

Disordering by Design: High-Entropy Alloy Nanocrystals via Galvanic Replacement Reactions for Catalytic Applications

Neus G. Bastús

Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and The Barcelona Institute of Science and Technology (BIST), Campus UAB, 08193, Bellaterra, Barcelona, Spain

E-mail neus.bastus@icn2.cat

High-entropy alloy (HEA) nanocrystals, composed of multiple metallic elements randomly distributed within a single crystalline phase, represent a powerful platform for catalysis. However, achieving uniform composition, well-defined morphology, and single-phase character under mild (room temperature) synthetic conditions remains a significant challenge. Building on our previous work employing galvanic replacement reactions (GRRs) for the synthesis of hollow nanocrystals¹⁻⁵, we present a sequential GRR strategy that enables spatially and temporally controlled incorporation of diverse metal precursors into a sacrificial template. The approach capitalizes on the high enthalpic penalty associated with phase segregation at the nanoscale, where the formation of internal interfaces and segregated domains is energetically disfavored due to high surface and interfacial energies⁶. To direct this transformation, the protocol systematically optimizes surfactants and co-reducing agents to finely tune reduction kinetics, suppress secondary nucleation, and promote controlled transformations. As a result, robust solid templates evolve into porous, anisotropic, and compositionally homogeneous HEA nanocrystals which exhibit significantly enhanced catalytic activity and durability. The work establishes a versatile and generalizable route for synthesizing architecturally complex, compositionally tunable HEA nanocatalysts, providing a foundation for the rational design of multimetallic materials.

References

1. Russo, L. Time- and Size-Resolved Plasmonic Evolution with nm Resolution of Galvanic Replacement Reaction in AuAg Nanoshells Synthesis. *Chem. Mater.* 2018, 30 (15), 5098-5107.
2. Gonzalez, E.; Enhanced reactivity of high-index surface Pt hollow NCs. *Journal of Materials Chemistry A* 2016, 4 (1), 200-208.
3. Merkoçi, F.; Understanding galvanic replacement reactions: the case of Pt and Ag. *Materials Today Advances* 2020, 5, 100037.
4. Genç, A.; Asymmetrical plasmon distribution in hybrid AuAg hollow/solid coded nanotubes. *Nanomaterials* 2023, 13 (6), 992.
5. Patarroyo, J.; Hollow PdAg-CeO₂ heterodimer nanocrystals as highly structured heterogeneous catalysts. *Sci Rep* 2019, 9 (1), 18776.
6. Yang, L.; Synthesis Strategies for High Entropy Nanoparticles. *Adv Mater* 2025, 37 (1), e2412337.