Supporting Information

Adsorbed emulsion droplets: capping agent for in-situ heterogeneous engineering of particle surfaces

Aijing Ma, Jie Xu, Li Yu, Xuehua Zhang, Dayang Wang, and Haolan Xu*

EXPERIMENTAL SECTION

Materials: Hydrogen tetrachloroaurate (ш) (99.9%, metal basis) was purchased from Alfa Aesar. $Cu(CH_3COO)_2\ H_2O$, glucose, hexadecane, acetone, ethanol, HCl and NaOH were purchased from Sigma-Aldrich and used without purification. Milli-Q water with the resistance of 18.2 MΩ cm^{-1} was used for all experiments.

Preparation of Cu_2O octahedra, cubes and truncated octahedra:

Synthesis of Cu_2O octahedra: 0.3 g of $Cu(CH_3COO)_2\ H_2O$ was dissolved in 5 mL of water. 3mL of NaOH solution (3 M) was added dropwise into the $Cu(CH_3COO)_2$ solution under constant stirring. Blue $Cu(OH)_2$ suspension was produced. Then, 0.06 g of glucose was added into the $Cu(OH)_2$ suspension. After stirring for 10 min, the mixture solution was placed in a water bath with temperature of 70 ^{o}C for 5 min. A Brick red precipitate was formed. The precipitate was cooled down to room temperature and then washed with water and ethanol several times. The obtained precipitate was dispersed in 2 mL of water for further experiments.

Synthesis of Cu_2O truncated octahedra: 0.3 g of $Cu(CH_3COO)_2\ H_2O$ was dissolved in 20 mL of water. Then 6 mL of NaOH solution (3 M) was added dropwise to the $Cu(CH_3COO)_2$ solution under constant stirring. After the blue suspension of $Cu(OH)_2$ was produced, 0.06 g of glucose was added into the suspension. After stirring for 10 min, the mixture solution was kept in water bath at 70 ^{o}C for 8 min. After the reaction, the brick red precipitate was cooled down to room temperature and then washed with water and ethanol several times. The obtained particles were dispersed in 2 mL of water for further experiments.

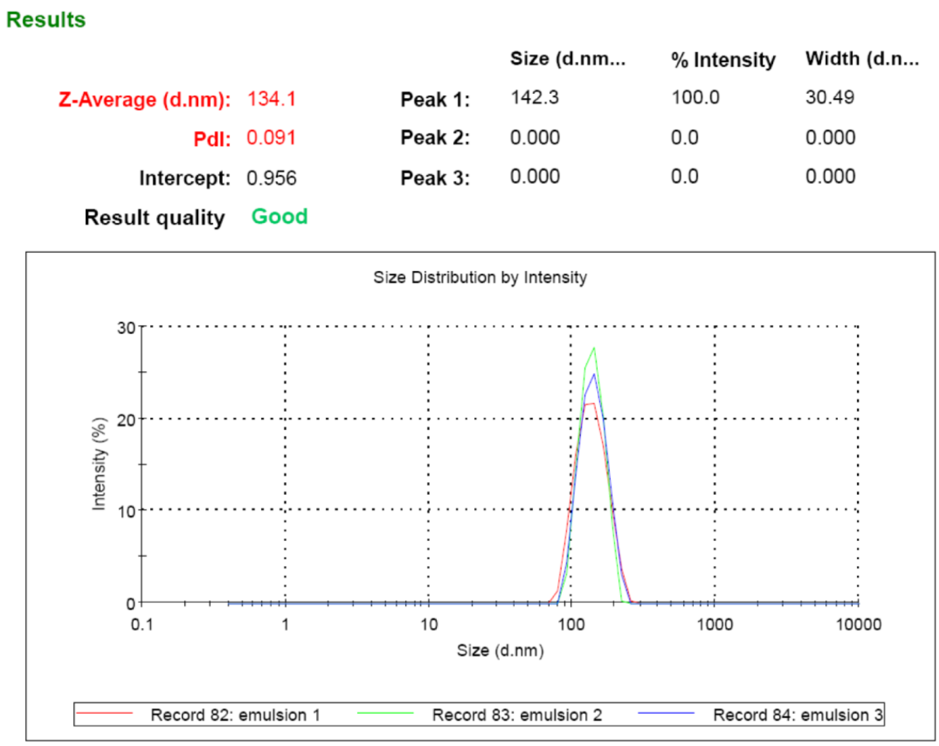
Synthesis of Cu_2O Cubes: Cu_2O cubes were synthesized according to literature.[58] 0.499 g of $Cu(CH_3COO)_2{\cdot}H_2O$ was dissolved in 50 mL of water. The solution was heated to 70 ^{o}C in water bath. 2.5 mL of NaOH solution (6 M) was added dropwise into the $Cu(CH_3COO)_2$ solution under constant stirring. Then 0.1 g of glucose was added. The mixture was maintained at 70 ^{o}C for 60 min. After the reaction, the red precipitate was filtered and washed with water and ethanol for several times. The obtained precipitate was dispersed in 5 ml of water for further experiments.

Preparation of oil-in-water emulsions: Hexadecane-in-water emulsions were prepared via a solvent-shifting method. Hexadecane was firstly dissolved in pure acetone at a volume fraction of 10^{-3}. Then the solution was mixed with a much larger volume (×20) of water quickly to form the hexadecane-in-water emulsions.

Adsorption of emulsion droplets onto the crystallographic facets of Cu_2O polyhedron particles: 0.02 mL of Cu_2O suspension was directly added into 20 mL of as prepared emulsions. The mixture was kept still for 20 min to reach the adsorption equilibrium. The mixtures were ready for the further reaction and etching.

Reaction and etching of the emulsion droplets capped Cu_2O crystals: (1) *galvanic reaction*: 1 mL of $HAuCl_4$ (2.9 mM) was added to the mixture to initiate the galvanic reaction between Cu_2O and $AuCl_4^-$. After reaction, the Cu_2O particles were collected and washed by water and ethanol several times. (2) *Etching*: 1 mL of HCl (29 mM) was added to the mixture. The reaction was incubated for 10, 30, and 60 min separately. After etching, the Cu_2O particles were separated and washed by water and ethanol several times.

Characterization: Scanning electron microscopy (SEM) images, Back-scattered Electron (BSE) images and energy dispersive X-ray spectrometer (EDX) spectrum were conducted with FEI Quanta 450 operated at 10-20 kV. The powder X-ray diffraction (XRD) analysis was performed with a ScintagARL X'tra diffractometer. The dynamic lighter scattering (DLS) size distribution of hexadecane-in-water emulsion droplets was measured on Malvern zetasizer nano ZS.



Results

Z-Average (d.nm): 134.1
PdI: 0.091
Intercept: 0.956
Result quality Good

	Size (d.nm...	% Intensity	Width (d.n...
Peak 1:	142.3	100.0	30.49
Peak 2:	0.000	0.0	0.000
Peak 3:	0.000	0.0	0.000

Figure S1. DLS size distribution of hexadecane-in-water emulsions prepared via a solvent-shifting method.

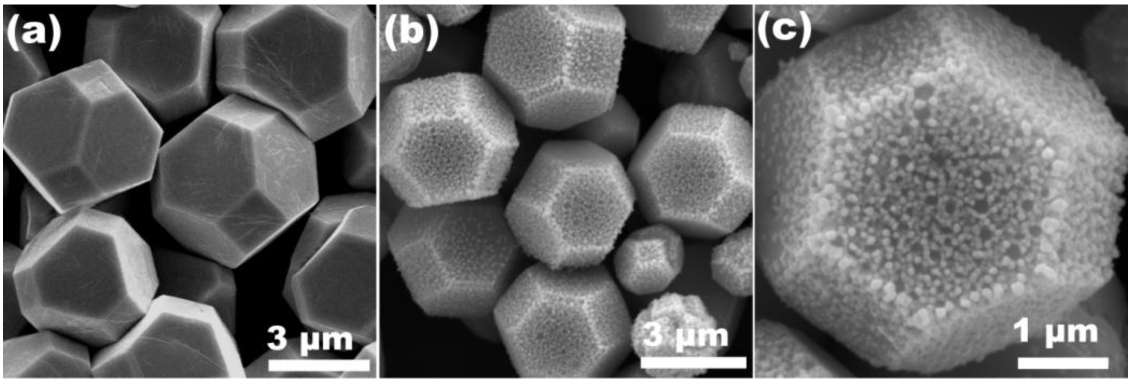


Figure S2. SEM images of (a) primary Cu_2O truncated octahedra, (b, c) Cu_2O-Au particles obtained via galvanic reaction between Cu_2O and $AuCl_4^-$ in the presence of emulsions.

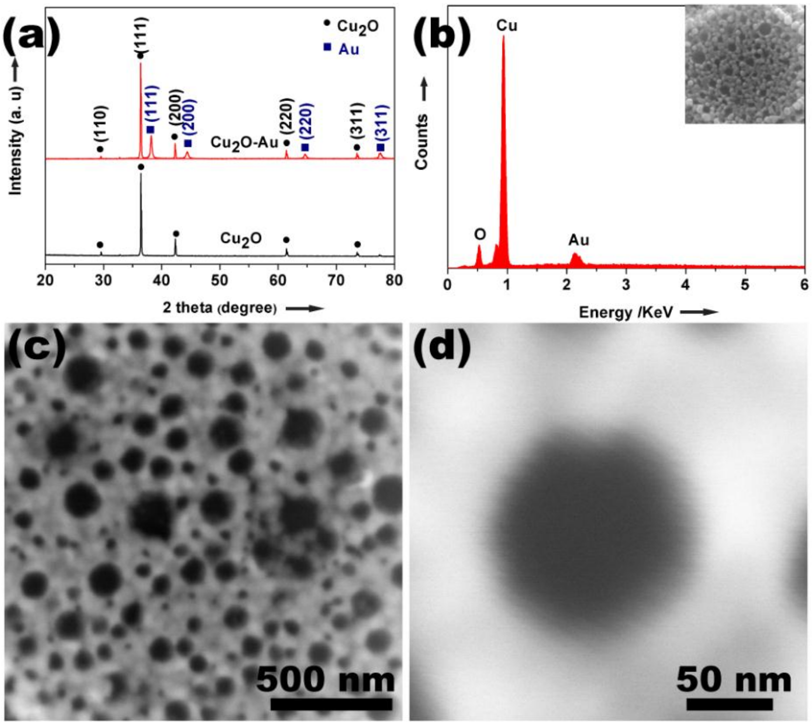


Figure S3. (a) XRD patterns of primary Cu_2O particles and Cu_2O-Au particles after galvanic reaction between Cu_2O and $AuCl_4^-$, (b) EDX spectrum of a Cu_2O-Au heterogeneous crystal facet (up inset), (c, d) BSE images of a Cu_2O-Au heterogeneous crystal facet.

The XRD pattern (Figure S3a) of primary Cu_2O particles clearly shows the diffraction peaks located at 29.61°, 36.49°, 42.41°, 61.45° and 73.62°, corresponding to the (110), (111), (200), (220), (311) planes of cubic phase Cu_2O [JCPDS 34-1354]. After galvanic reaction between Cu_2O and $AuCl_4^-$, except for the typical Cu_2O diffraction peaks, new peaks which can be indexed to the Au crystal [JCPDS 65-2870] arise, confirming the formation and deposition of Au NCs at the surface of Cu_2O. EDX spectrum (Figure S3b) of a Cu_2O crystallographic facet after galvanic reaction clearly demonstrates the co-existence of Cu and Au element. BSE images were recorded to illustrate the element distribution on the heterogeneous crystal facets of Cu_2O-Au particles. BSE model can provide image contrast as a function of elemental composition, as well as surface topography. BSE are produced by the electrostatic interactions between the sample and the incident electron beam. Larger atoms with a greater atomic number have a higher probability of producing an elastic collision due to their greater cross-sectional area. Therefore, the number of BSE collected by a BSE detector is proportional to the mean atomic number of the sample, which results in image contrast as a function of composition. Higher atomic number element appears brighter than low atomic number element in BSE image. In the case of Cu_2O-Au surfaces, the atomic number of Cu is 29, O is 8 and Au is 79. The large discrepancy between Au and Cu, O gives rise to an obvious brightness contrast in BSE image. In BSE images (Figure S3c,d) of a crystallographic facets of a Cu_2O-Au particle with different magnifications, apparent brightness contrast, the holes are dark and the frameworks are bright can be distinguished, indicating the different composition. Combined with the XRD patterns, SEM images, EDX spectrum, one can confirm that the holes are composed of intact Cu_2O crystal facets, while the frameworks are consisted of deposited Au nanoparticles formed by galvanic reaction.

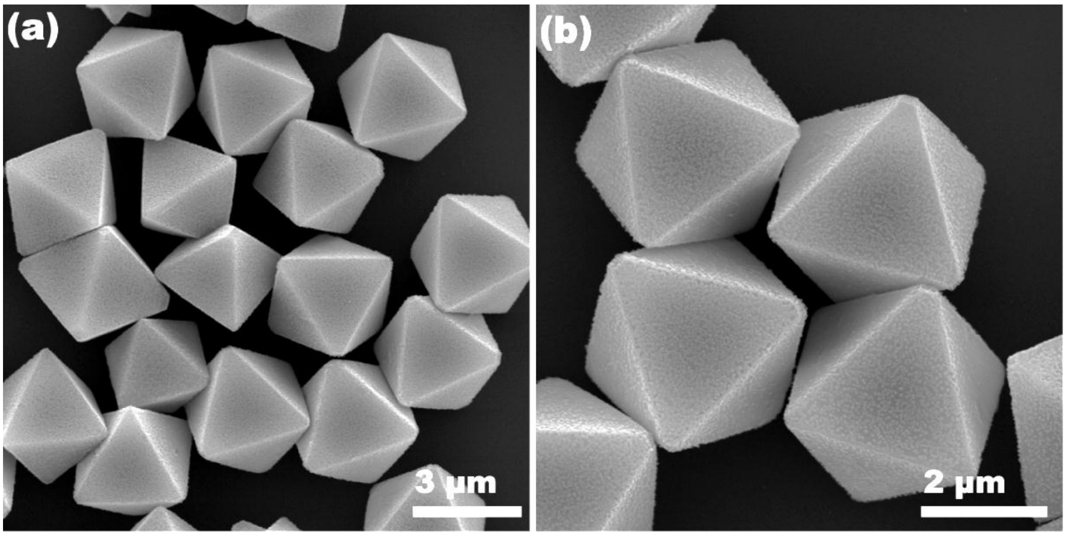


Figure S4. Cu_2O-Au particles obtained via galvanic reaction between Cu_2O and $AuCl_4^-$ in water without the presence of emulsions.

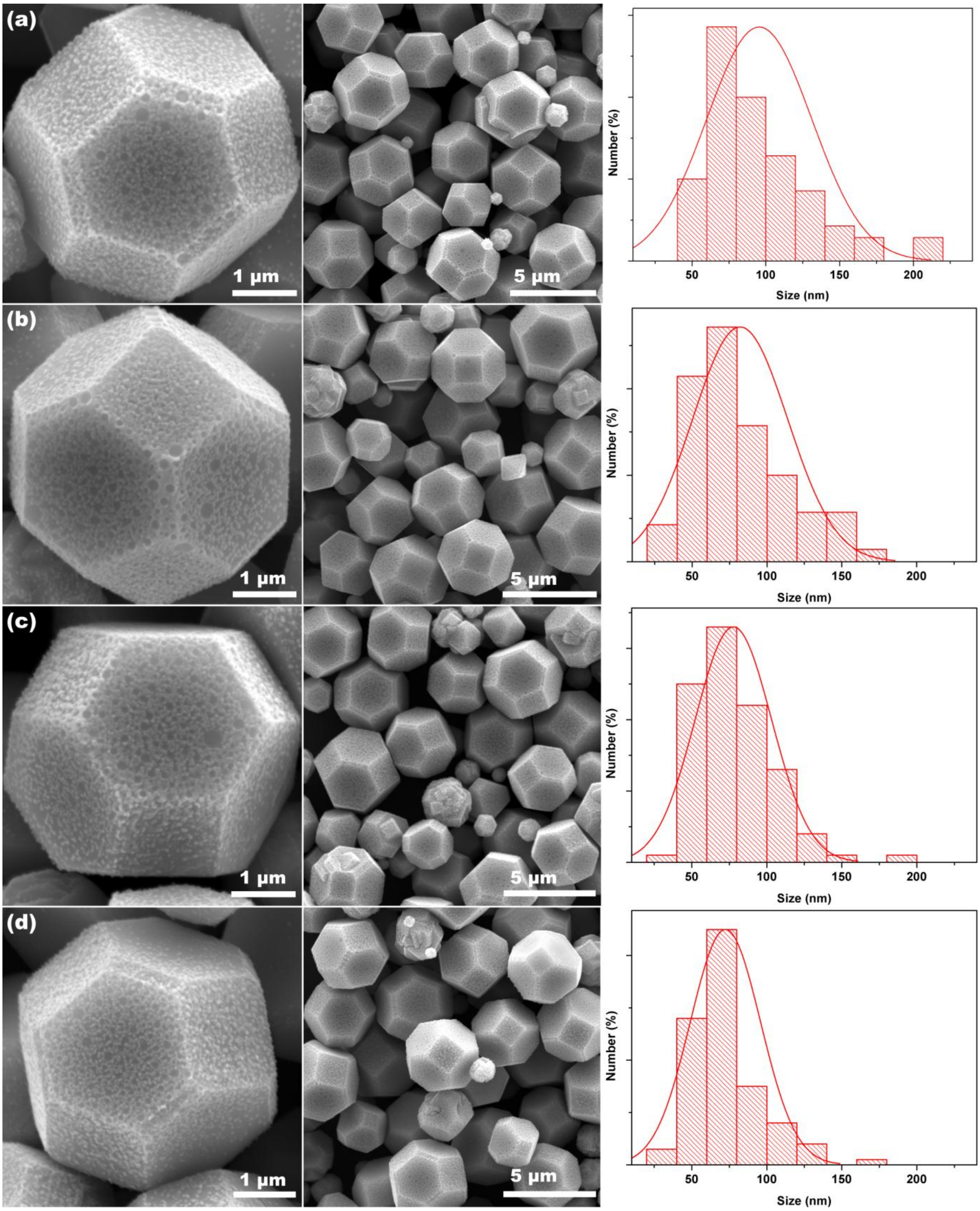


Figure S5. SEM images and corresponding size distributions of the holes on the surfaces of Cu_2O-Au particles obtained via galvanic reaction after (a) 5 min, (b) 1 h, (c) 5 h, (d) 24 h emulsion droplets adsorption.

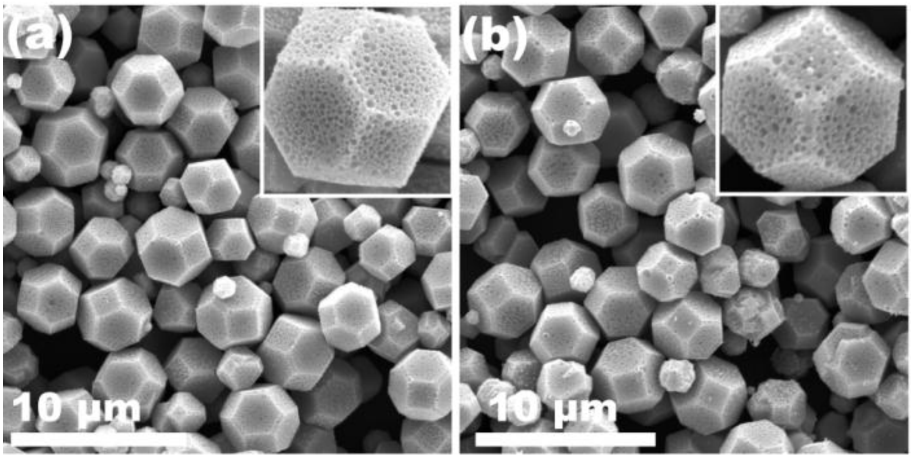


Figure S6. SEM images of Cu_2O-Au particles obtained via (a) 1 h and (b) 3 h galvanic reaction between Cu_2O and $AuCl_4^-$ after 10 min emulsion droplets adsorption. The upper insets are the corresponding Cu_2O-Au particles with high magnification.

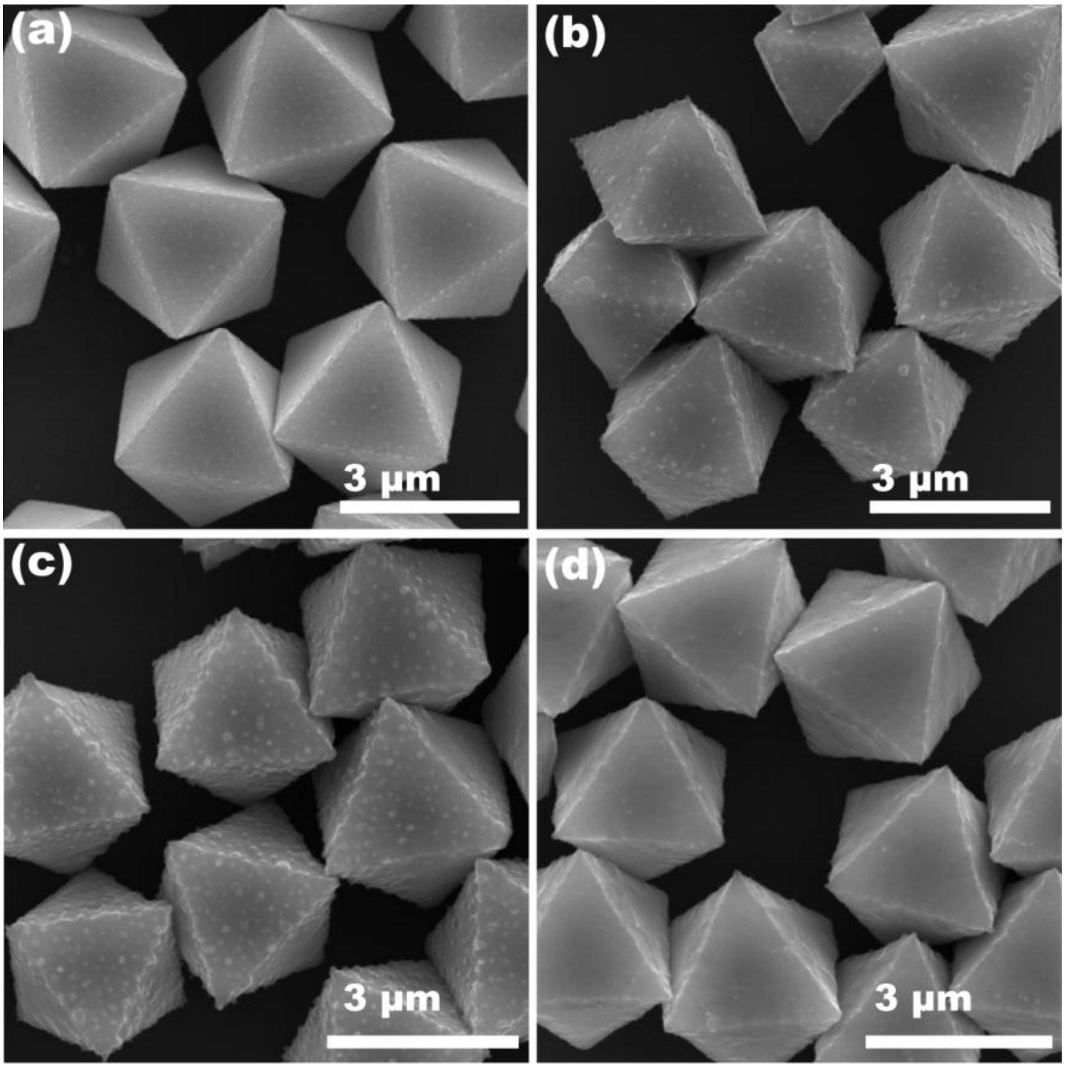


Figure S7. SEM images of Cu_2O octahedra etched by HCl (a) 10 min with adsorbed emulsion droplets, (b) 30 min with adsorbed emulsion droplets, (c) 60 min with adsorbed emulsion droplets, (d) 60 min without adsorbed emulsion droplets.