Copper oxide nanocubes wrapping metals
by microwave synthesis

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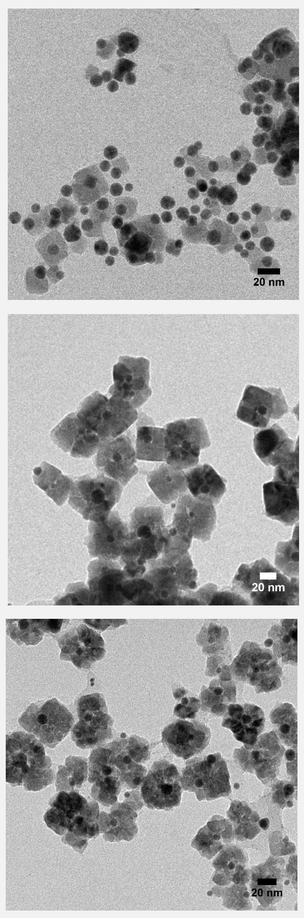
Abstract

- **The fabrication of noble metal NPs [Au, Ag, Pd, Pt] and Cu_2O heterostructures (HS) by a microwave (MW)-assisted synthesis is presented.**
- MW selectivity with a fast two-step protocol enabled us to easily prepare these multicomponent nanoparticles in a short time (~ 40 min).
- First, metal NPs (Au, Ag, or Pd) are synthesized through a MW-assisted polyol approach and those NPs serve as nucleation seeds for a cubic Cu_2O wrapping.
- Other types of HS were found when using smaller Pt NPs.
- For Au NPs as the core, we analyzed the effect of gold to copper molar ratio on the shape-yield of the nanocubes, reported their optic and plasmonic properties and demonstrated the reproducibility and scalability of the synthetic routes.

Au-Cu_2O HS

Gold to copper molar ratio

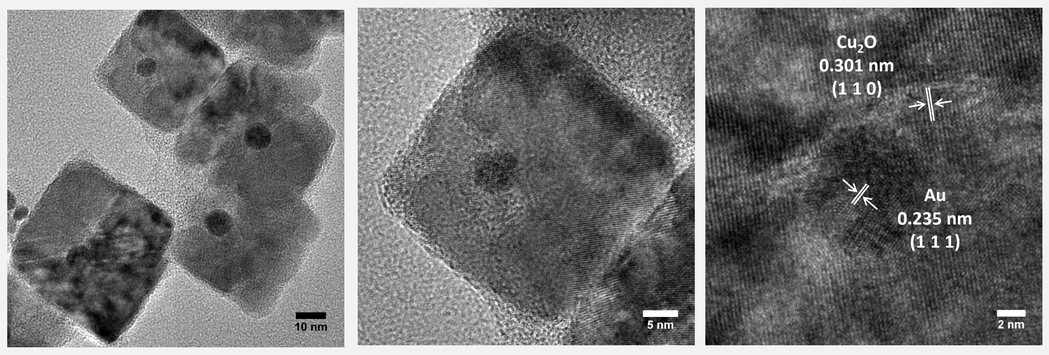


(Increasing gold seeds)

Isolated Au NPs
incomplete shape-oriented formation

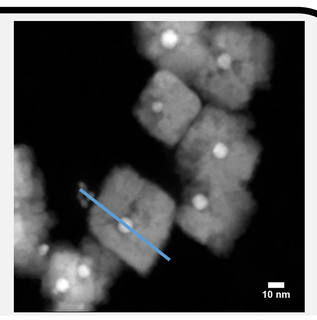
Irregular, flower-like structures

HR-TEM

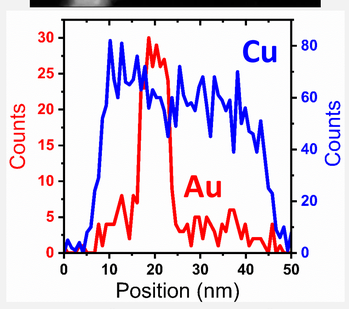


- Cu_2O nanocubes of 30-50 nm edge length wrapping the smaller Au NPs (9 ± 1 nm).
- Homogeneous covering and contact, growth mechanism based on a single cube growth with {1 0 0} facets. No epitaxy relation.

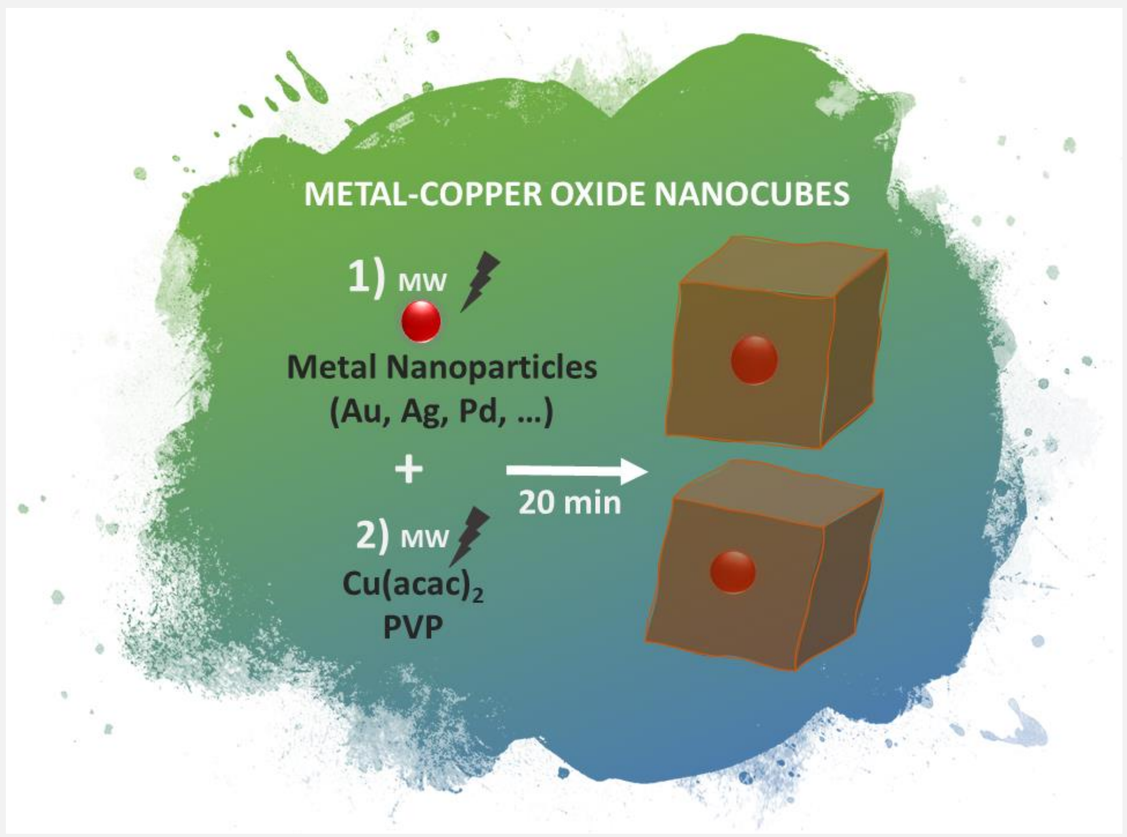
HAADF STEM



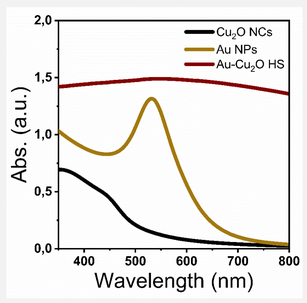
Element profile



Summary

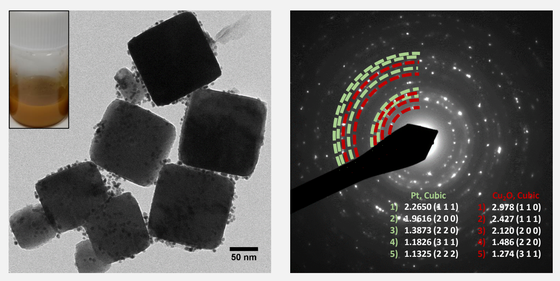


Optic and plasmonic properties



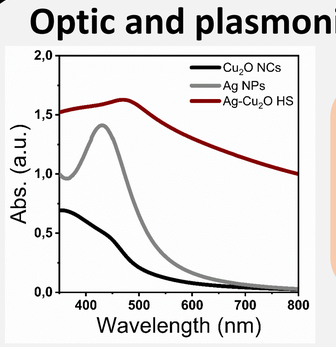
- Au plasmon attenuated and red-shifted.
- Broad light-scattering band in the red and near-IR regions.

Pt-Cu_2O HS



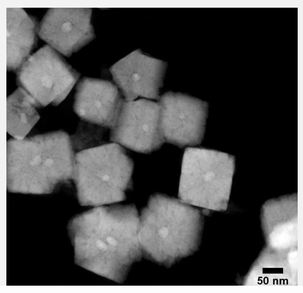
- Cu_2O nanocubes of 100-120 nm edge length with Pt NPs (5 ± 1 nm) attached to the side-facets.

Optic and plasmonic properties

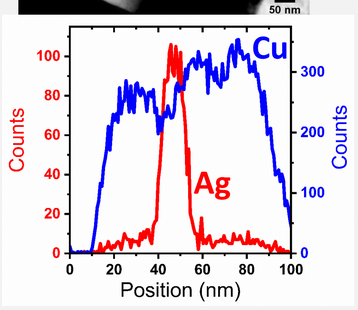


- Ag plasmon attenuated and red-shifted.
- Broad light-scattering band in the red and near-IR regions.

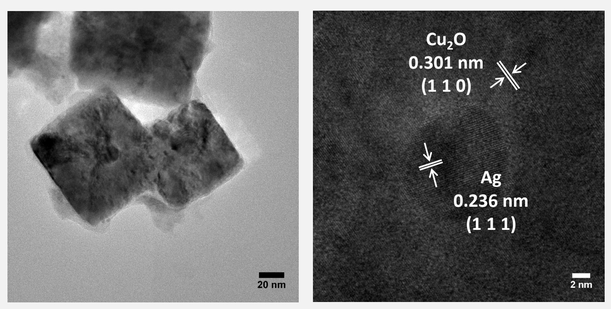
HAADF STEM



Element profile



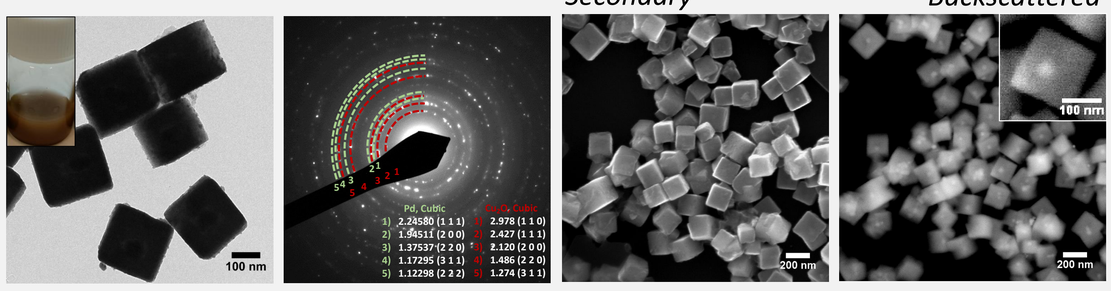
HR-TEM



- Cu_2O nanocubes of Cu_2O 60-80 nm edge length wrapping Ag NPs of 13 ± 4 nm.

Ag-Cu_2O HS

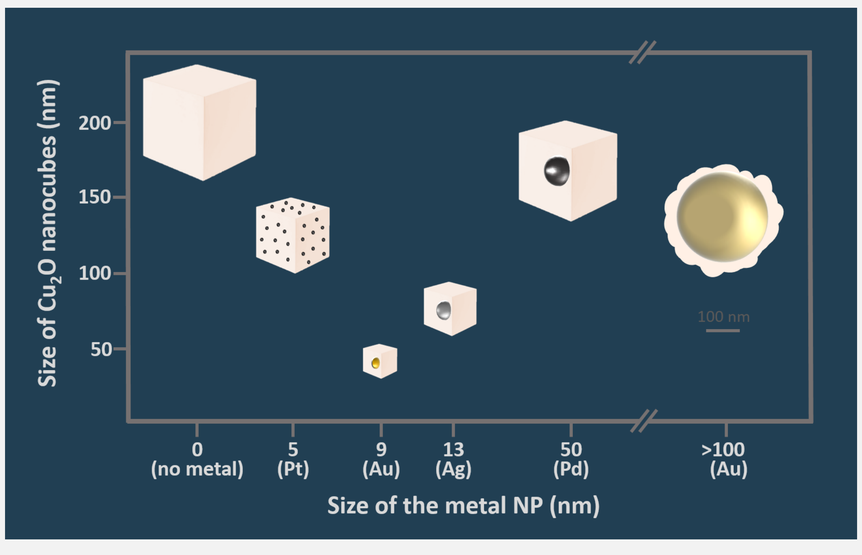
TEM **SAED** **SEM** *Secondary* *Backscattered*



- Cu_2O nanocubes of 150-180 nm edge length wrapping Pd NPs of 50 ± 9 nm.

Pd-Cu_2O HS

M-Cu_2O HS comparison



Conclusions

- Noble metal-Cu_2O HS consisting of Cu_2O cubes wrapping a metal core (Au, Ag and Pd) by a universal MW-assisted synthesis have been presented thanks to the MW selectivity and controlling the synthetic parameters such as the molar ratio of metal NPs to $Cu(acac)_2$.
- The overall synthesis time was less than 40 min, no shaping-template agents were used, and the metal-Cu_2O HS were readily dispersible in water.
- With Au NPs used, the HS consisted of Cu_2O cubes ca. 30-50 nm wrapping smaller crystalline Au NPs of ca. 9 nm. HRTEM highlighted a homogeneous covering and contact, indicating a growth mechanism based on a single cube growth with {1 0 0} facets but with no epitaxy relation.
- Regarding optical and plasmonic properties, the spectrum mostly reflected the absorption characteristics of Cu_2O crystals and a broad light-scattering band in the red and near-IR regions, while the characteristic plasmon peak of the Au NPs was attenuated and red-shifted.
- The presented route could be generalized to other metals (Ag and Pd).

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