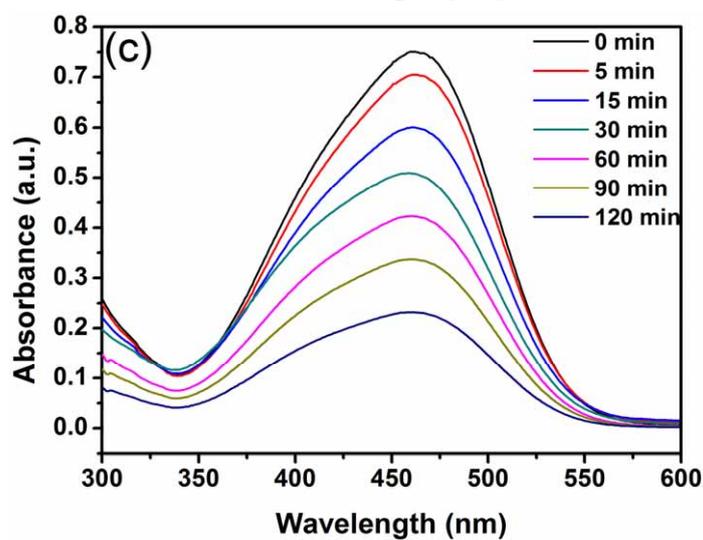
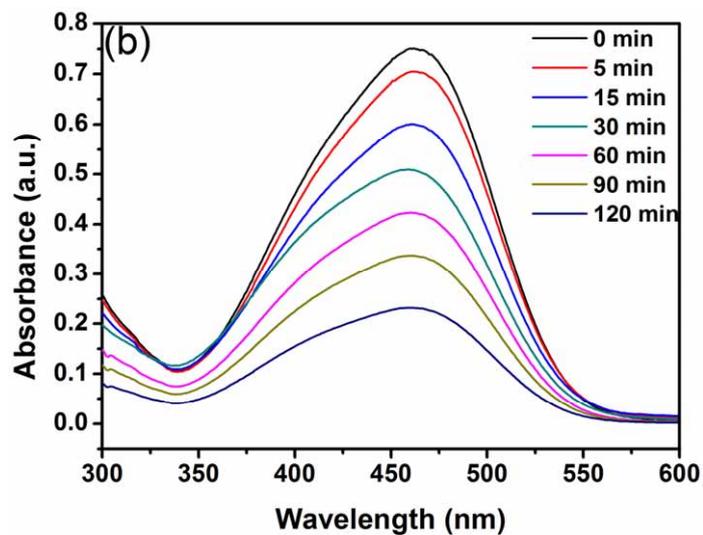
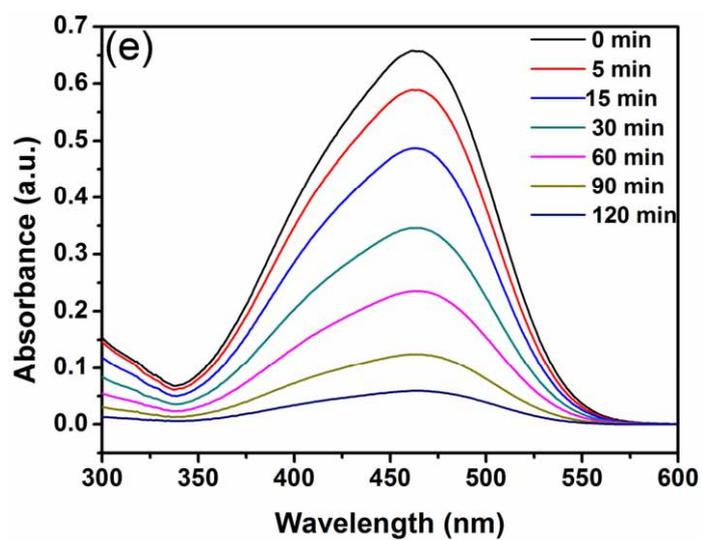


Fig. S7 The Cu LMM Auger peaks of (a)  $\text{Cu}_2\text{O}$  octahedrons and (b)  $\text{Cu}_2\text{O-Au}$  heterostructures.







**Fig. S8** UV-Vis absorption spectra of methyl orange as a function of irradiation time using (a)  $\text{Cu}_2\text{O}$  octahedrons, (b)  $\text{Cu}_2\text{O}$  decorated by 0.25 mL  $\text{HAuCl}_4$ , (c)  $\text{Cu}_2\text{O}$  decorated by 0.5 mL  $\text{HAuCl}_4$ , (d)  $\text{Cu}_2\text{O}$  decorated by 0.75 mL  $\text{HAuCl}_4$ , (e)  $\text{Cu}_2\text{O}$  decorated by 1 mL  $\text{HAuCl}_4$ .