Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary information

Gold-copper nanostars as photo-thermal agents: synthesis and advanced electron microscopy characterization

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Specifically, the solidus-liquidus curves of a regular solution model are given by:

$$\begin{cases} kT\ln\left(\dfrac{x_{solidus}}{x_{liquidus}}\right)=\Delta H_m^A\left(1-\dfrac{T}{T_m^A}\right)+\Omega_l\left(1-x_{liquidus}\right)^2-\Omega_s\left(1-x_{solidus}\right)^2 \\ kT\ln\left(\dfrac{1-x_{solidus}}{1-x_{liquidus}}\right)=\Delta H_m^B\left(1-\dfrac{T}{T_m^B}\right)+\Omega_l x_{liquidus}^2-\Omega_s x_{solidus}^2 \end{cases} \quad (1)$$

Here $x_{solidus}$ ($x_{liquidus}$) denote the compositions of the solid (liquid) phases at given temperature T; T_m^A and T_m^B, the size-dependent melting temperatures of gold (A) and copper (B); ΔH_m^A and ΔH_m^B, their respective size-dependent melting enthalpies; Ω_l and Ω_s, the respective size-dependent interactions parameters in the liquid and solid phases; and kT, the characteristic thermal energy. To calculate the phase diagram at the nanoscale, the size-dependent parameters must be evaluated. The size-dependent melting temperature of each element is calculated according to equation (2).

$$\frac{T_m}{T_{m,\infty}}=1-\left(\frac{\gamma_s-\gamma_l}{\Delta H_{m,\infty}}\right)\frac{A}{V} \quad (2)$$

A/V is the surface to volume ratio of the nanostar. $\Delta H_{m,\infty}$ is the bulk melting enthalpy. γ_l and γ_s are the respective surface energies in the liquid and solid state. The surface of the pointed nanostar is mainly composed of (hhl) planes due to a surface reconstruction of {111} terraces and {002} steps (Figure 2), therefore the surface can be considered as constituted by {111} planes. The solid surface energy used in the calculation of the pointed nanostar is the one corresponding to (111) faces. The surface of the rounded nanostar is mainly composed of (220) planes (Figure 5) therefore the solid surface energy used in the calculation is the one corresponding to (110) faces.

Once we have used equation (2) to obtain the set of size-dependent parameters $\{T_m^A, T_m^B, \Delta H_m^A, \Delta H_m^B, \Omega_l, \Omega_s\}$ for the sizes considered in this manuscript, we can introduce these parameters into equations (1) to generate the Au-Cu phase diagram at the nanoscale (Figure 8). The material parameters used in this calculation are the ones tabulated in Ref.[14]

Table S1. Melting temperature of the pointed and rounded nanostars made of pure gold or pure copper only.

Type of nanostar	T_m^{Au} (K)	T_m^{Cu} (K)
Pointed*	859	890
Rounded**	455	543

*The dimensions of the nanostar used for this calculation are a=50 nm and h=10nm.

**The dimensions of the nanostar used for this calculation are a=25nm, b =40nm, c=15nm, d=7nm and t=10nm.

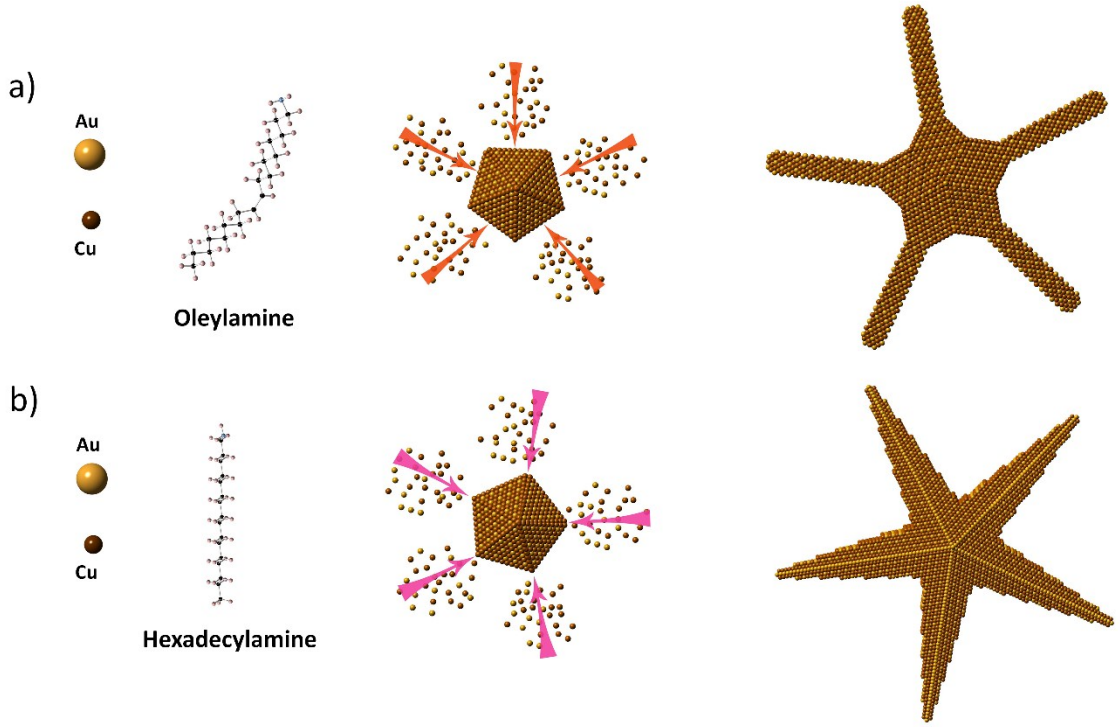

Figure S1. Schematic representation of the growth mechanism for the rounded (a) and pointed (b) pentagonal nanostars. Gold-copper decahedral seeds were formed at the early stages of the chemical reaction by exposing {111} and {100} facets. Then, the rounded and pointed nanostars grew by following a layer-by-layer deposition growth mode in the <100> direction for the rounded ones while in the <112> direction for the pointed ones, due to the preferential attachment of OLA and HDA on certain facets.

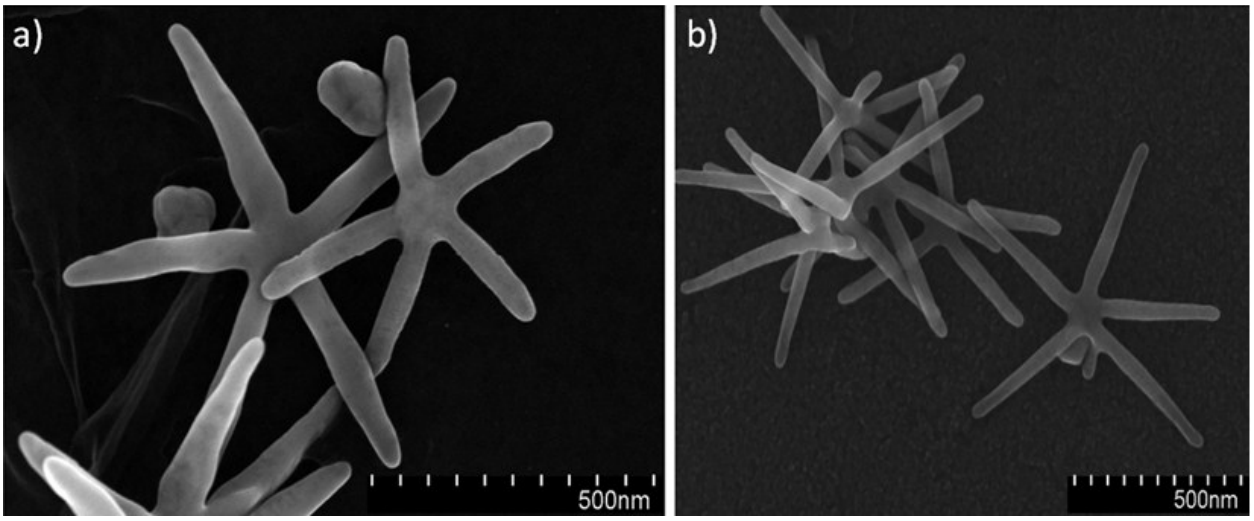

Figure S2. Gold-copper nanostars synthesized by changing the Au-Cu molar ratio to a) 2:3 and b) 1:6, respectively. Longer branches are obtained in both cases and the pentagonal structure is preserved.