

Rational Design and Synthesis of Silver-Based Nanocrystals for Plasmonics and Catalysis

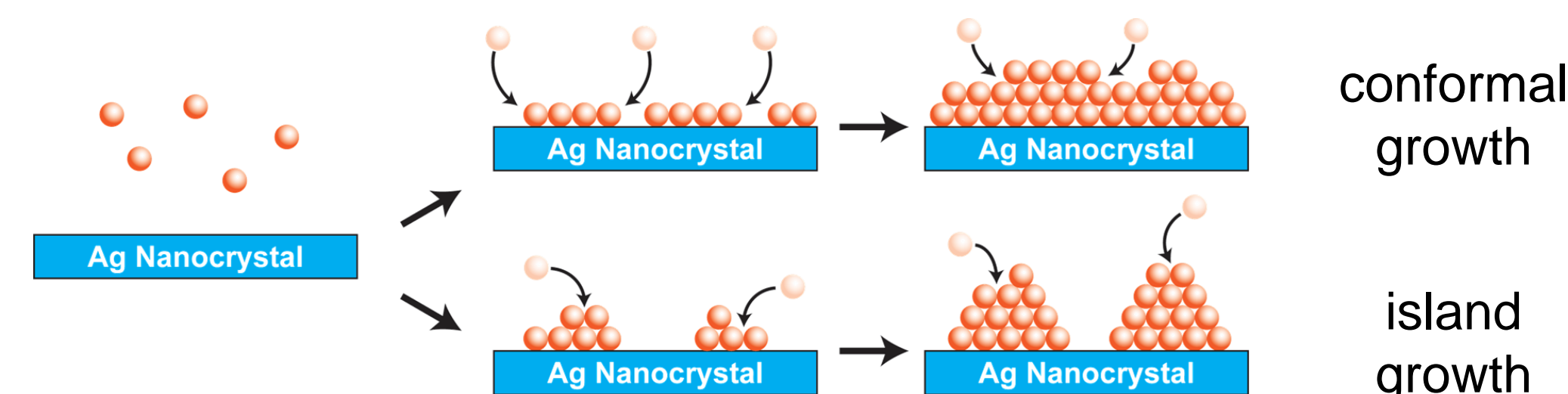
Silver nanocrystals are excellent plasmonic materials for use in surface-enhanced Raman spectroscopy (SERS). By adding a second metal such as Au, Pd, Pt, Rh, Ru, or Ir, having impactful catalytic properties, we could produce nanocrystals with combined plasmonic and catalytic properties to greatly expand the application landscape.

Seed-mediated growth: Ag nanocrystals are prepared first as “seeds,” followed by the deposition of the second metal atoms (M: Au, Pt, Pd, Ru, Rh, Ir) onto the surface of the seeds.

Determining growth modes (thermodynamics):

Material properties

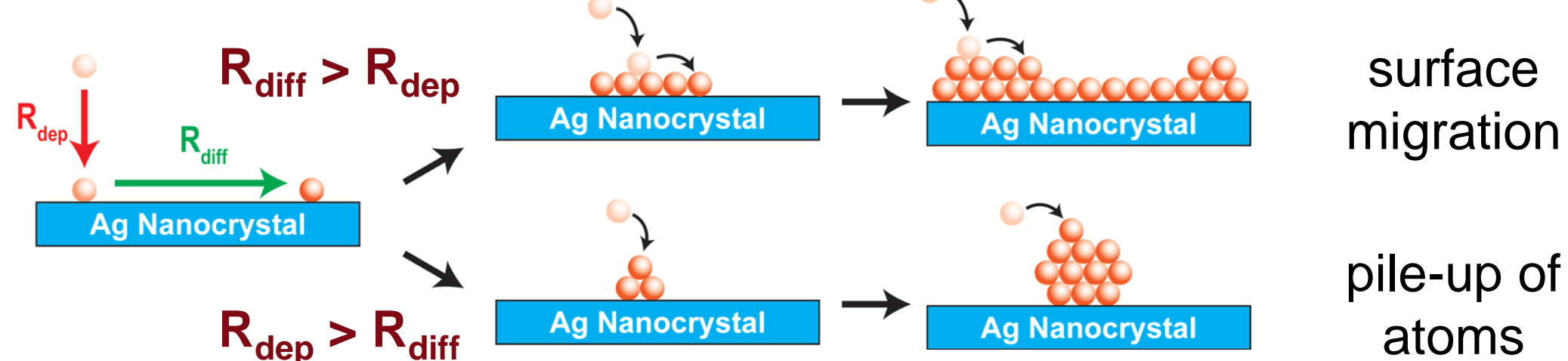
- Cohesive energy
- Lattice parameter
- Electronegativity



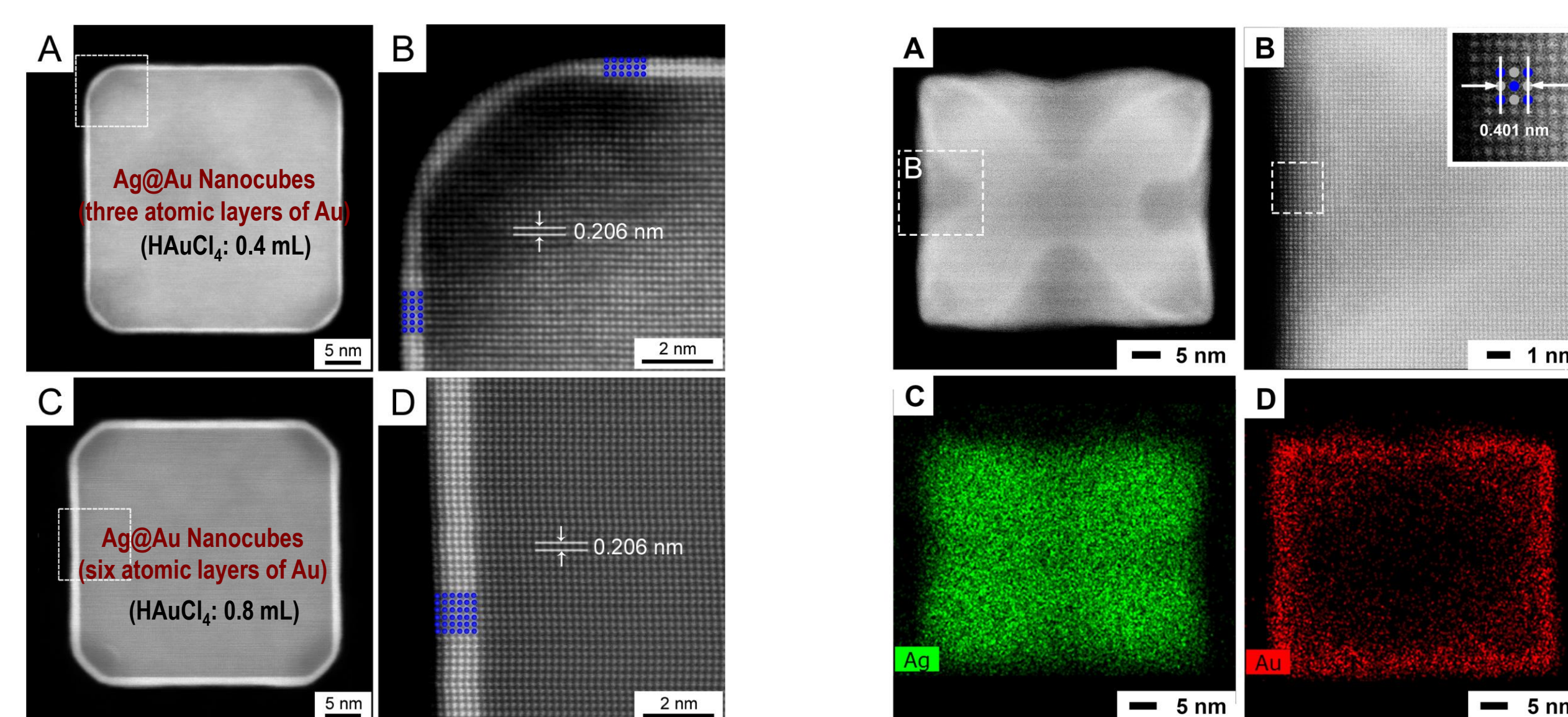
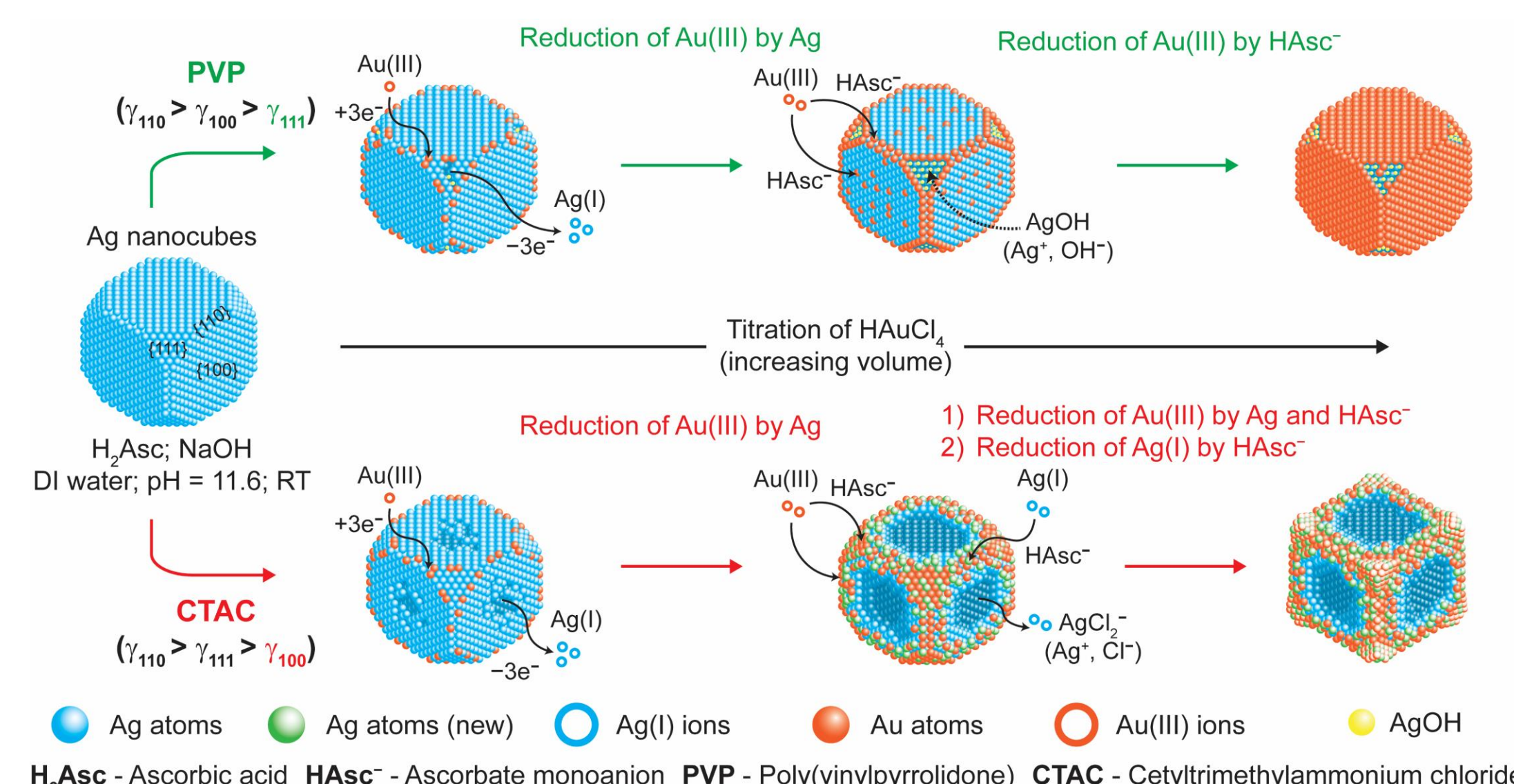
Controlling reaction rates (kinetics):

Experimental knobs

- Temperature
- Injection rate



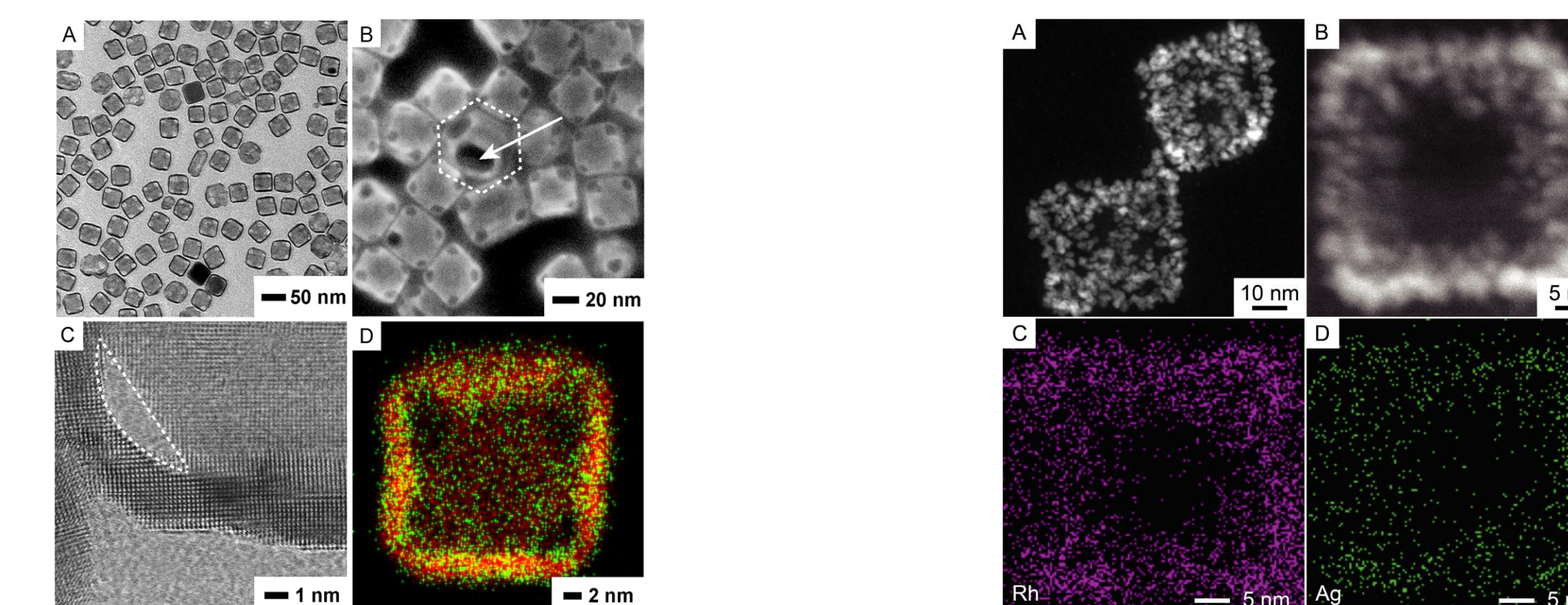
For the growth of Au on Ag nanocubes, we demonstrated that the involvement of either poly(vinylpyrrolidone) (PVP) or cetyltrimethylammonium chloride (CTAC) would respectively activate a completely different reaction route.



Galvanic replacement-free deposition of Au on Ag for core-shell nanocubes with enhanced chemical stability and SERS activity
Yang, Y.; Liu, J.; Fu, Z. W.; Qin, D. *J. Am. Chem. Soc.* **2014**, *136*, 8153–8156.

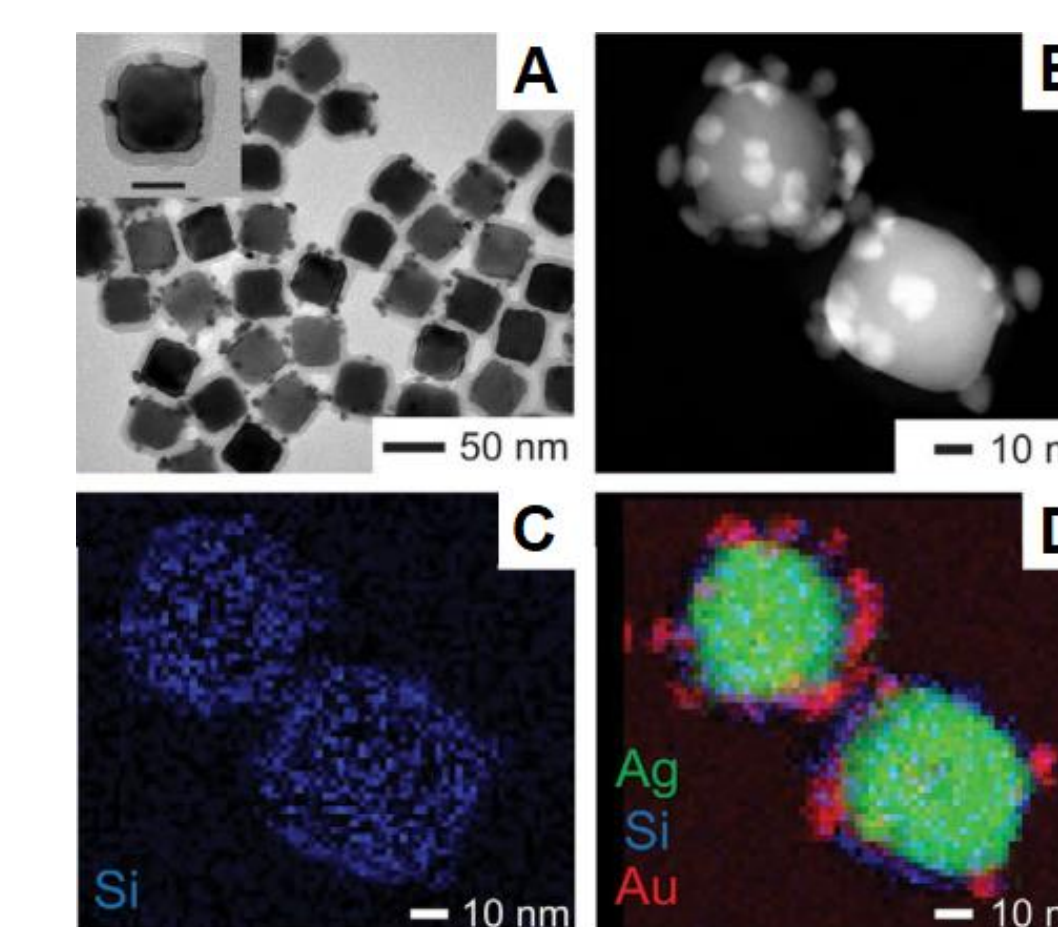
Site-Selective Carving and Co-Deposition: Transformation of Ag Nanocubes into Concave Nanocrystals Encased by Au-Ag Alloy Frames
Ahn, J.; Wang, D.; Ding, Y.; Zhang, J.; Qin, D. *ACS Nano* **2018**, *12*, 298–307.

We have reported previously, and are currently working toward a rational design and synthesis of various Ag-based nanocrystal systems and their derivatives.

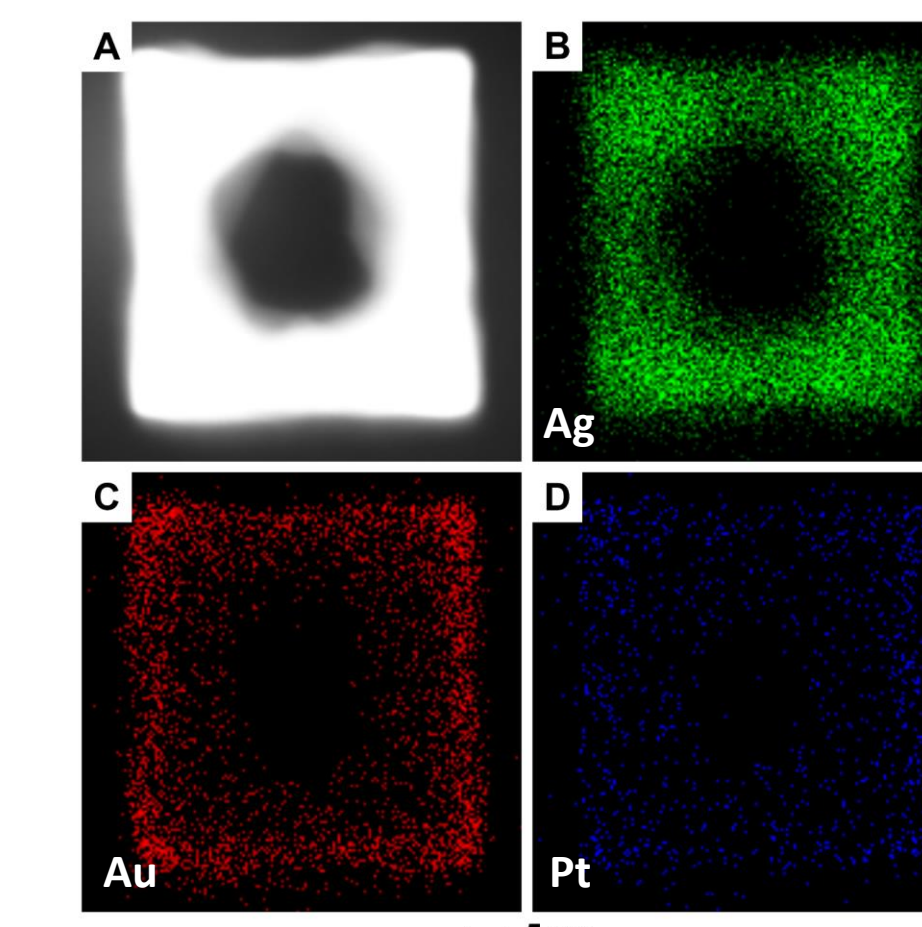


Au nanoboxes having thin (< 2 nm) walls, with well-defined openings at corners.

Rh nanoboxes with highly porous walls



Ag@SiO₂/Au hybrid nanocrystals



Ag-Au-Pt hollow trimetallic nanocrystals

Gold-Based Cubic Nanoboxes with Well-Defined Openings at the Corners and Ultrathin Walls Less Than Two Nanometers Thick
Sun, X.; Kim, J.; Gilroy, K. D.; Liu, J.; König, T. A. F.; Qin, D. *ACS Nano* **2016**, *10*, 8019–8025

Syntheses, Plasmonic Properties, and Catalytic Applications of Ag-Rh Core-Frame Nanoboxes and Rh Nanoboxes with Highly Porous Walls
Zhang, Y.; Ahn, J.; Liu, J.; Qin, D. *Chem. Mater.* **2018**, *30*, 2151–2159.

Bifunctional Ag@SiO₂/Au Nanoparticles for Probing Sequential Catalytic Reactions by Surface-Enhanced Raman Spectroscopy
Wu, Y.; Su, D.; Qin, D. *Chem. Mater.* **2017**, *3*, 245–251.

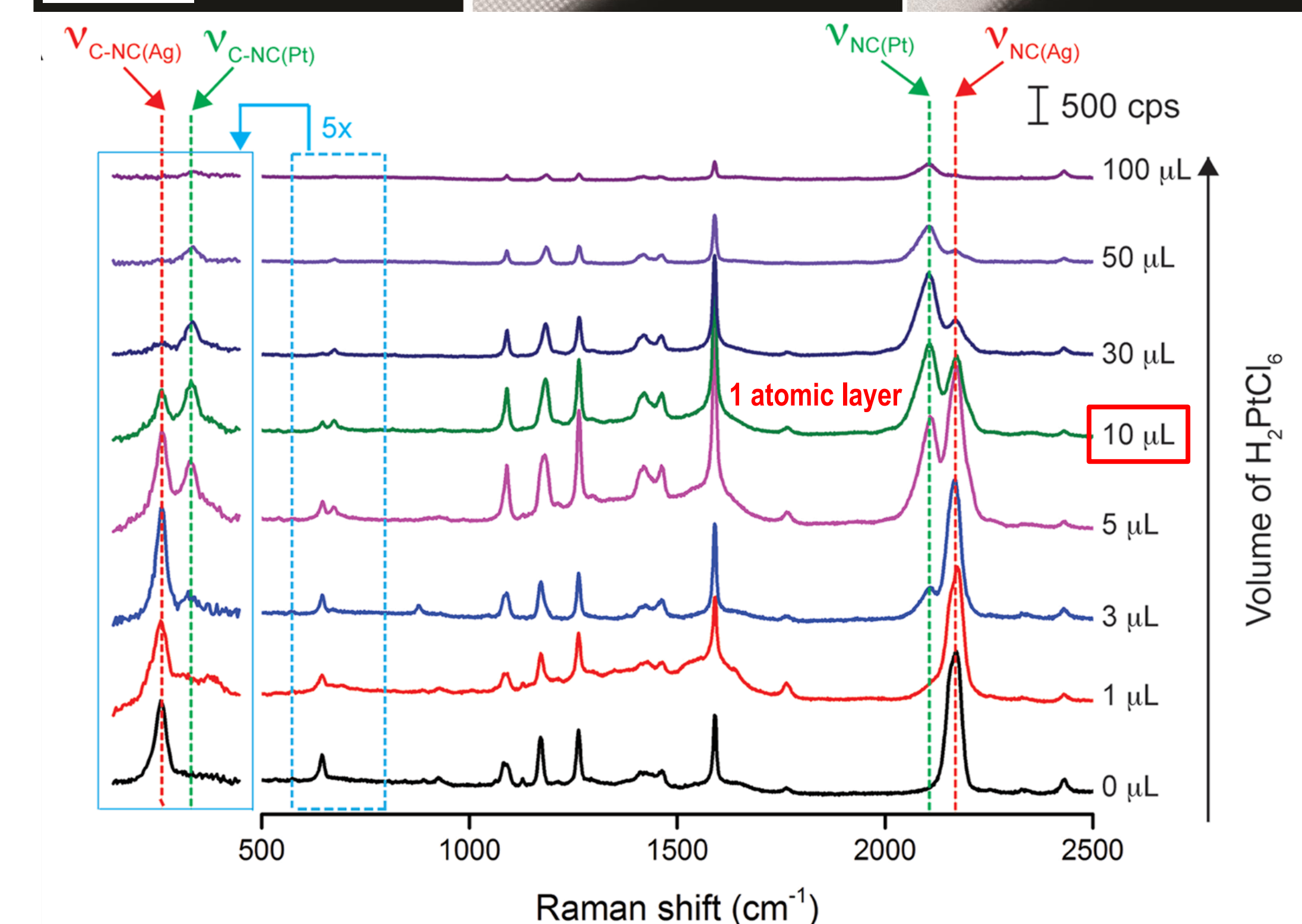
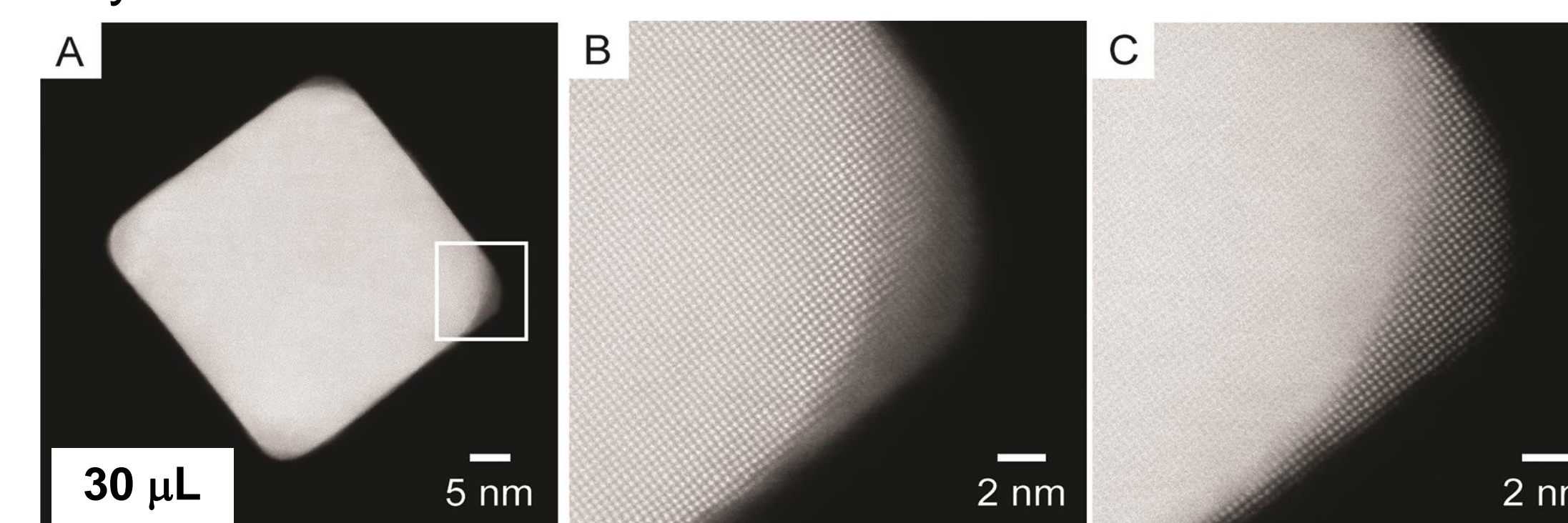
Fabrication of Nanoscale Cage Cubes by Drilling Orthogonal, Intersected Holes through All Six Side Faces of Ag Nanocubes
Ahn, J.; Qin, D. *Chem. Mater.* **2019**, *31*, 9179–9187.

Understanding Heterogeneous Nucleation and Growth Using an Isocyanide-based Molecular Probe

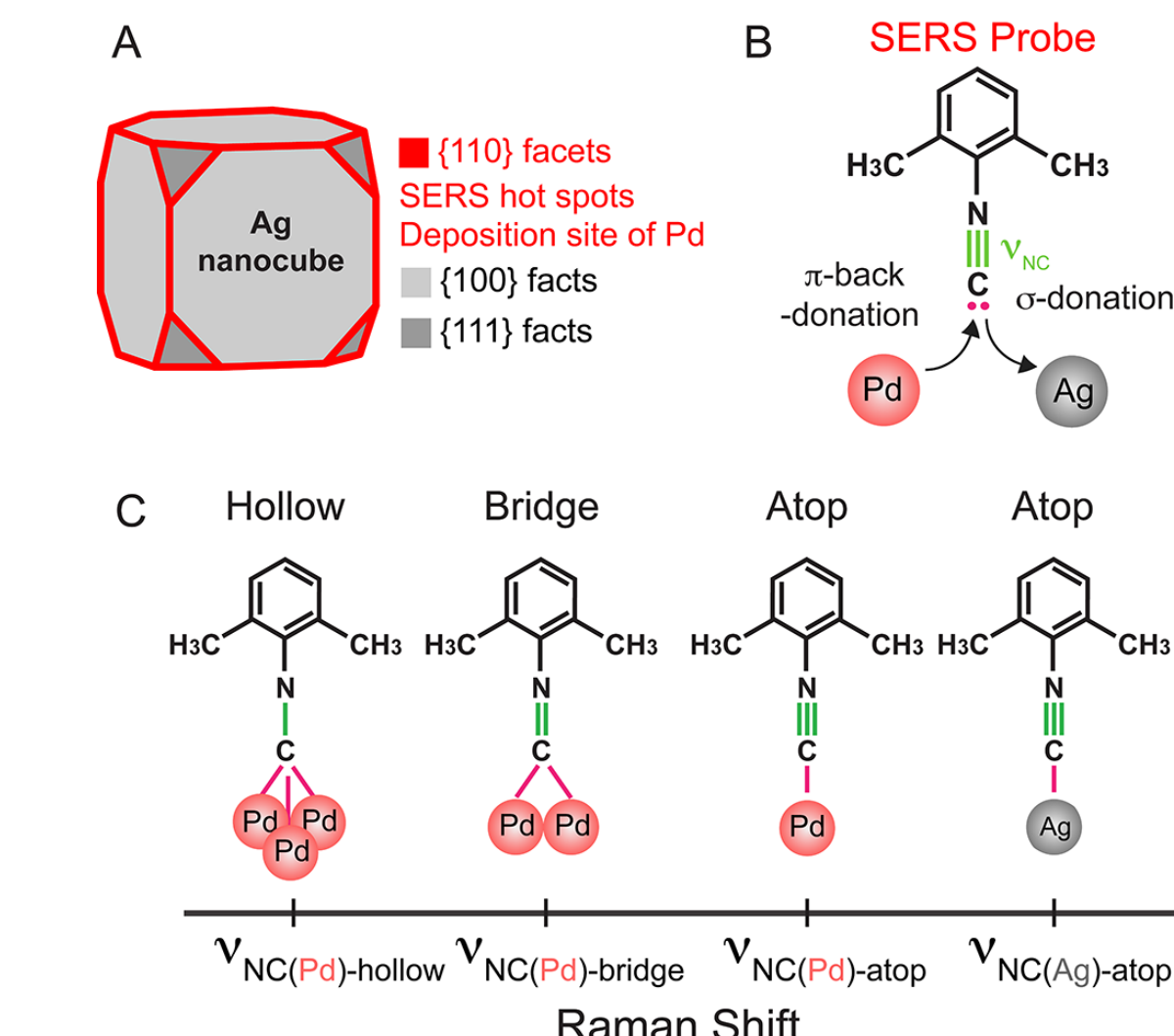
We developed an isocyanide-based molecular probe for *in situ* characterization of the nucleation and growth of the second metal on the edges of Ag nanocube seeds in solution by surface-enhanced Raman scattering (SERS). Our success relies on the difference in the vibrational frequency of the isocyanide (-NC) group in 2,6-dimethylphenyl isocyanide (2,6-DMPI) as NC group binds to different metal surfaces.

- Ag and Au: electrons from the σ^* antibonding orbital of the NC group are transferred to the d-band of the metal, strengthening the NC bond and blue-shifting its stretching frequency. (σ -donation)
- Pd and Pt: electrons from the d-band of the metal are transferred to the π^* antibonding orbital of the NC group, weakening the NC bond and red-shifting its stretching frequency. (π -back-donation)

While it is difficult to capture the sub-monolayer nucleation of the second metal (e.g. Pt atoms) using high-resolution electron microscopy (HREM), the isocyanide-based molecular probe is sensitive to report the deposition below one monolayer.

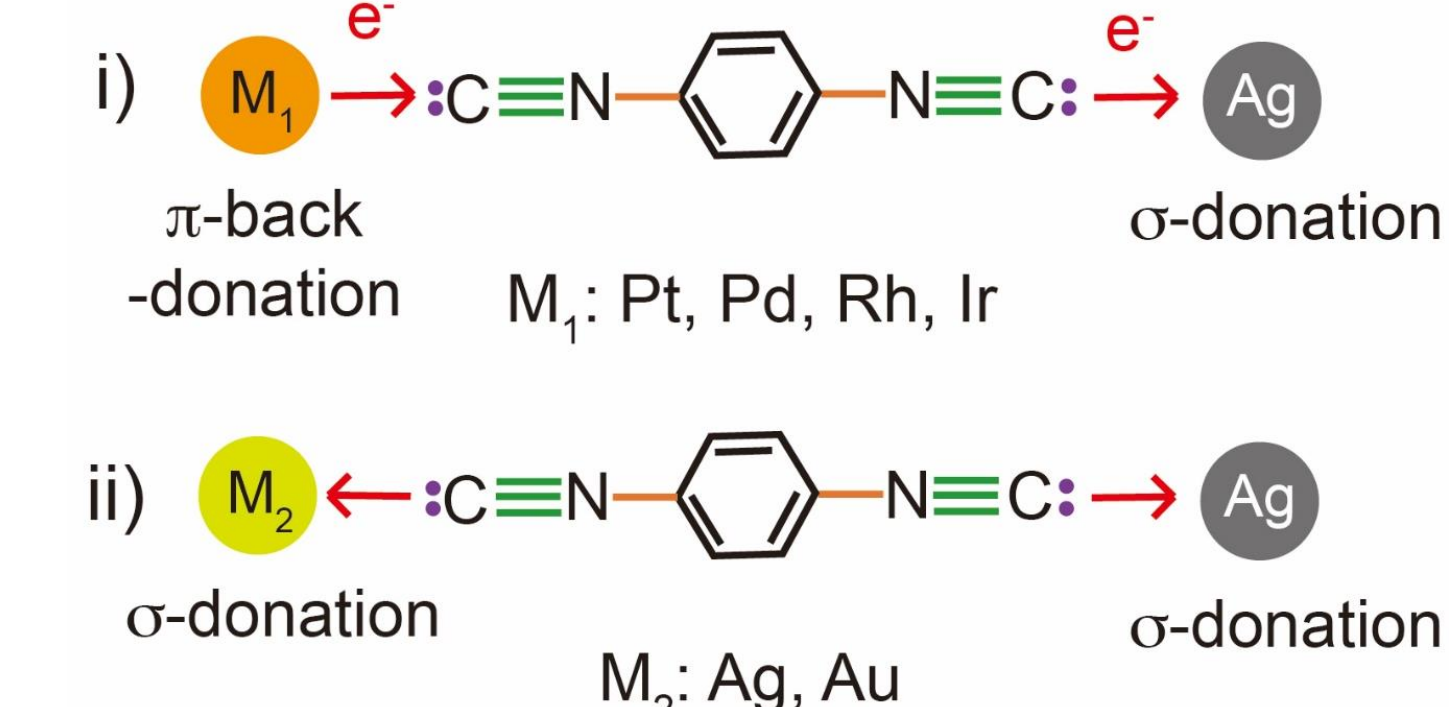
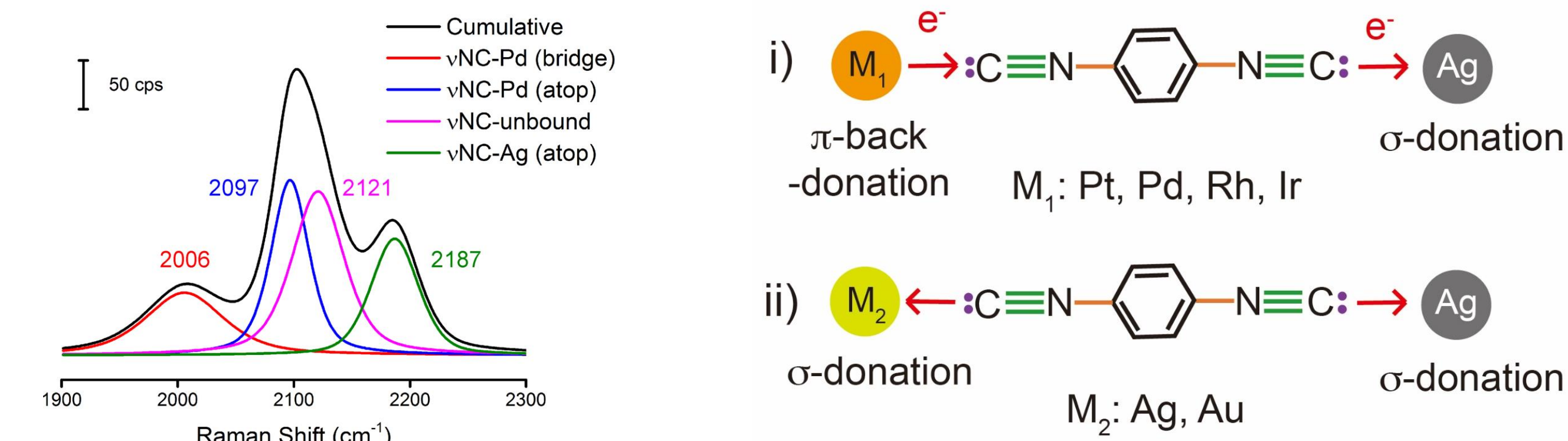


For metals such as Pd, the NC group may bind to multiple atoms at once and form different configurations.



When the NC group is bound to more Pd atoms (to form *bridge* or *hollow* configurations), the NC bond will become increasingly weaker, leading to the red-shifting of its stretching frequency.

In addition, 1,4-phenylene diisocyanide (PDI), having two isocyanide groups in opposite positions, could bond to dissimilar metals and induce a charge transfer to the Ag atoms, activating Ag for catalytic applications.



Moving forward, we aim to apply the isocyanide-based molecular probe for characterizing catalytically significant interfaces, specifically toward detecting single atoms of catalytic metals (Pd, Pt, Rh, Ru, Ir), by using SERS to monitor surface reactions.