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Letter

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Disorder-to-Order Transition Mediated by Size Refocusing: A Route toward Monodisperse Intermetallic Nanoparticles

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Size-Dependent Disorder–Order Transformation in the Synthesis of Monodisperse Intermetallic PdCu Nanocatalysts

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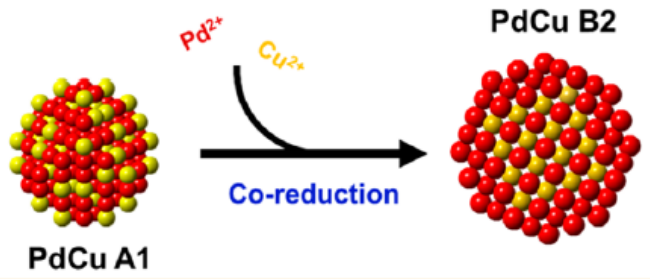


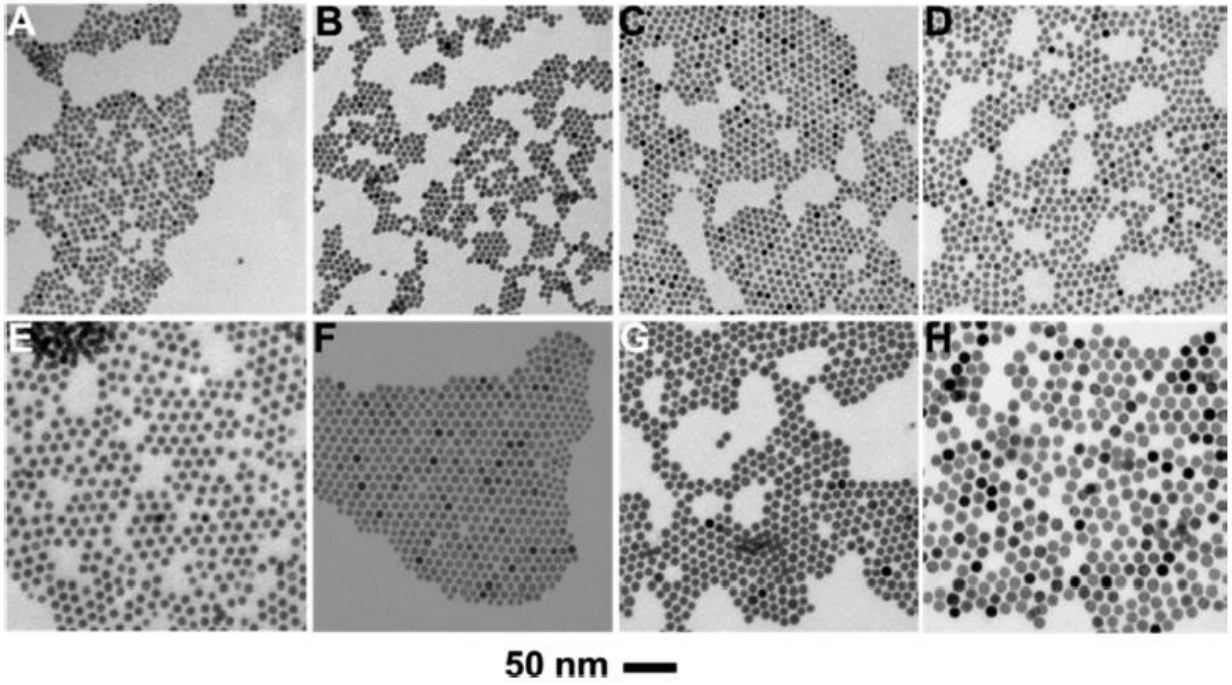
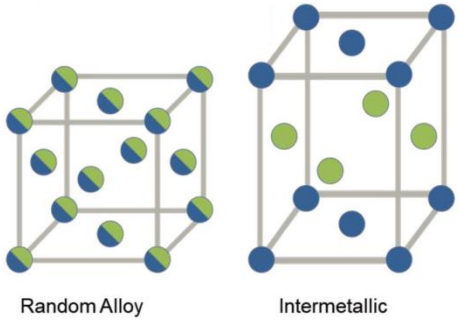


Figure 5. TEM images of PdCu NPs synthesized by seed-mediated coreduction: (A) PdCu A1 seeds; (B) specimen collected at 230 °C during the rise of temperature; (C–H) samples collected at 270 °C after (C) 0 min, (D) 3 min, (E) 6 min, (F) 9 min, (G) 15 min, and (H) 30 min.

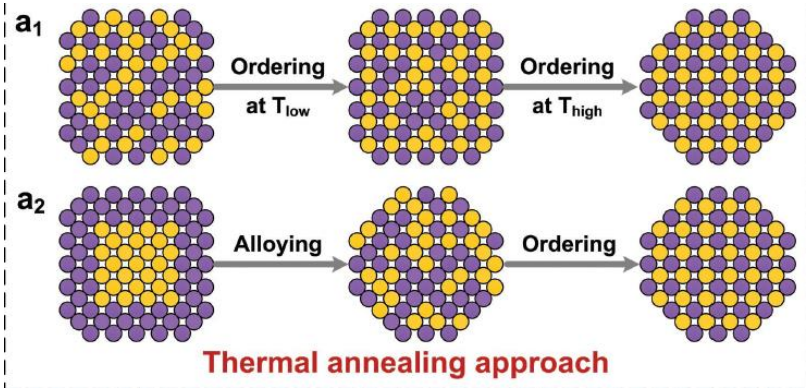
Intermetallic Nanoparticles

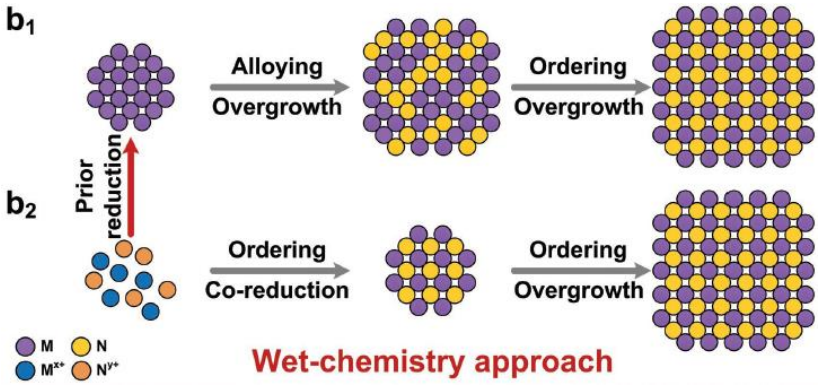


Reported Synthetic Methods for Intermetallic NPs

1. **Thermal annealing** of alloys or heterostructures in reduced or inert atmosphere (or vacuum) at temperatures lower than the order-to-disorder transition point

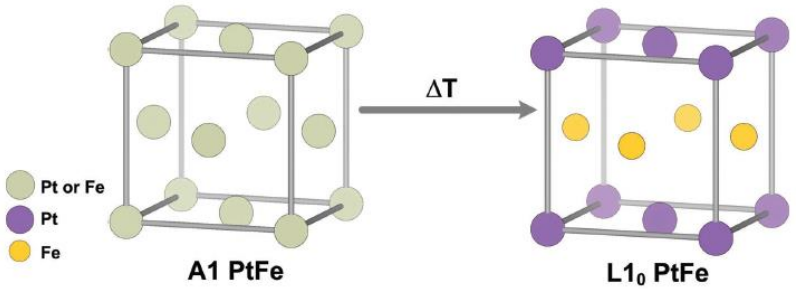
2. **Wet-chemistry approach:** seed-mediated diffusion growth in the presence of preformed seeds or direct one-pot syntheses, involving the simultaneous reduction and/or decomposition of two metal precursors

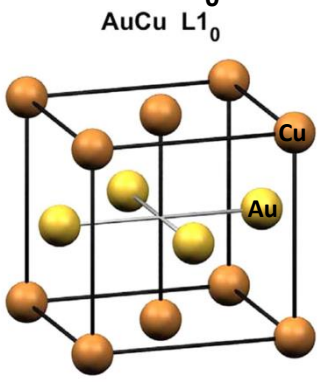




Introduction

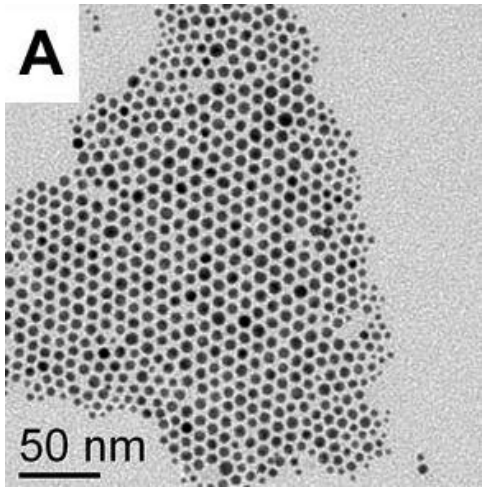
- Random alloy NPs need to overcome size-dependent activation barrier to achieve ordering.
- Thermodynamics and Kinetics parameters influence size-dependency
  1. ΔG = negative, on going from disordered-to-ordered phase, although total surface free energy increases with decreasing size.
  2. Atomic diffusion facilitates phase transitions , smaller NPs more facile.
- In conclusion: Optimal size of NP is required as smaller NP with faster atomic diffusion restricts formation of new phase.
- At the annealing temperature, ordering impossible as disordered state is more stable.
- Hence, random alloy AuCu NP to ordered AuCu NP in solution using **overgrowth conditions** (Seed-mediated deposition).
- Small sacrificial NPs rapidly dissolve, leading to deposition of their material onto the larger nanoparticles; this process refocused the ensemble to a narrow size distribution, this process to achieve a narrow size distribution.
- **In this paper, Random alloy A1 phase AuCu NPs on overgrowth goes to intermetallic $L1_0$ phase AuCu NPs.**

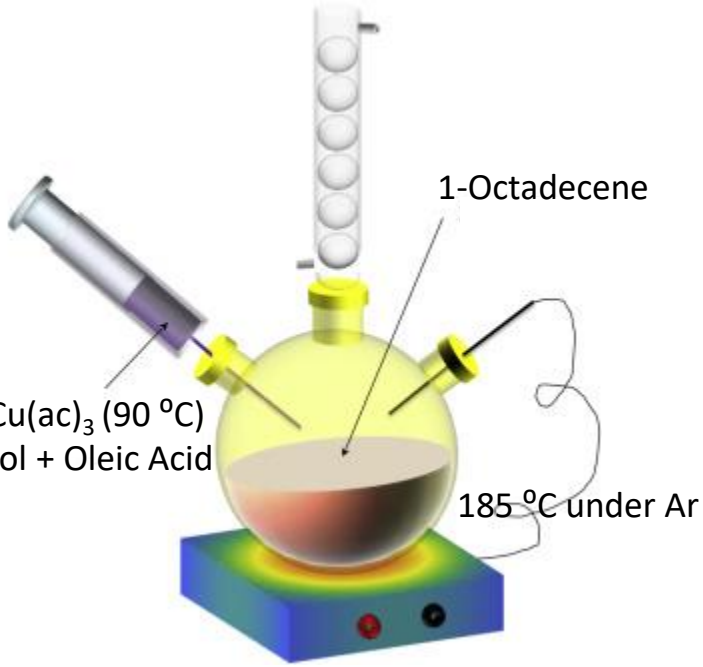


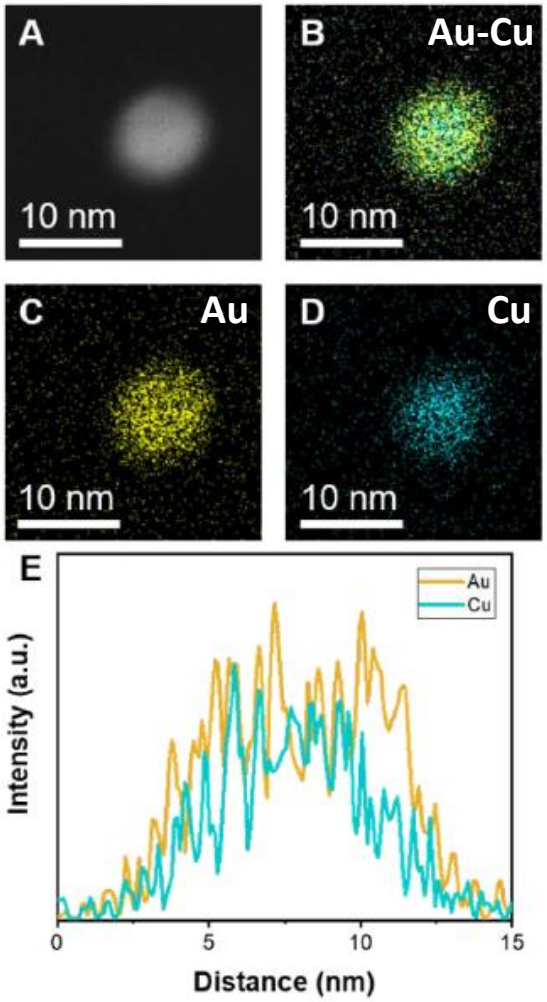


Seed Synthesis via Hot injection Method

6.5 ± 1.2 nm







EDX-Line scan

*Figure S1

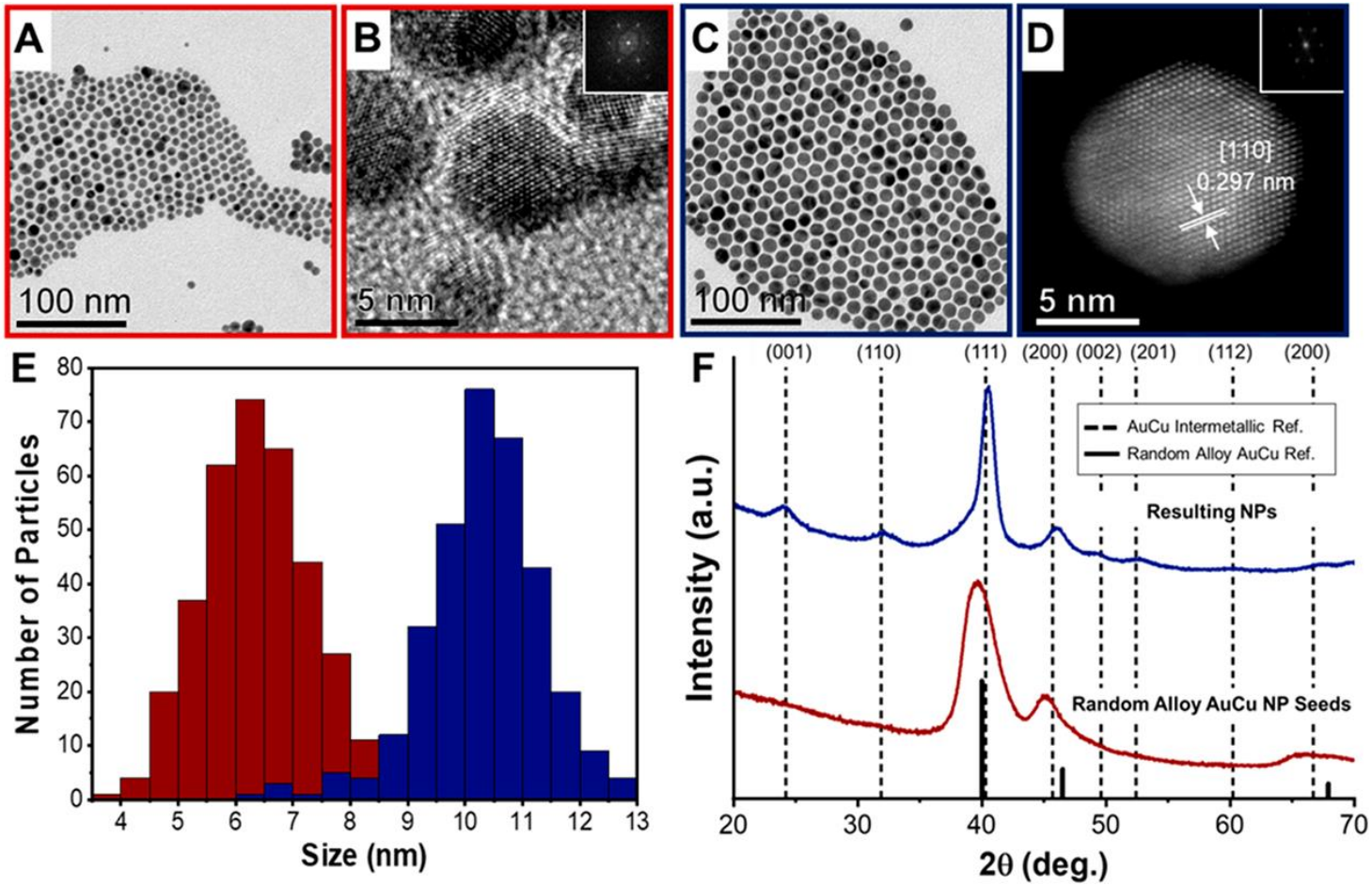
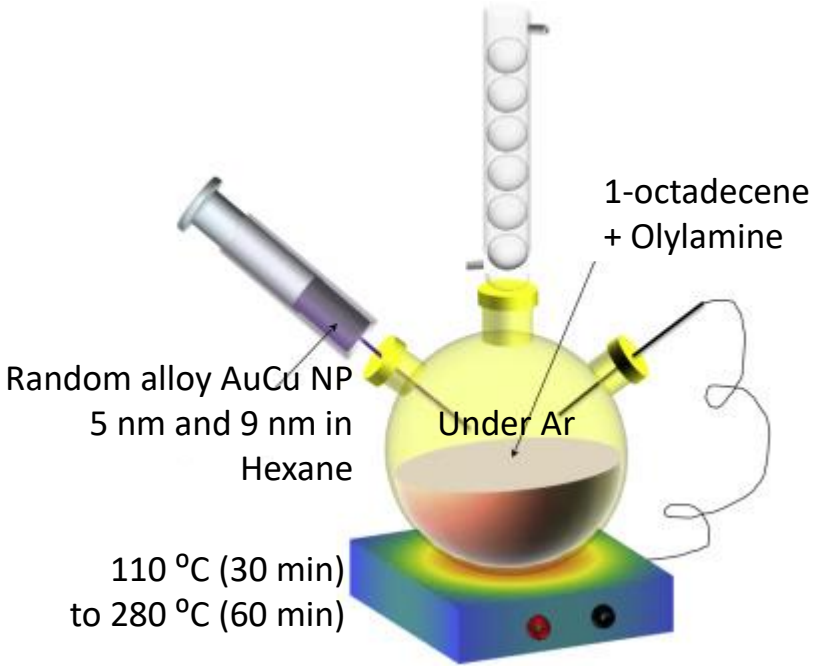


Figure 1. (A) TEM image of monodisperse random alloy AuCu NPs of A1 structure; (B) HRTEM image of individual random alloy AuCu NP with inset of the corresponding selected area FFT; (C) TEM image of monodisperse AuCu NPs obtained with overgrowth; (D) high-angle annular dark-field/STEM image along the [110] zone axis (confirmed by the FFT in the inset); (E) histogram of particle distribution of random alloy AuCu NPs (red) and AuCu NPs resulting from overgrowth (blue); (F) PXRD patterns of AuCu nanoparticles (NP) with face-centered cubic random alloy configuration (red) and face-centered tetragonal intermetallic configuration (blue).

Size Refocusing by Ostwald Ripening



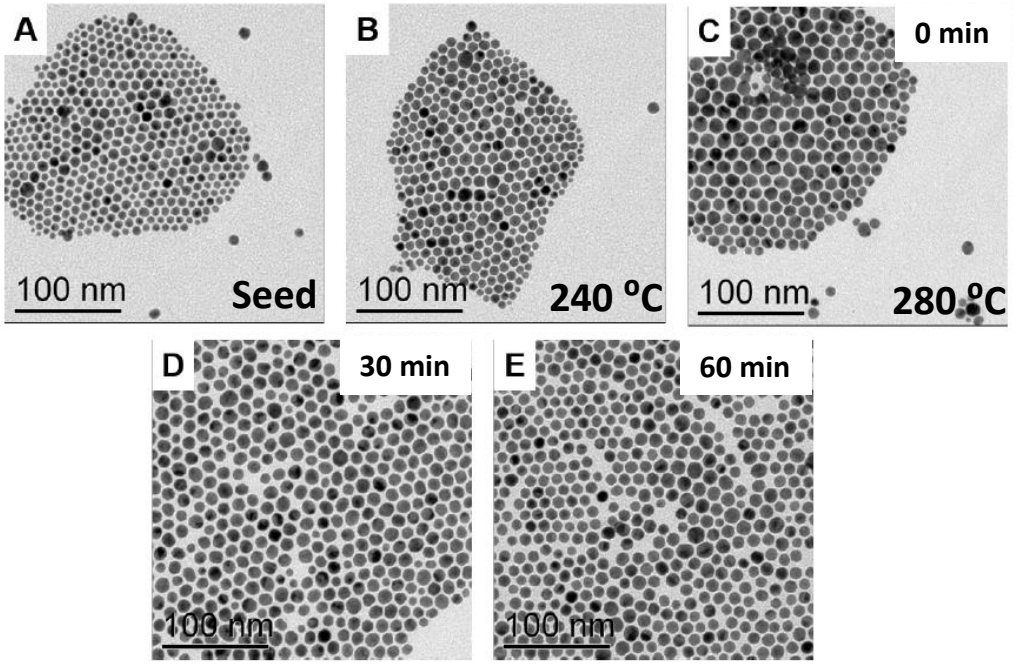


*Figure S5

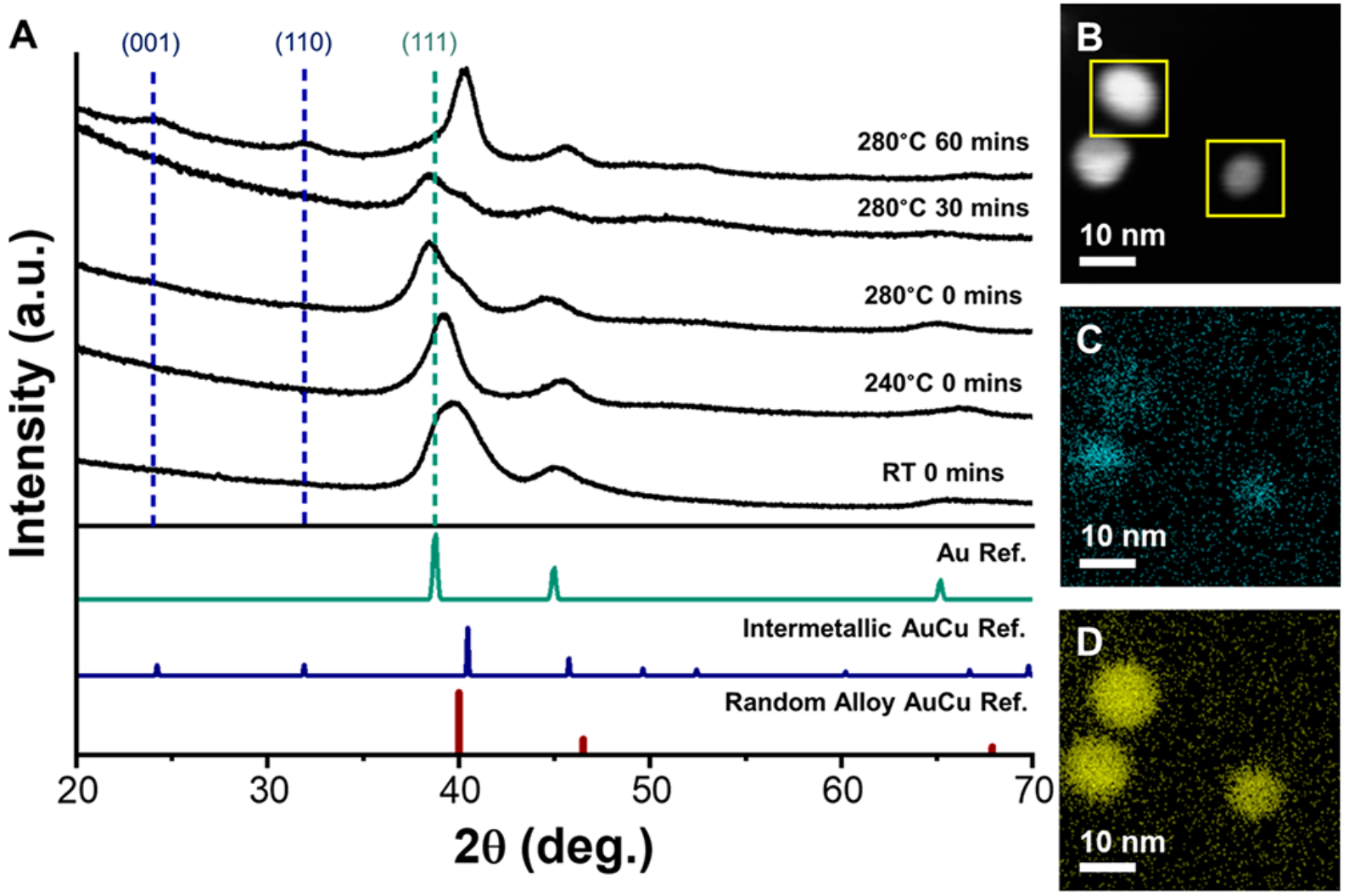


Figure 2. (A) Time-evolution XRD patterns of AuCu NPs sampled during the overgrowth process, with the dashed lines indicating the superlattice peaks of intermetallic AuCu (blue) and for the facecentered cubic Au fundamental peak (green); (B) STEM image of selected AuCu NPs after 0 min at 280 °C for STEM-EDX analysis, and yellow boxes highlight the nanoparticles composed of mostly Au. Elemental mapping of selected area (B) denotes the presence of (C) Cu (blue) and (D) Au (yellow).

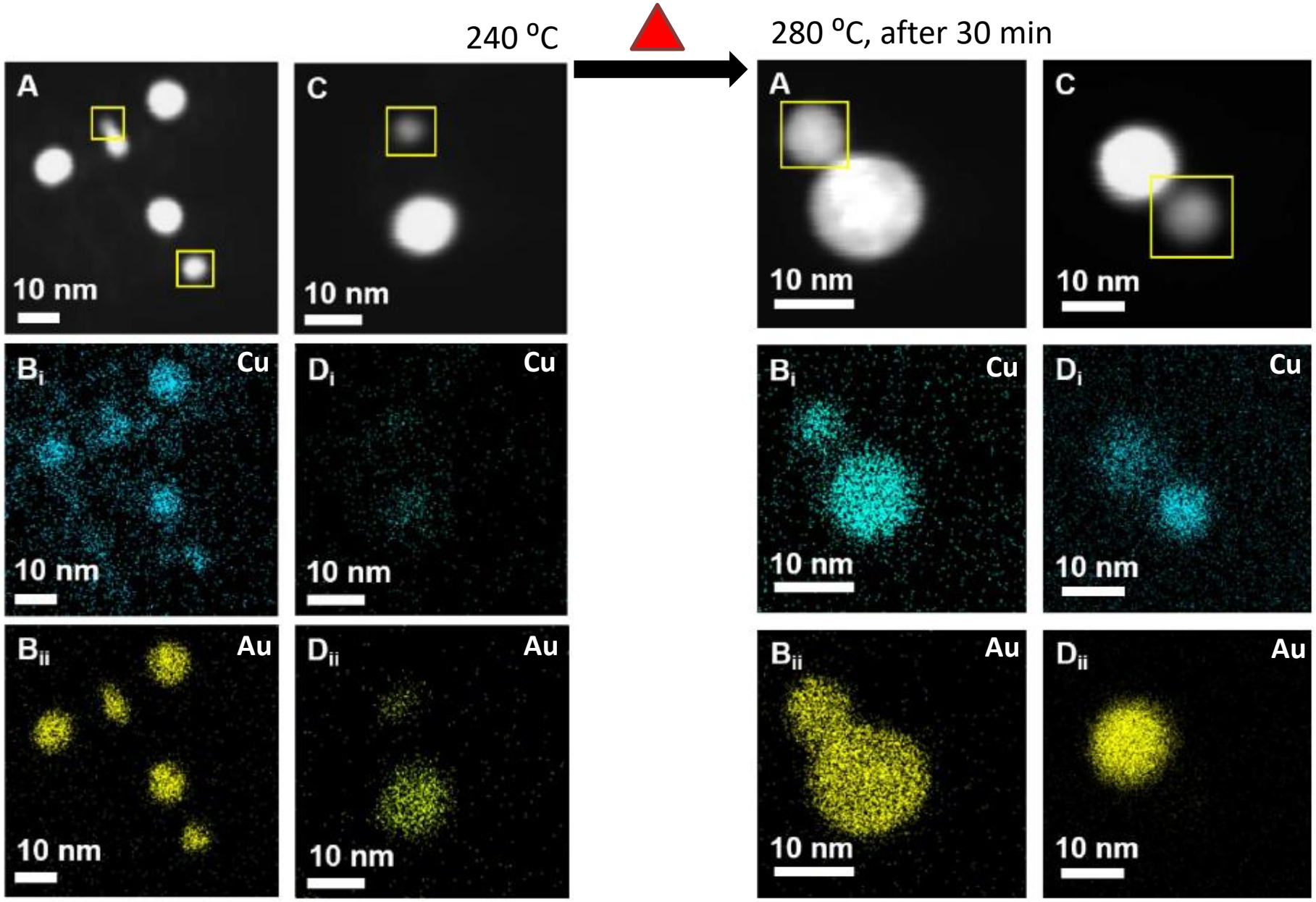


*Figure S7

*Figure S8

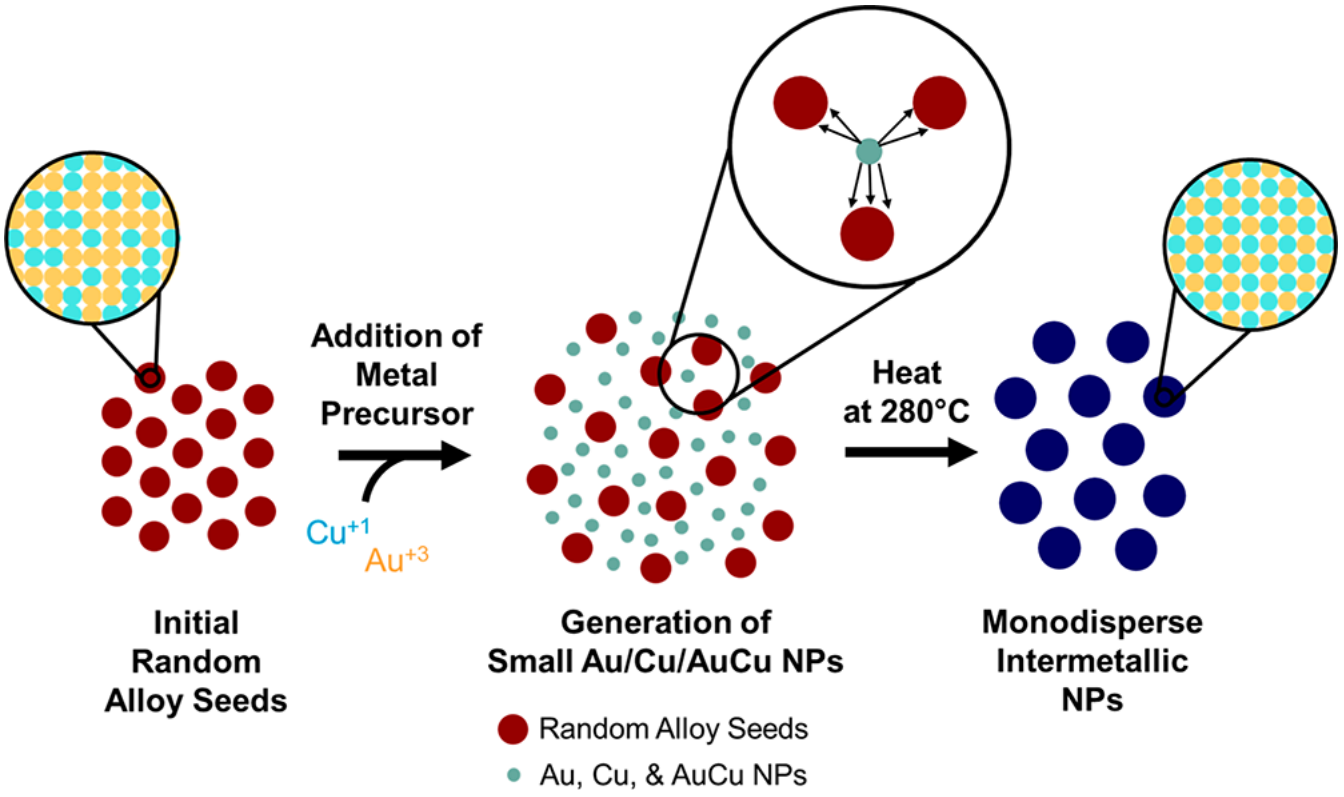


Figure 3. Scheme depicting the proposed mechanism for the formation of monodisperse intermetallic NPs.

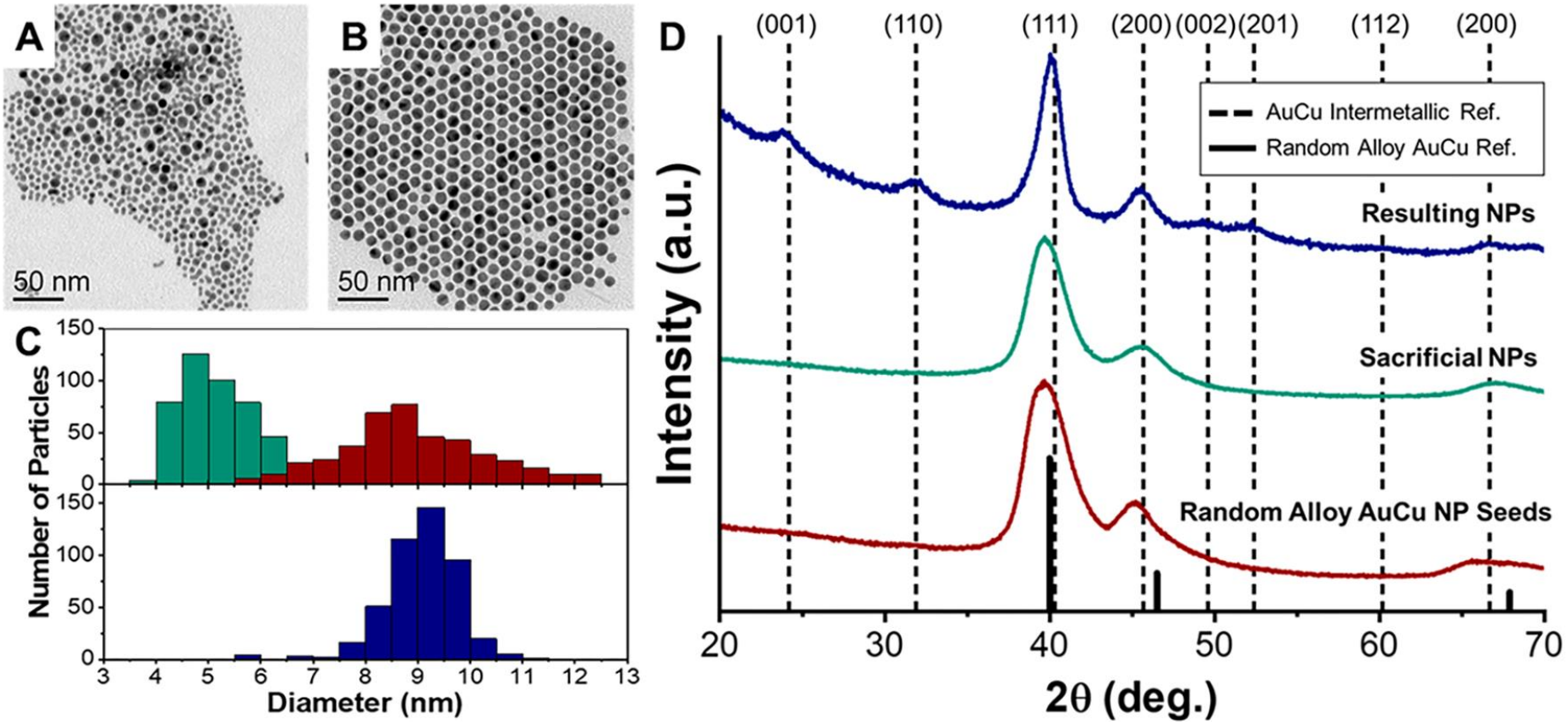


Figure 4. (A) TEM image of the synthesized the combined random alloy AuCu NP seeds and sacrificial nanoparticles; (B) TEM image of the resulting nanoparticles after heating in solution of ODE and OLA; (C) histogram of the random alloy AuCu NPs (red), sacrificial nanoparticles (green), and resulting nanoparticles (blue); (D) corresponding XRD patterns of the nanoparticles.

Insights from the Paper

- Necessary condition for size refocussing is 2 population of different sized NPs, the resulting NP forms at the cost of sacrificial NP.
- Size refocusing facilitates disorder-to-order phase transfer.
- Seed vs Sacrificial NP ratio to be optimized, as a large population of sacrificial nanoparticles will shift the critical radius size and prevent dissolution
- Size of sacrificial NP < size of seeds, to guarantee dissolution.
- Peng *et. al.*, synthesis of semiconductor NPs needs rapid dissolution of sacrificial NPs within a time frame of reaction to avoid defocusing of the size distribution by Ostwald ripening.
- Temperature can be manipulated to control the rate of diffusion to control the effect of size focussing.
- Both reaction Time and Temperature are important factor to ensure complete dissolution along with the disorder-to-order transformation.

Conclusions

- Monodisperse intermetallic NPs were achieved by depositing uniform overgrowth on random alloy seeds.
- Overgrowth was observed to proceed through size refocussing mechanism.
- Size refocusing proposed as a mechanism to facilitate the disorder-to-order phase transformation in multimetallic NP resulting in sample monodispersity.
- The work can in future contribute to the development of electrocatalysts and magnetic storages materials by advancing the understanding of intermetallic nanoparticle formation in colloidal syntheses