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Shape regulation of high-index facet nanoparticles by dealloying

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Relevance to our group

1. Bimetallic and trimetallic nanoparticle synthesis
2. Noble metal recovery
3. Recovery of metals from degradation of tyres

Terminologies

1. Dealloying: **Dealloying** is the selective corrosion of one or more components of a solid solution alloy. It is also called parting, selective leaching or selective attack.
   Common **dealloying** examples are decarburization, decobaltification, denickelification, dezincification, and graphitic corrosion.

2. Tetra hexahedron (THH): A solid in the isometric system, bounded by twenty-four equal triangular faces, four corresponding to each face of the cube.

Background work

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Synthesis of Tetrahexahedral Platinum Nanocrystals with High-Index Facets and High Electro-Oxidation Activity

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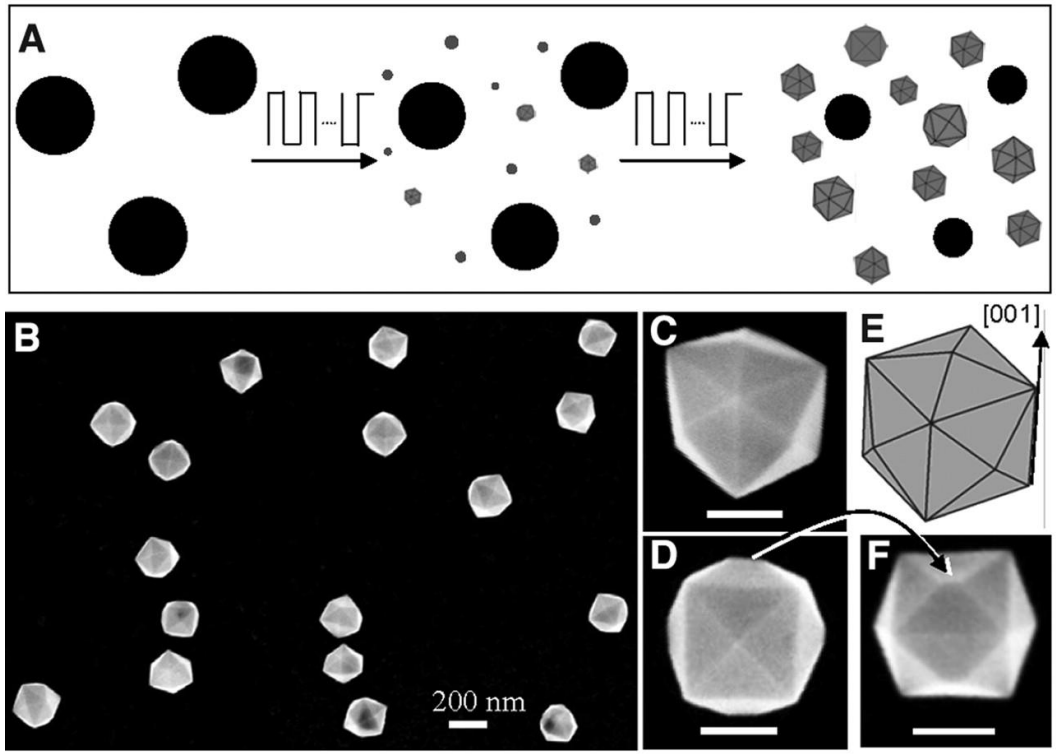


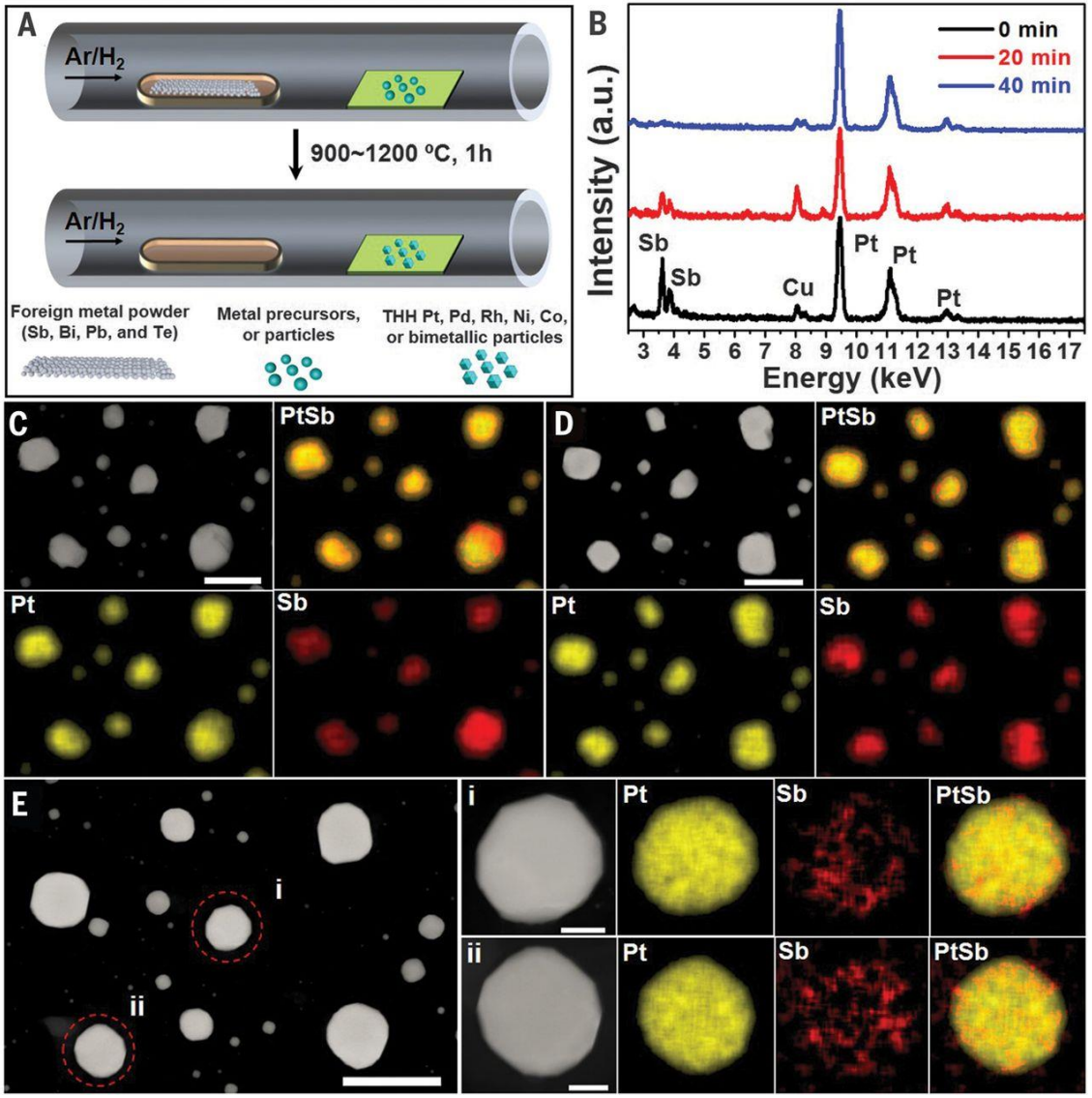
Scheme of electrochemical preparation of THH Pt NCs from nanospheres. The Pt nanosphere is an agglomeration of tiny Pt nanoparticles of irregular shapes. Under the influence of the square wave potential, new Pt NCs of THH shape grow at the expense of the large nanospheres (the large nanosphere is “dissolved” into smaller ones, which eventually transform into THH shape). (B) Low-magnification SEM image of THH Pt NCs with growth time of 60 min. (C and D) High-magnification SEM images of Pt THH viewed down along different orientations, showing the shape of the THH. (E) Geometrical model of an ideal THH. (F) High-magnification SEM image of a THH Pt NC, showing the imperfect vertices as a result of unequal size of the neighboring facets. Scale bars in (C), (D), and (F), 100 nm.

Introduction

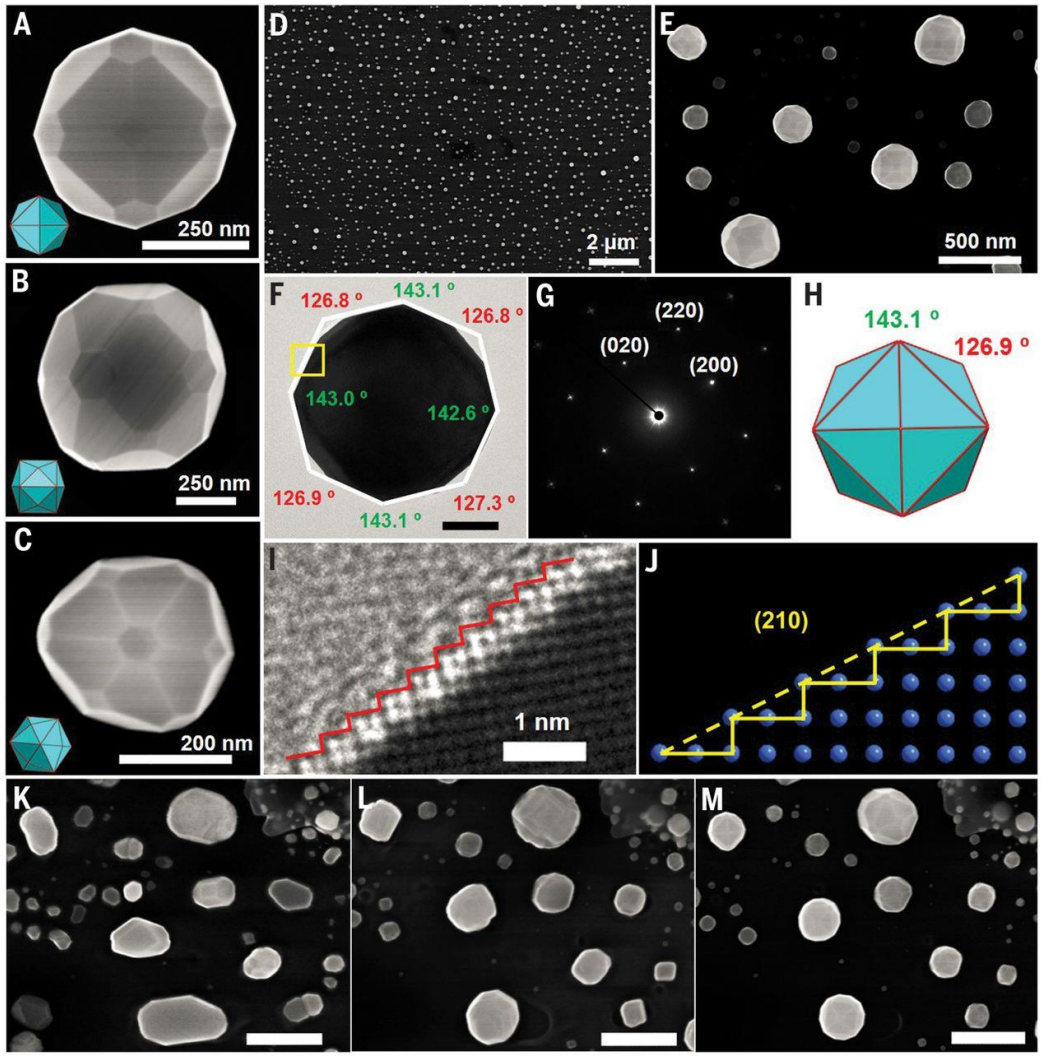
- Thermolysis of solid-state precursors, a method widely used in industry for producing noble metal NPs at scale, typically yields thermodynamically favoured NPs that have flat low-index facets that can have much lower catalytic activity for certain reactions than those with high-index facets with low coordination metal sites.

- Higher throughput solution-phase methods to control particle shape typically rely on stabilizing ligands that are often difficult to remove and can adversely affect catalytic activity by blocking active sites.

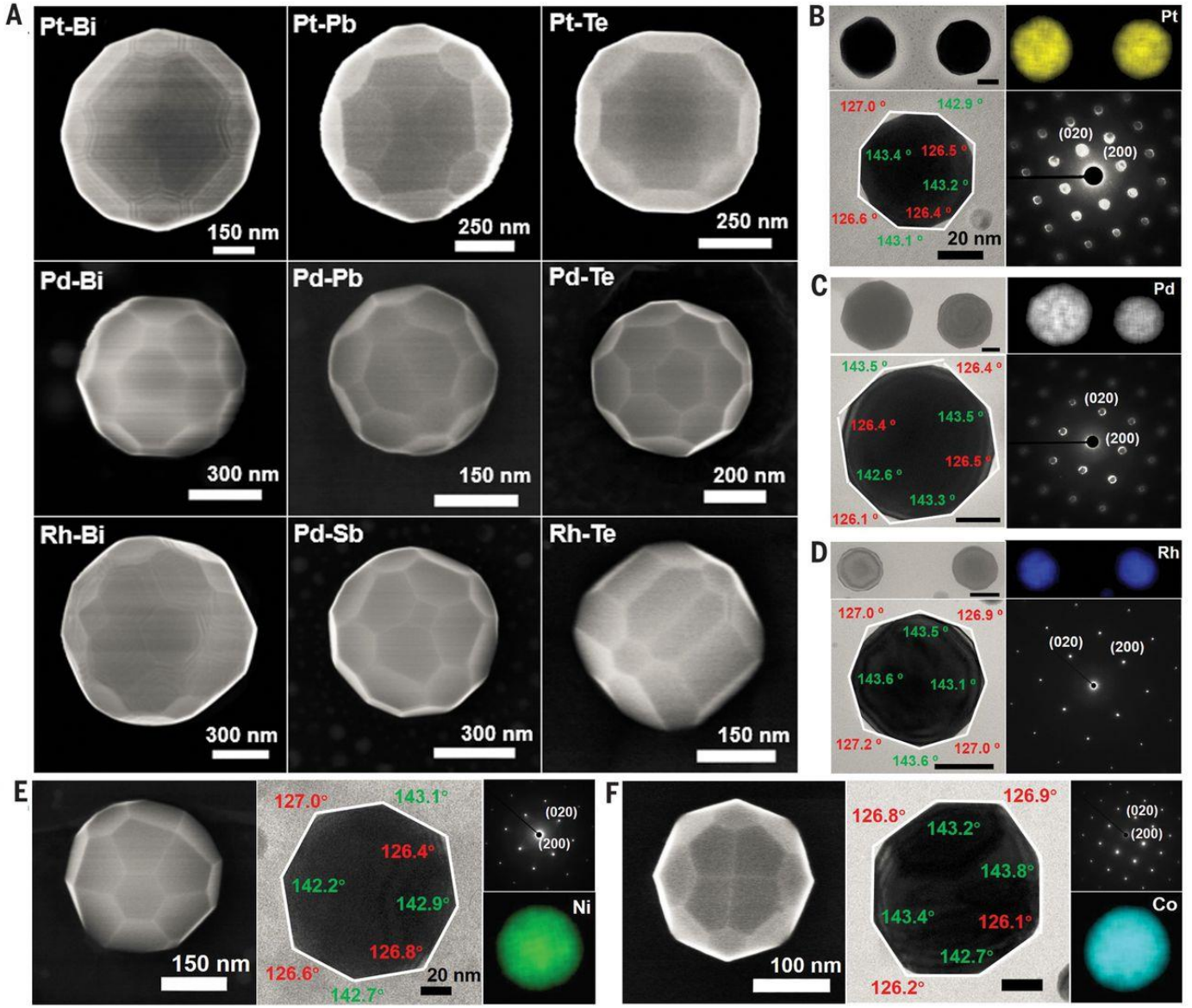
- Inspired by the observation that under potential deposition (UPD)of trace amounts of shape regulating metal elements can be used to synthesize NPs with high-index facets. Solid-state metal precursors of interest were heated in a tube furnace with a foreign metal (Sb, Bi, Pb, and Te) atmosphere to influence NP growth.



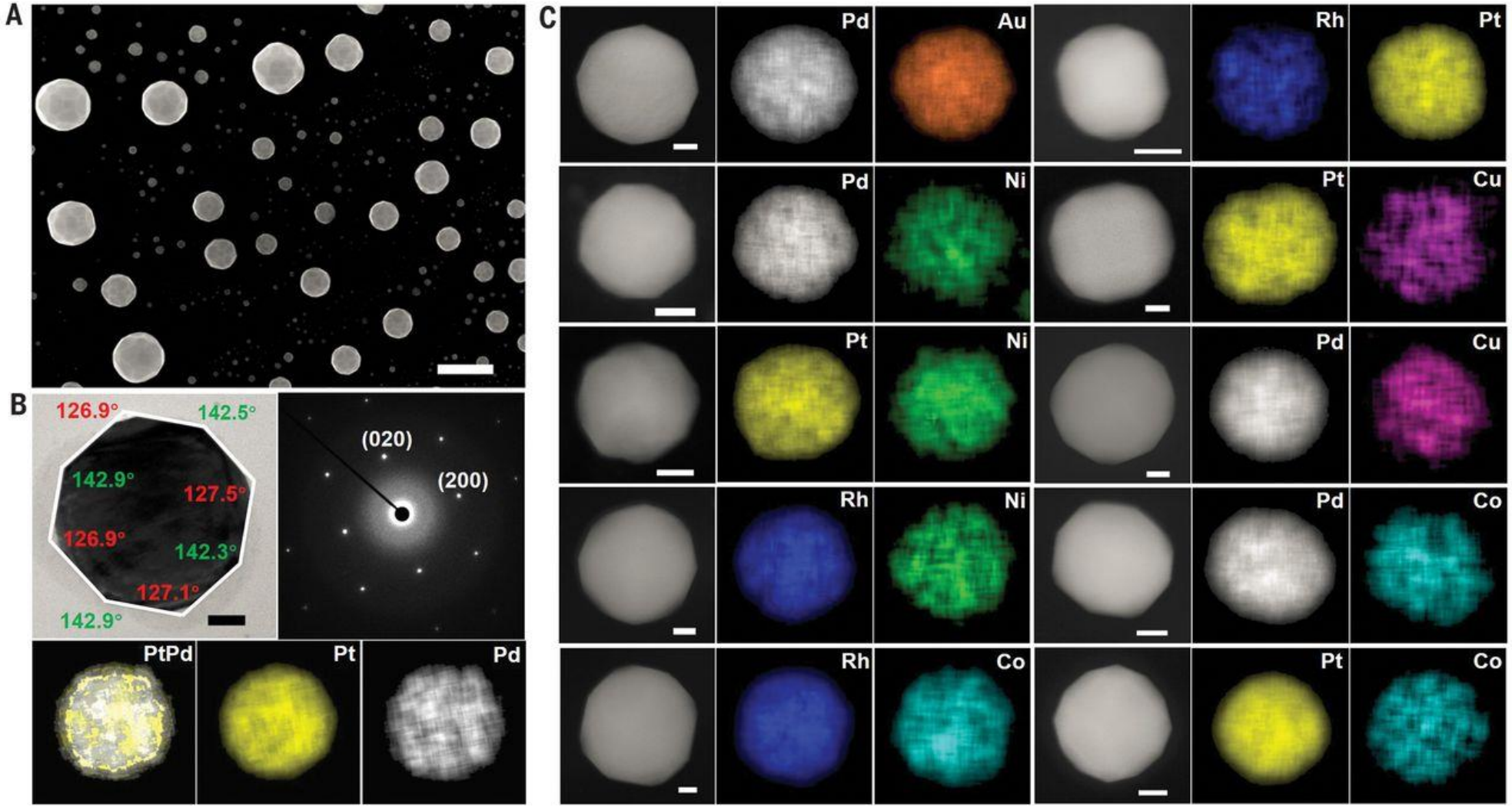
Synthesizing THH particles through alloying/dealloying with foreign metals (Sb, Bi, Pb, and Te). (**A**) Scheme for synthesizing THH particles with a CVD setup. (**B**) EDS spectra of the synthesized particles after reacting at 900°C as a function of time. The Cu signals are from the TEM sample holder. (**C** to **E**) STEM images and EDS elemental maps of the synthesized particles in the same area after reacting at 900°C for 0 min (26.3% Pt, 73.7% Sb) (C), 20 min (37.9% Pt, 62.1% Sb) (D), and 40 min (84.9% Pt, 15.1% Sb) (E). In (E), STEM images and corresponding EDS elemental maps (right) for the particles circled in red provide a clear view of particle morphology and elemental distribution. Scale bars in (i) and (ii), 50 nm; others, 300 nm.



THH Pt particles synthesized through Sb modification. (**A** to **E**) Representative SEM images of THH Pt particles recorded along the [100], [110], and [111] crystal directions [(A) to (C)], and THH Pt particles dispersed on a silicon wafer [(D) and (E)]. (**F**) TEM image of a THH Pt particle recorded along the [001] direction. White lines are used to highlight the particle facets as a guide to the eye. (**G**) Corresponding diffraction pattern for the particle in (F). (**H**) An ideal model of a THH particle surrounded by {210} facets projected along the [001] direction. A careful measurement of angles between surface planes of the nanoparticle in (F) indicates that the Miller indices of exposed high-index facets are {210}. (**I**) A HRTEM image recorded from the boxed area in (F). Red lines are drawn to highlight the surface (210) plane as a guide to the eye. (**J**) An atomic model of the (210) plane. (**K** to **M**) SEM images of Pt particles synthesized on a silicon wafer by thermally decomposing H_2PtCl_6 at 700°C for 30 min without using Sb powder (K), heating the sample shown in (K) at 900°C for 30 min using 1 mg Sb powder (L), and heating the sample shown in (L) at 900°C for 30 min without using Sb powder (M). Scale bars, 20 nm (F), 300 nm [(K) to (M)].



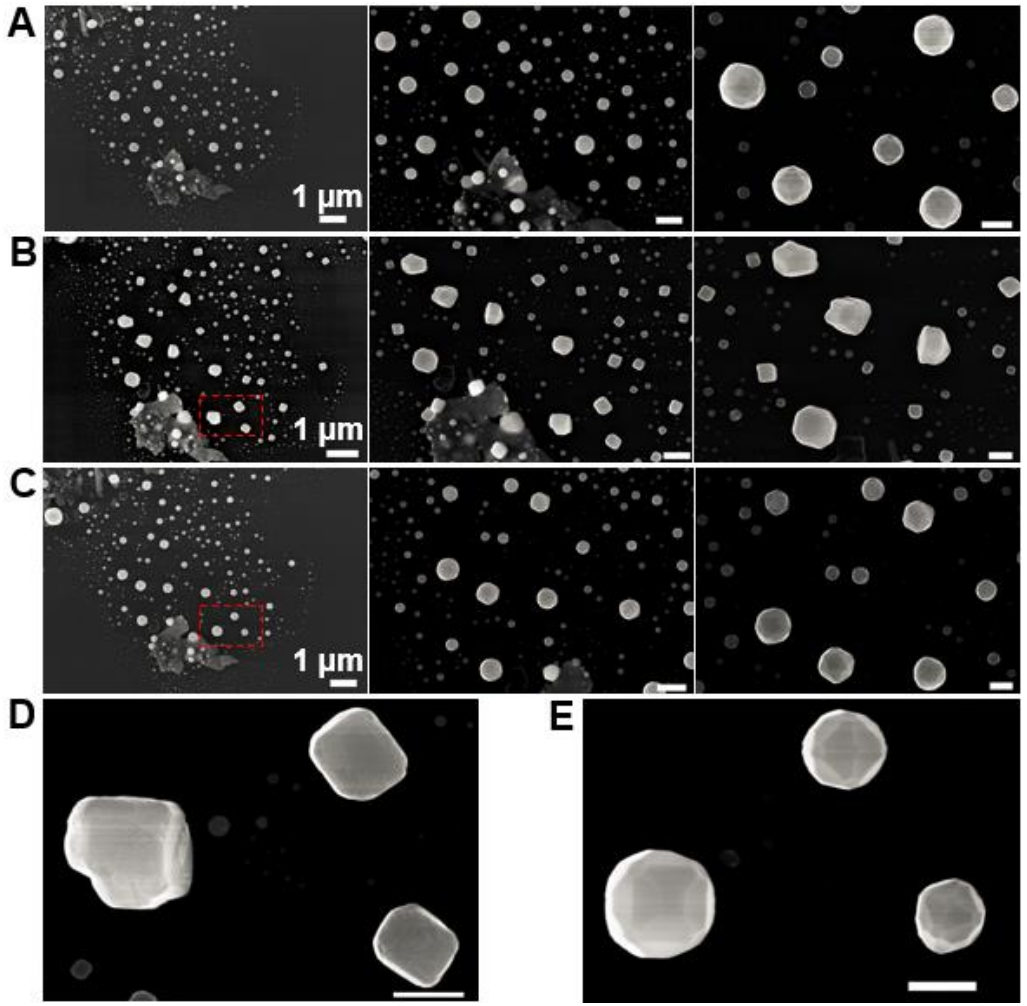
THH Pt, Pd, Rh, Ni, and Co particles synthesized through foreign metal (Sb, Bi, Pb, and Te) modification. (**A**) SEM images of Pt, Pd, and Rh particles synthesized through Sb, Bi, Pb, and Te modification. (**B** to **D**) STEM images, EDS elemental maps, TEM images, and corresponding diffraction patterns of the Pt-Bi (96.5% Pt, 3.5% Bi) particles (B), Pd-Bi (98.8% Pd, 1.2% Bi) particles (C), and Rh-Bi (99.8% Rh, 0.2% Bi) particles (D). (**E** and **F**) SEM images, TEM images, corresponding diffraction patterns, and EDS elemental maps of the Ni-Bi (99.4% Ni, 0.6% Bi) particles (E) and the Co-Bi (99.6% Co, 0.4% Bi) particles (F). Scale bars, 50 nm unless otherwise noted.



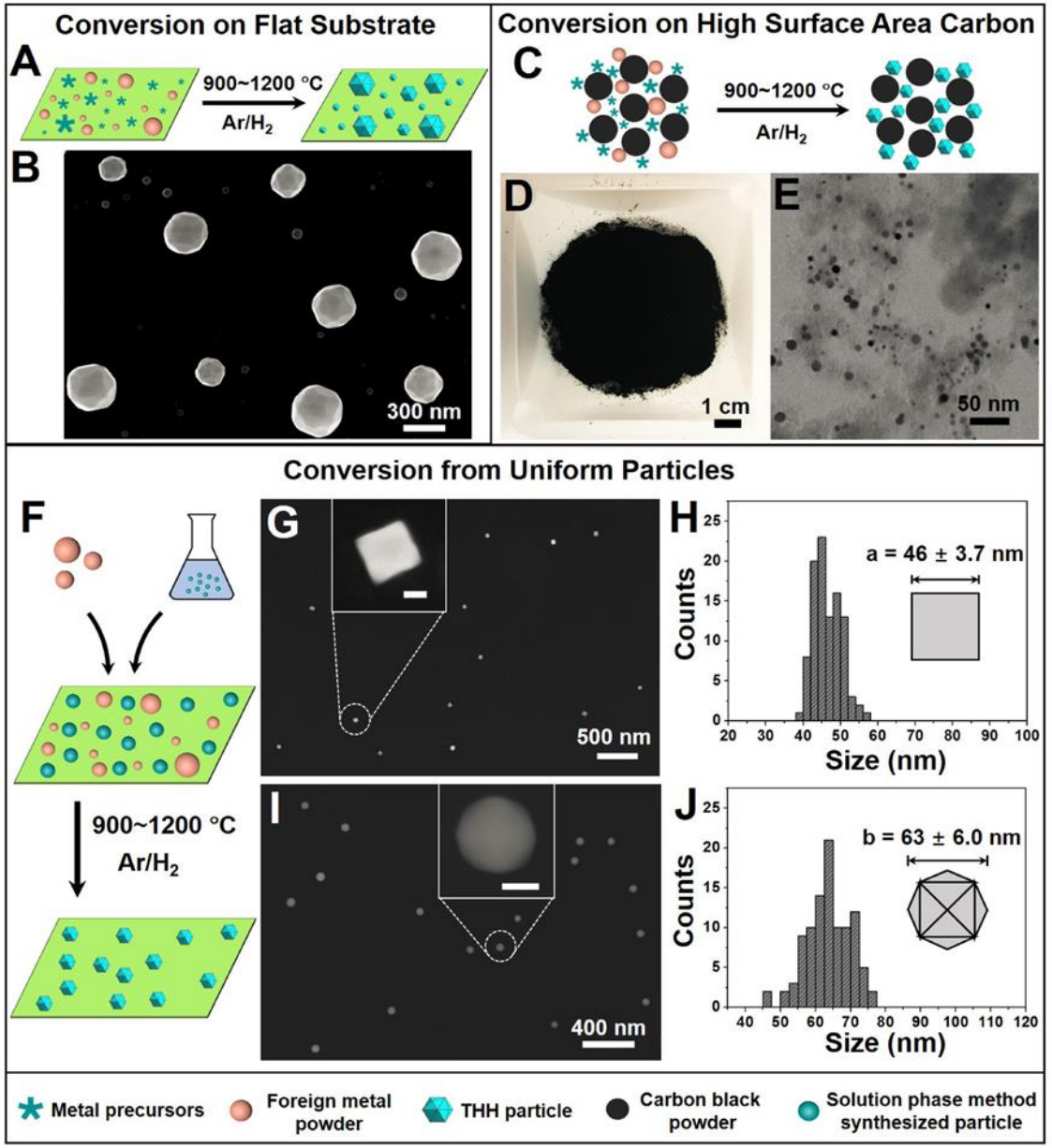
THH-shaped bimetallic particles synthesized through Bi modification. (**A**) SEM image of THH-shaped PtPd particles synthesized on a silicon wafer. (**B**) TEM image, corresponding diffraction pattern, and EDS elemental maps for a THH-shaped PtPd-Bi (18.1% Pt, 81.7% Pd, 0.2% Bi) particle. (**C**) STEM images (columns 1 and 4) and EDS elemental maps (columns 2, 3, 5, and 6) for THH-shaped PdAu-Bi (89.3% Pd, 10.6% Au, 0.1% Bi), RhPt-Bi (82.1% Rh, 17.6% Pt, 0.3% Bi), PdNi-Bi (57.3% Pd, 41.1% Ni, 1.6% Bi), PtCu-Bi (88.5% Pt, 11.4% Cu, 0.1% Bi), PtNi-Bi (55.1% Pt, 44.5% Ni, 0.4% Bi), PdCu-Bi (77.6% Pd, 22.1% Cu, 0.3% Bi), RhNi-Bi (74.8% Rh, 25.1% Ni, 0.1% Bi), PdCo-Bi (70.7% Pd, 29.1% Co, 0.2% Bi), RhCo-Bi (66.5% Rh, 33.4% Co, 0.1% Bi), and PtCo-Bi (78.4% Pt, 21.1% Co, 0.5% Bi) particles. Scale bars, 500 nm (A), 20 nm [(B) and (C)].

Conclusion

THANK YOU ☺



SEM images of Pt particles in the same area on a silicon wafer. (A) As-synthesized truncated THH Pt particles on a silicon wafer, (B) Pt particles synthesized after annealing the sample in (A) at 900 °C for 30 min with 1 mg Sb powder, and (C) truncated THH Pt particles synthesized after annealing the sample in (B) at 900 °C for 30 min without Sb powder. Each column is a magnified view of the former column. (D) and (E) are magnified view of the boxed areas in (B) and (C) respectively. Scale bars: 500 nm (second column) and 250 nm (third column) in (A to C), 250 nm in (D and E).


Conversion on Flat Substrate
A
900~1200 °C
Ar/H2
B
300 nm
Conversion on High Surface Area Carbon
C
900~1200 °C
Ar/H2
D
1 cm
E
50 nm
Conversion from Uniform Particles
F
900~1200 °C
Ar/H2
G
500 nm
H
a = 46 ± 3.7 nm
Counts
Size (nm)
I
400 nm
J
b = 63 ± 6.0 nm
Counts
Size (nm)
Metal precursors
Foreign metal powder
THH particle
Carbon black powder
Solution phase method synthesized particle