Facile synthesis of complex shaped Pt-Cu alloy architectures

Experimental details

**Chemicals:** Chloroplatinic acid hexahydrate (H$_2$PtCl$_6$·6H$_2$O) was analytical reagent (A.R.) grade and purchased from Beijing Research Institute for Nonferrous Metals. Copper chloride (CuCl$_2$), poly(vinylpyrrolidone) (PVP, K30), aspartic acid, glutamic acid, ethanolamine (ETA), NaI, isopropanolamine, ethylene diamine, diethylamine, ethylene glycol and ethanol were A.R. and purchased from Sinopharm Chemical Reagent Co. Ltd. All reagents were used as received without further purification.

**Synthesis of hexapod backbone with thin stretchers (thinHBS):** In a typical synthesis, PVP (400 mg), aspartic acid (133 mg), NaI (35 mg), 1 mL of 20 mM CuCl$_2$ aqueous solution, 1 mL of 20 mM H$_2$PtCl$_6$ aqueous solution and 1 mL ETA were added into 3 mL deionized water, and magnetically stirred at room temperature. The homogeneous solution was then heated in a Teflon-lined stainless steel autoclave at 160 °C for 8 h and allowed to cool naturally to room temperature. The resulting products were separated by centrifugation.

**Synthesis of hexapod backbone with thick stretchers (thickHBS):** Elongating the reaction time of thinHBS from 8 h to 14 h would lead to the formation of thickHBS. Other conditions were exactly the same as thinHBS.

**Synthesis of caved octahedron like hexapod (COLD):** In a typical synthesis, PVP (400 mg), aspartic acid (133 mg), NaI (75 mg), 1 mL of 20 mM CuCl$_2$ aqueous solution, 1 mL of 20 mM H$_2$PtCl$_6$ aqueous solution and 0.35 mL ETA were added into 3.65 mL deionized water, and magnetically stirred at room temperature. The homogeneous solution was then heated in a Teflon-lined stainless steel autoclave at 200 °C for 3 h and allowed to cool naturally to room temperature. The resulting products were separated by centrifugation.

**Characterization:** The X-ray diffraction (XRD) patterns were performed on a Bruker D8 ADVANCE X-ray powder diffractometer operated at 40 kV voltage and 40 mA current with Cu Kα radiation (λ = 1.5406 Å). The morphology and size of the products were determined by a Hitachi H-7700 transmission electron microscope (TEM) at 100 kV, a FEI Tecnai G2 F20 S-Twin high-resolution transmission electron microscope (HRTEM) equipped with energy dispersive X-ray spectroscopy (EDS) at 200 kV, and a JEOL 2100F HRTEM equipped with energy dispersive X-ray spectroscopy (EDS) at 200 kV. TEM samples were prepared by depositing an ethanol dispersion of the final products onto carbon-coated Cu grids followed by the solvent evaporation. EDX and high-angle annular dark-field scanning TEM (HAADF-STEM) were determined by a FEI Tecnai G2 F20 S-Twin HRTEM operating at 200 kV and JEOL 2100F HRTEM operating at 200kV. EDX samples were prepared by using Mo grids. Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to determine the composition of the Pt-Cu nanostructures.
Fig. S1 XRD results of thinHBS (green line) and COLD (red line). The black and blue vertical lines indicate the peak positions of Pt (JCPDS: 65-2868) and Cu (JCPDS: 04-0836) respectively. The peaks shift a little comparing with the pure metals, indicating the formation of alloys. According to Vegard’s law, the lattice distance of alloy is smaller than pure Pt and larger than pure Cu, leading to the peak shift to higher angle of Pt and lower angle of Cu. The signals of thinHBS were very weak, this may be due the fact that thinHBS is very thin and poorly crystallized. The signal of COLD are positioned between pure Pt and Cu, indicating the formation of alloy. Considering the fact that COLD and HBS were prepared in very similar conditions, thus their crystal structures might be very similar. CuI particles will be formed at the beginning of the reactions and then convert to the final morphology as time elongated. The unmatched peak marked by the star can be assign to the (220) diffraction of CuI (JCPDS: 06-0623) due to contamination.
Fig. S2 The High angle annular dark field-scanning TEM (HAADF-STEM) image of COLD (a,b) and its element mapping results, (c) is the signals of Cu and (d) is Pt, (e) is the overlapping results, indicating a evenly distribution.
Fig. S3 Time profile experiments in the synthesis of HBS.
Fig. S4 Time profile experiments in the synthesis of COLD.
Fig. S5 Changing the ratio of Pt to Cu in the synthesis of COLD, the amount of water was changed respectively to make sure the total amount of liquid is 6 mL.
Fig. S6 When the amount of NaI is reduced to 35 mg in the synthesis of COLD. Changing the ratio of Pt to Cu also showed similar trends with that in the synthesis of COLD.
Fig. S7 Changing the total amount of metal precursors in the synthesis of COLD.
Fig. S8 The influence of NaI in the synthesis of thickHBS. (a) NaI was excluded; (b) NaI was replaced by NaBr, and (c) was NaCl. Though the TEM images of relevant products showed dark aggregations, some hollow structures could also be recognized in the red circles indicate. (d, e, f) are the images using different amount of NaI, (d, e) were 15 mg, and (f) was 150 mg. The results of 75 mg looked the same as 150 mg, thus image is not posted here. The novel structures in (d,e) are structures constituted by octahedron shells and all equatorial planes.
Fig. S9 Replacing the CuCl$_2$ with CuI (a) and CuAc$_2$ (b, c). Icosahedron frameworks can be seen inside (b, c).
Fig. S10 Changing the amount of aspartic acid in the synthesis of thickHBS. (a) 0 mg; (b) 10 mg; (c) 50 mg; (d) 300 mg. Only a proper amount of aspartic acid (133 mg) could lead to good results.
Fig. S11 Changing the amount of aspartic acid in the synthesis of COLD. (a) 10 mg; (b) 50 mg; (c) 200 mg; (d) 300 mg. The amount of aspartic acid in the synthesis would dramatically change the morphologies from solid to hollow particles without changing the shape a lot, adding more aspartic acid would further stabilize the [111] domains, leading to HBS structures because of the difficulties of growth on them.
**Fig. S12** The aspartic acid was replaced by threonine (a, b) or glutamic acid (c, d) in the synthesis of COLD. Some COLD with hollow center can be seen in (b). The pentagon like structures are hollow decahedron shells with all equatorial planes. The structure was further characterized by HRTEM (Fig. S18, 19).
Fig. S13 Changing the amount of ETA in the synthesis of COLD. (a), 0 mL; (b), 0.15 mL; (c), 0.25 mL; (d), 0.45 mL; (e), 0.65 mL; (f), 4 mL.
Fig. S14 Changing the amount of ETA in the synthesis of thickHBS. (a), 0.15 mL; (b), 0.75 mL.
Fig. S15 The ETA was replaced by diethylamine (a), isopropanolamine (b), ethylene glycol (c), ethylene diamine (d), butylamine (e) or ethanol (f) in the synthesis of thickHBS.
Fig. S16 Changing the amount of PVP in the case of thickHBS.
Fig. S17 Using 35 mg NaI and 0.5 mL ETA in the synthesis of COLD would lead to more novel structures (a). In the image (a), the triangle with arrows are commonly seen, as well as some other partly etched structures. (b-d) are the HRTEM images of the triangle with arrows, (b) is the basal plane, (c) is the linker and (d) is the arrow. Inset of them are the corresponding fast Fourier transform (FFT) patterns of the areas inside the red squares, the numbers in FFT patterns indicate the reciprocal of distance in the relevant directions (hereafter).
Fig. S18 HRTEM images of the hollow decahedron shells with all equatorial planes (a-c). (b) is the pentagonal plane and (c) is the core. (d) is the FFT patterns of the area in the red square of (c).
Fig. S19 Tilted TEM images of the hollow decahedron shells with all equatorial planes by rotating the sample holder.
Fig. S20 Other novel structures (a, d, g), their enlarged images (b, e, h) and corresponding FFT patterns (c, f, i) respectively.
Fig. S21 HRTEM images of petals (a) and core (b) of the structures shown in (c). (e, f) show the enlarged images of (d).
Fig. S22 HRTEM images of framed triangle structure (a). (b) the lateral frame. (c, d) the basal plane.
Using RhCl$_3$ instead of H$_2$PtCl$_6$ as precursor could also result in frame structures in the synthesis. The reaction conditions were the same as that of thickHBS, then we varied the amount of NaI. (a) 75 mg NaI, (b) 35 mg NaI.