Ordered bcc CuPd nanoalloy synthesised from the thermal decomposition of Pd nanoparticles covered with a metal-organic framework under hydrogen gas

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1. Synthesis of Pd@HKUST-1

Pd nanoparticles with a flat surface were used to form the composite with HKUST-1. Pd nanoparticles with an average edge length of 10 nm were synthesized in an aqueous solution by reducing Na_2PdCl_4 with L-ascorbic acid in the presence of bromide ions as the capping agents to promote the formation of {100} facets, as reported previously[1]. The hybridization of Pd nanoparticles and HKUST-1 was performed by stirring at room temperature for 48 h in the presence of $Cu(NO_3)_2 \cdot 3H_2O$ and trimesic acid in enthanol solution.

2. Measurement condition

TEM measurement. TEM image of samples were recorded using a Hitachi HT7700 TEM instrument operated at 100 kV acceleration voltage

Powder XRD. Powder XRD at various temperatures at at BL02B2 beam line at SPring-8 and an X-ray wavelength of 1.001 (1) Å.

HAADF–STEM, and EDX analyses. The samples were dispersed in ethanol, dropped onto a carbon-coated nickel grid, and dried by exposure to ambient conditions for 24 h. HAADF–STEM, and EDX mapsmeasurements were performed using a JEM-ARM200F operated at 200 kV.

3. TEM image of Pd@HKUST-1 as synhesized

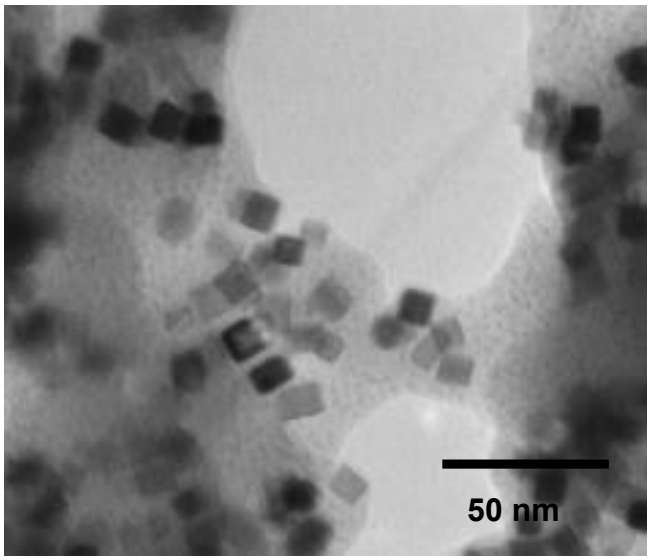

Figure S1. TEM image of Pd@HKUST-1 as synthesized.

4. XRD of Pd@HKUST-1

The powder X-ray diffraction (XRD) pattern of Pd@HKUST-1 was performed at 303 K at the BL02B2 beam line at the Super Photon Ring (SPring-8) and an X-ray wavelength of 1.000 Å. The XRD pattern of Pd@HKUST-1 consisted of two kinds of Pd and HKUST-1 patterns as shown in Figure S2.

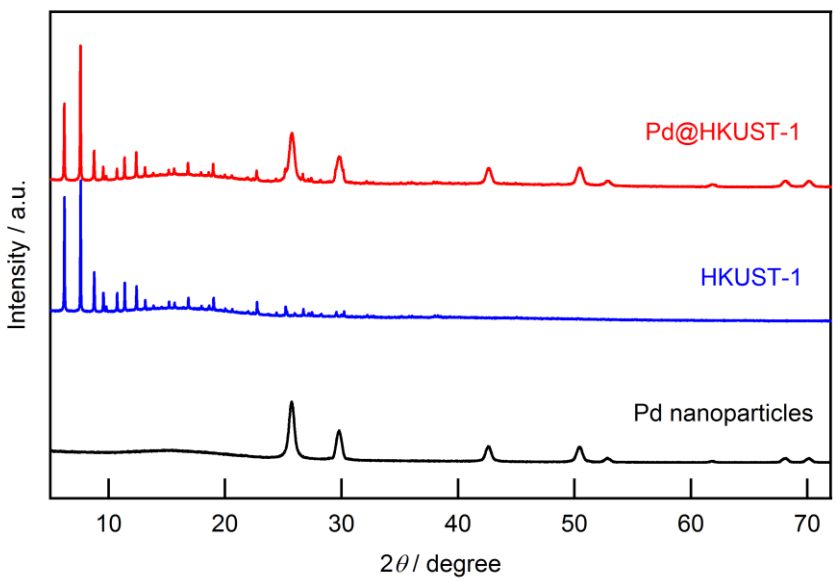

Figure S2. The XRD patterns of Pd@HKUST-1, HKUST-1, and Pd nanocubes.

5. Rietveld refinement of decomposed Pd@HKUST-1 under H_2 gas

After heating, the sample was cooled to 303 K, Rietveld refinement results of XRD pattern of cooled sample, bcc CuPd alloy, Pm-3m, a = 2.967(1) Å, Rexp=6.30, Rwp=6.58. Atomic ratio, Pd : Cu = 4: 6.

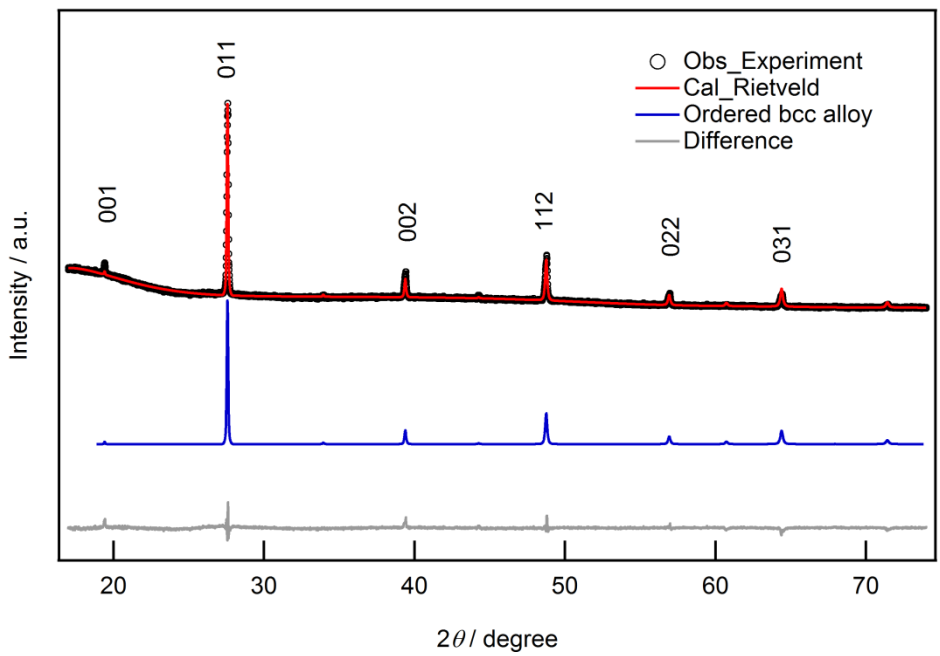

Figure S3. Rietveld refinement of the in situ XRD pattern of Pd@HKUST-1 at 303 K after heated at 773 K.

Rietveld refinement results of XRD patterns at 303 K, Pd, Fm-3m, a =4.036(1) Å, crystal size: 13.0 ± 0.1 nm, Rexp = 6.11, Rwp = 3.58.

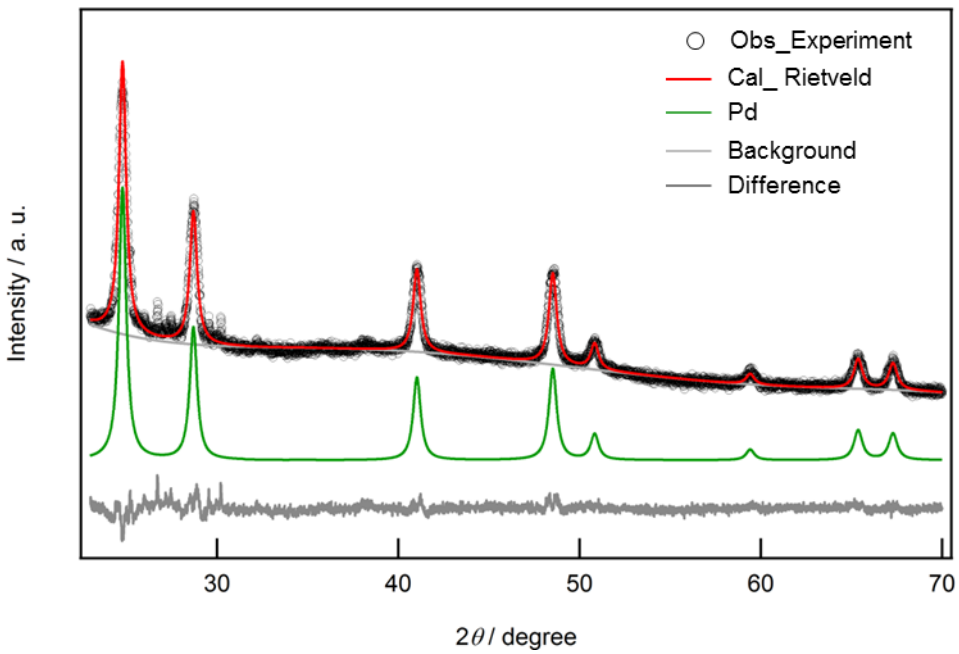

Figure S4. Rietveld refinement of the in situ XRD pattern of Pd@HKUST-1 at 303 K under H_2 gas.

Rietveld refinement results of XRD patterns at 373 K, Pd, Fm-3m, a =4.025(1) Å, crystal size: 13.2 ± 0.1 nm, Rexp = 6.15, Rwp = 3.26.

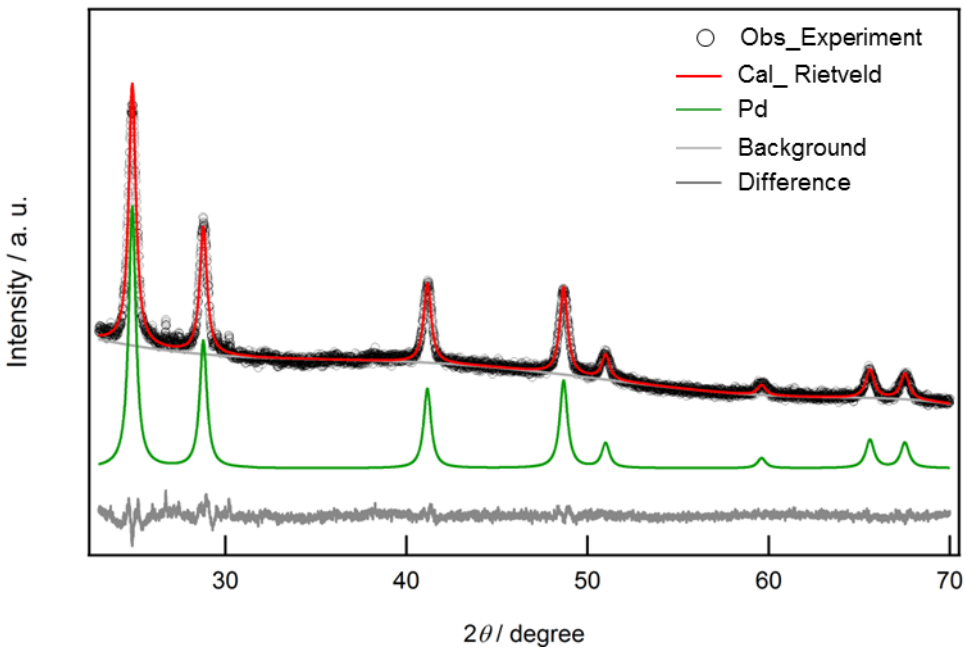

Figure S5. Rietveld refinement of the in situ XRD pattern of Pd@HKUST-1 at 373 K under H_2 gas.

Rietveld refinement results of XRD patterns at 423 K, Pd, Fm-3m, a =3.899(1) Å, crystal size: 12.9 ± 0.1 nm, Rexp = 6.21, Rwp = 3.27.

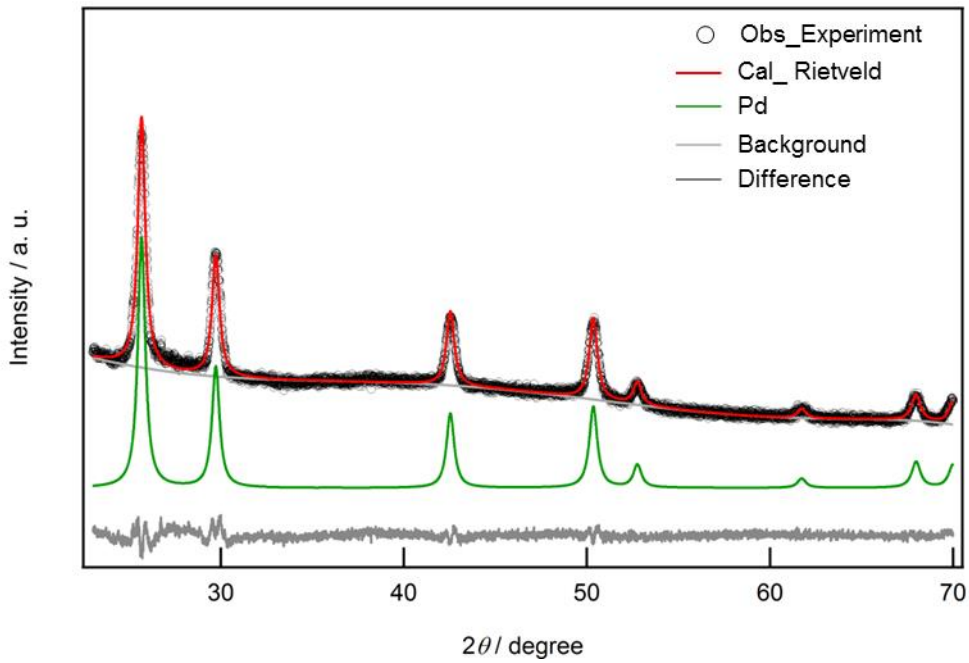

Figure S6. Rietveld refinement of the in situ XRD pattern of Pd@HKUST-1 at 423 K under H_2 gas.

Rietveld refinement results of XRD patterns at 473 K, Pd, Fm-3m, a =3.898(1) Å, 62.54%, crystal size: 12.1 ± 0.1 nm; Cu, Fm-3m, 3.632(1) Å, 37.46%, crystal size: 5.2 ± 0.1 nm, Rexp = 6.21, Rwp = 3.27.

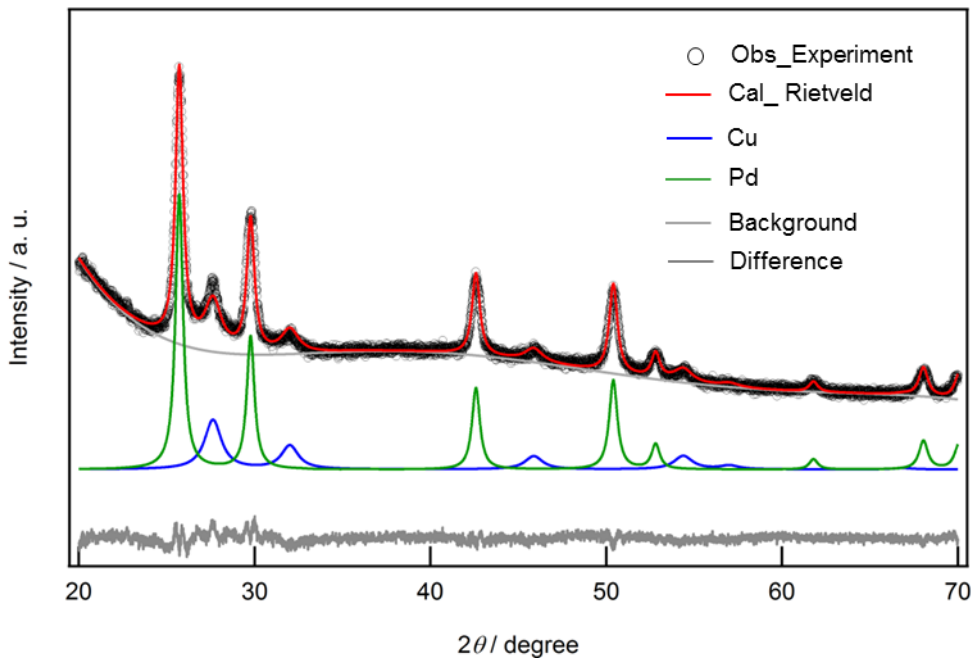

Figure S7. Rietveld refinement of the in situ XRD pattern of Pd@HKUST-1 at 473 K under H_2 gas.

Rietveld refinement results of XRD patterns at 523 K, Pd, Fm-3m, a =3.894(1) Å, 44.25%, 11.3±0.1nm; Cu, Fm-3m, a =3.641(1) Å, 19.29%, 14.7±0.6nm; CuPd, Fm-3m, a =3.742(2) Å, 36.47%, 4.0±0.2nm, Rexp=6.42, Rwp=4.04.

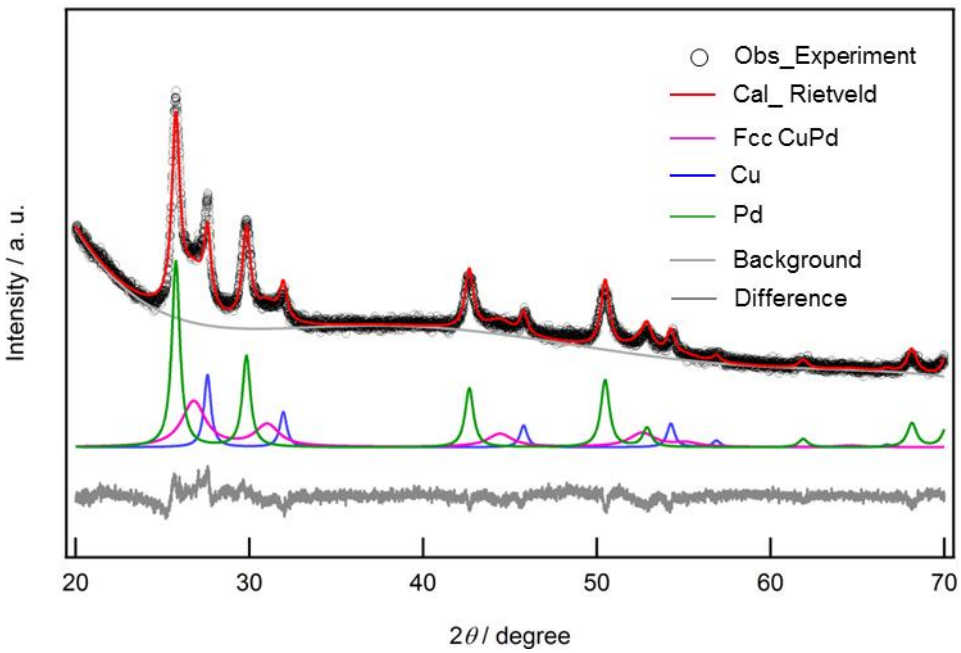

Figure S8. Rietveld refinement of the in situ XRD pattern of Pd@HKUST-1 at 523 K under H_2 gas.

Rietveld refinement results of XRD patterns at 573 K, Pd, Fm-3m, a =3.884(1) Å, 35.84%, crystal size: 10.1 ± 0.3 nm; fcc CuPd, Fm-3m, 3.734(1) Å, 48.74%, crystal size: 6.9 ± 0.2 nm; bcc CuPd, Pm-3m, 2.974(1) Å, 15.42%, crystal size: 33.1 ± 0.2 nm, Rexp = 6.21, Rwp = 3.27.

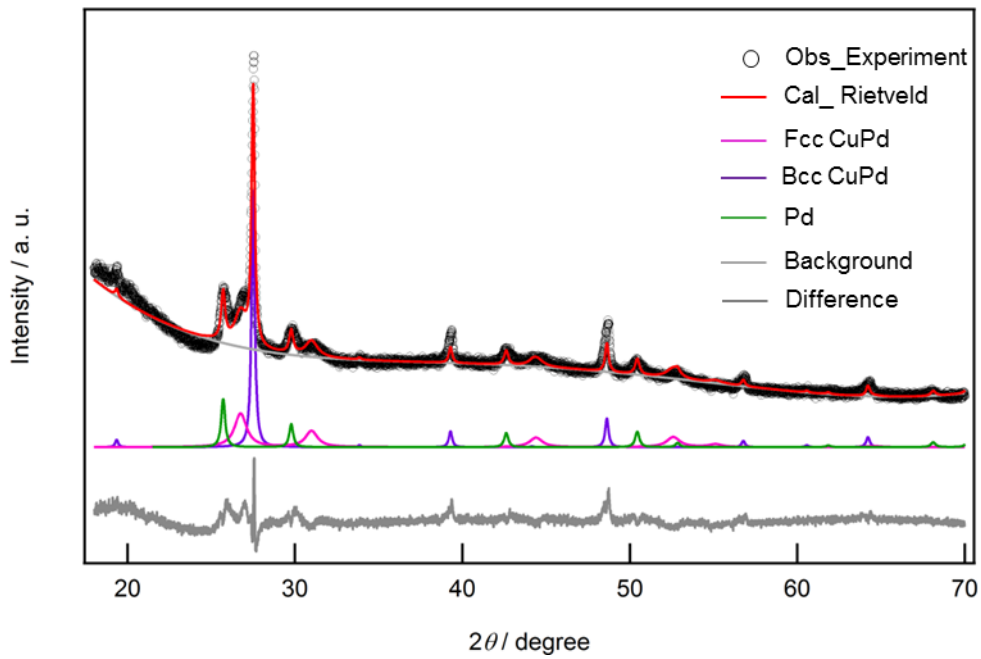

Figure S9. Rietveld refinement of the in situ XRD pattern of Pd@HKUST-1 at 573 K under H_2 gas.

Rietveld refinement results of XRD patterns at 623 K, Pd, Fm-3m, a =3.877(2) Å, 25.12%, crystal size: 9.9 ± 1.1 nm; fcc CuPd, Fm-3m, 3.759(1) Å, 33.41%, crystal size: 8.7 ± 1.0 nm; bcc CuPd, Pm-3m, a =2.975(1) Å, 41.47%, crystal size: 49.2 ± 0.7 nm, Rexp = 7.02, Rwp = 5.09.

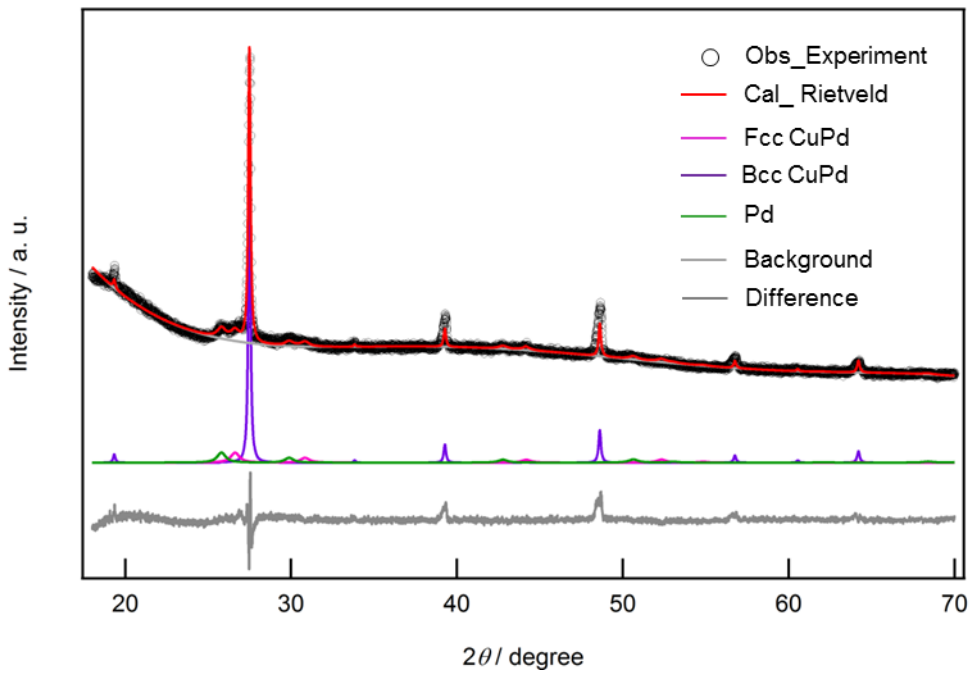

Figure S10. Rietveld refinement of the in situ XRD pattern of Pd@HKUST-1 at 623 K under H_2 gas.

Rietveld refinement results of XRD patterns at 673 K, bcc CuPd alloy, Pm-3m, a = 2.983(1) Å, 100%, Rexp=7.18, Rwp=5.55.

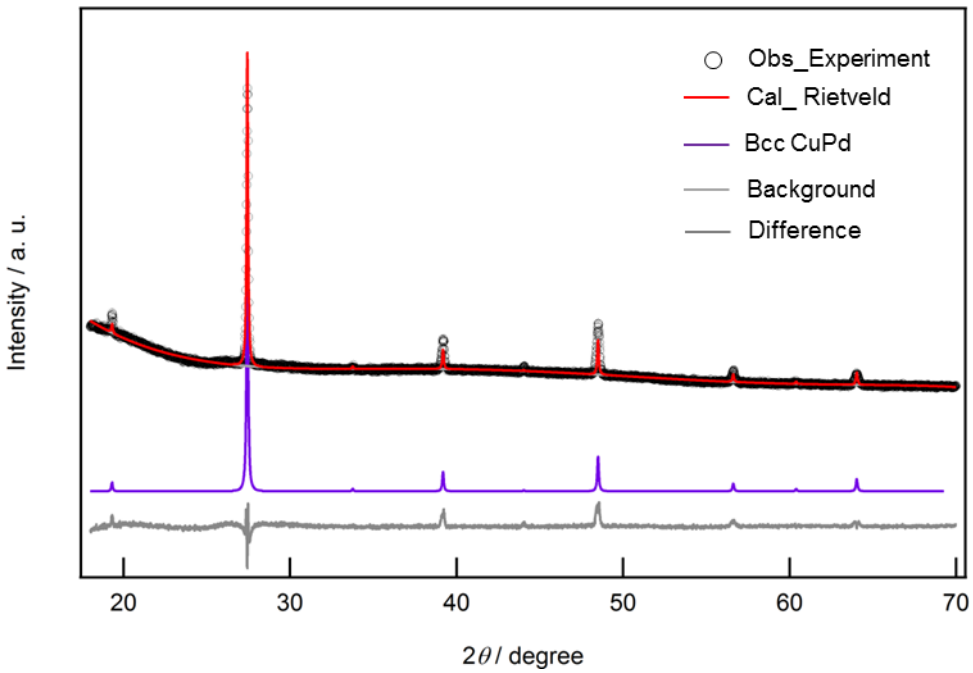

Figure S11. Rietveld refinement of the in situ XRD pattern of Pd@HKUST-1 at 673 K under H_2 gas.

Rietveld refinement results of XRD patterns at 723 K, bcc CuPd alloy, Pm-3m, a = 2.985(1) Å, 100%, Rexp=7.22, Rwp=5.44.

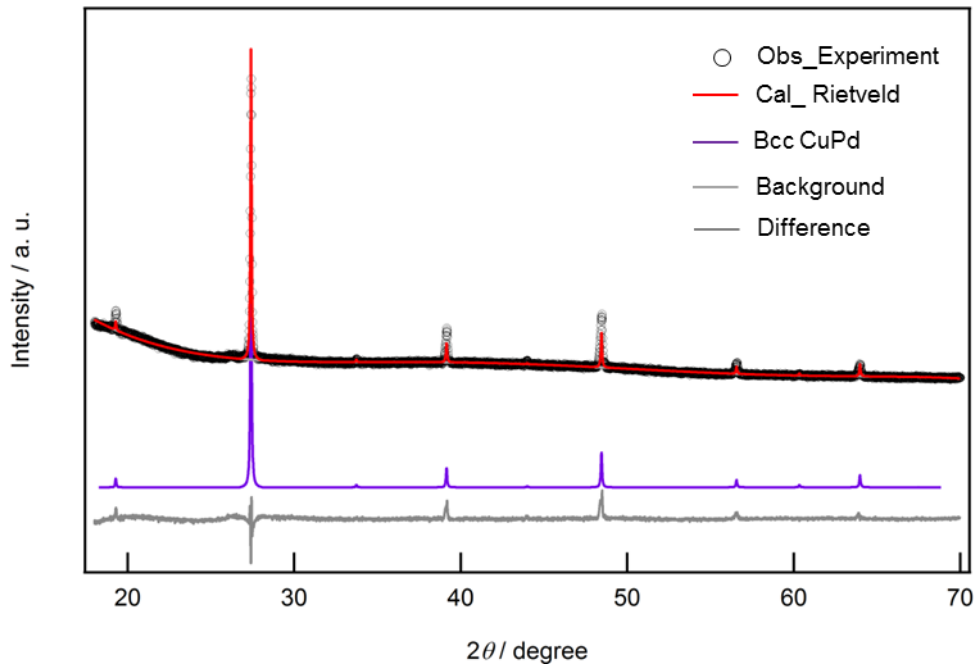

Figure S12. Rietveld refinement of the in situ XRD pattern of Pd@HKUST-1 at 723 K under H_2 gas.

Rietveld refinement results of XRD patterns at 773 K, bcc CuPd alloy, Pm-3m, a = 2.987(1) Å, 100%, Rexp=7.26, Rwp=5.25.

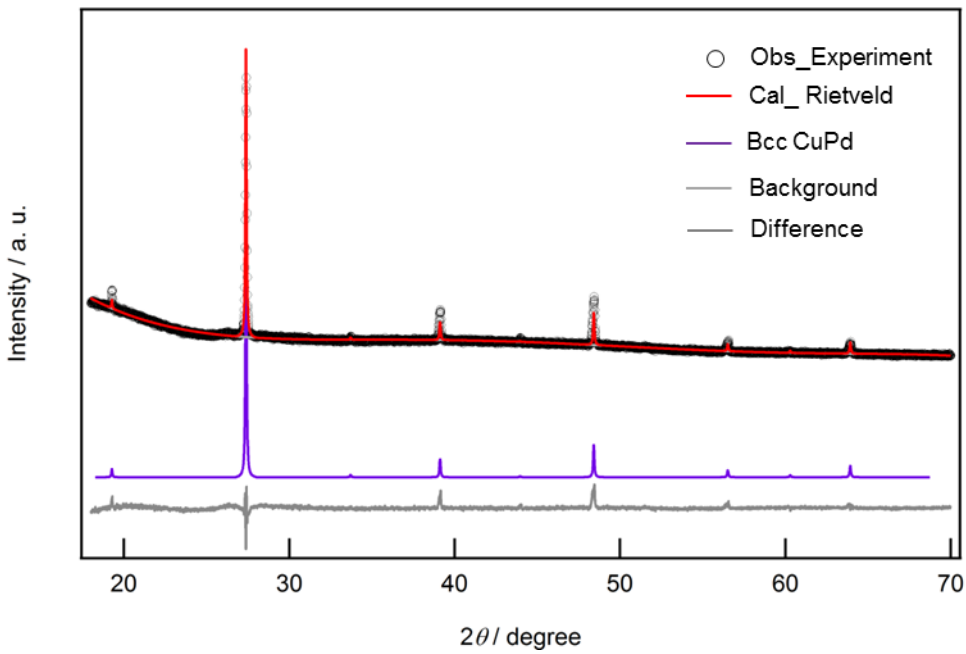

Figure S13. Rietveld refinement of the in situ XRD pattern of Pd@HKUST-1 at 773 K under H_2 gas.

6. Temperature dependency of *in situ* XRD patterns of Pd@HKUST-1 in vacuum

the specimen of Pd@HKUST-1 was placed in a capillary and then evacuated and heated 15 min at 423 K in vacuum to remove the water molecules. Subsequently, Pd@HKUST-1 was performed heating in vacuum from 303 K to773 K and annealing to 303 K. The structural change in Pd@HKUST-1 in vacuum was monitored via in situ powder XRD at various temperatures at at BL02B2 beam line at SPring-8 and an X-ray wavelength of 1.000 Å (Figure S14).

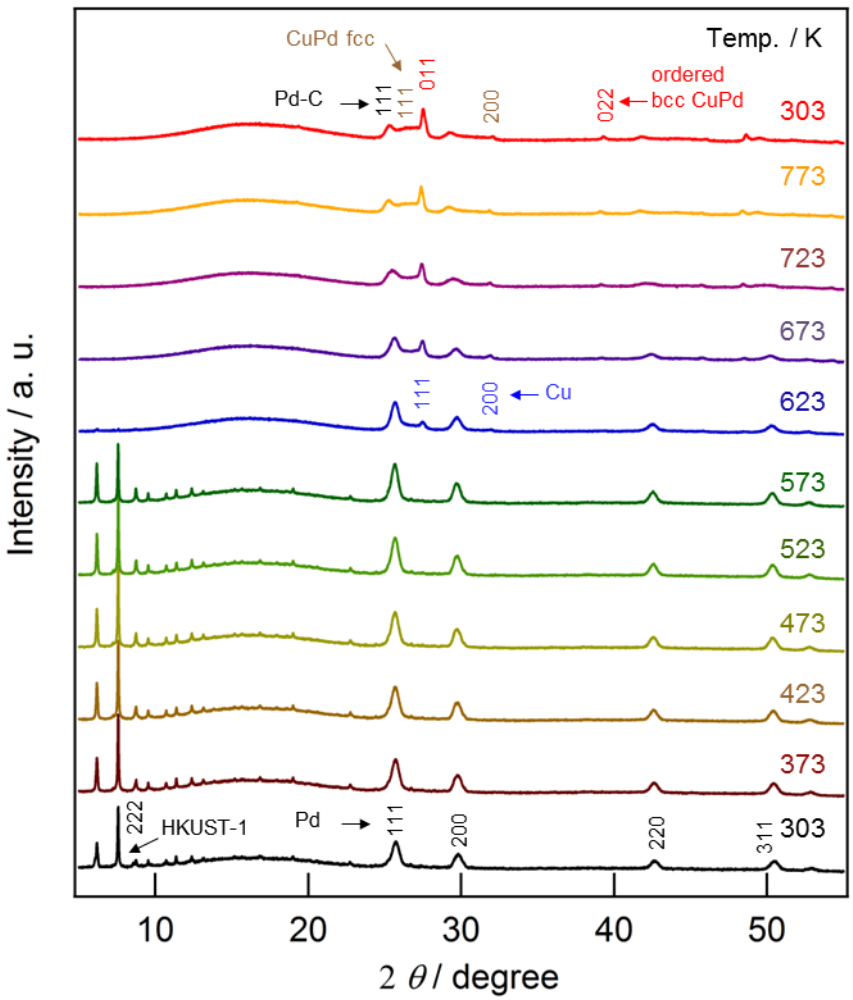

Figure S14. Temperature dependency of *in situ* XRD patterns of Pd@HKUST-1 in vacuum. The temperature is listed on the right side. The measurement order is from bottom to top.

7. Retveld refinement of in situ XRD patterns of Pd@HKUST-1 in vacuum

After heating and cooling to 303 K, XRD pattern was did Rietveld refinement. The results of fitting as follows. PdC, Fm-3m, a =3.956(2) Å, CuPd fcc, Fm-3m, a =3.770(4) Å, Cu, Fm-3m, a =3.635(2) Å, CuPd bcc, Pm-3m, a =2.972(1) Å, Rexp=4.91, Rwp=3.64.

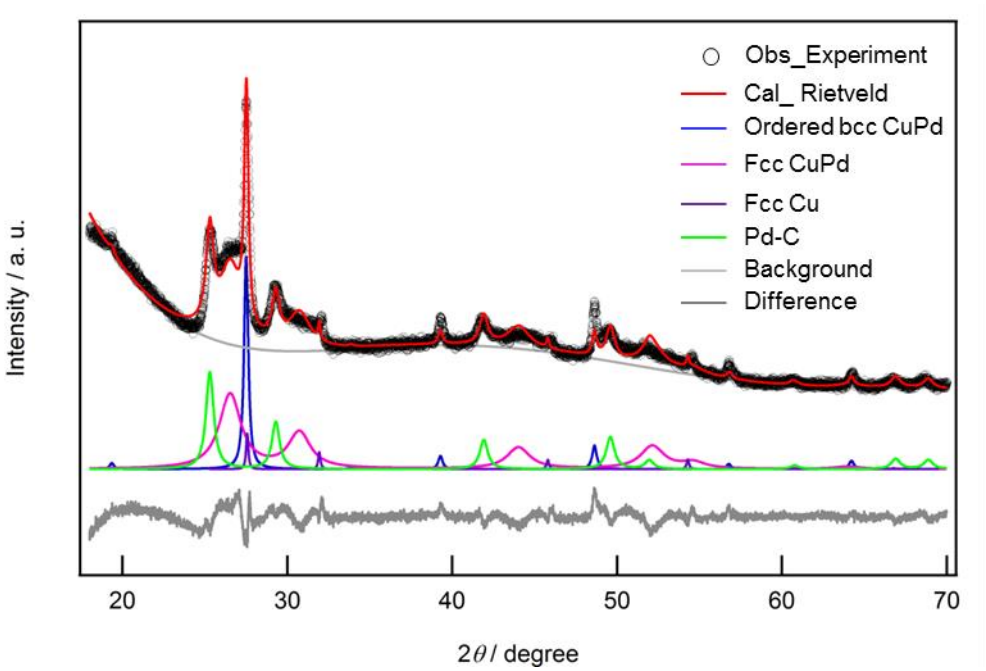

Figure S15. in situ XRD pattern of Pd@HKUST-1 in vacuum at 303 K after heating.

8. EDX mapping of Pd@HKUST-1 after heating in vacuum

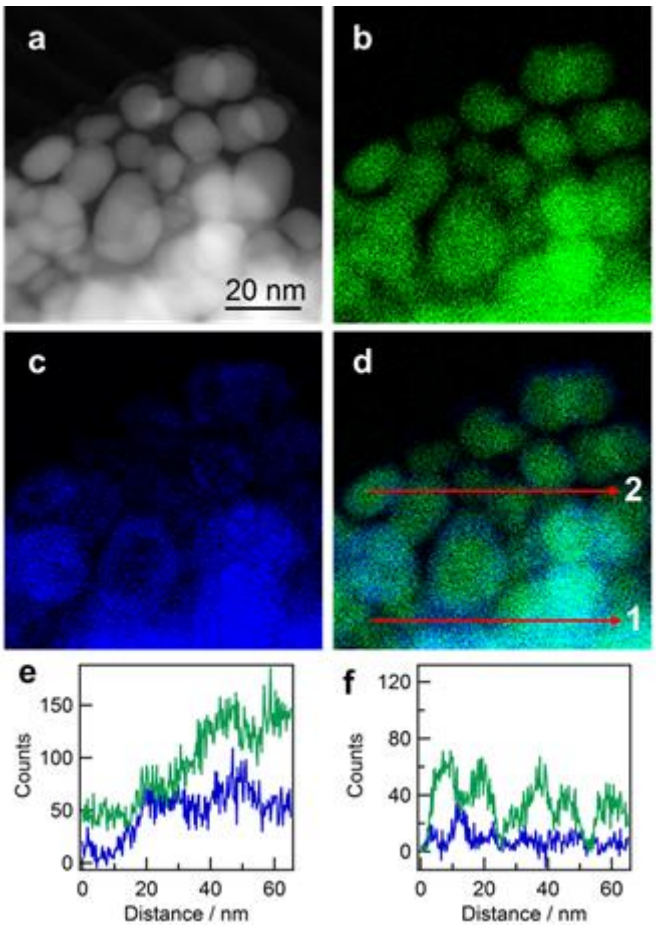

Figure S16. (a) HAADF-STEM image and (b-d) EDX mappings of (b) Pd element, (c) Cu element and (d) the overlay of Pd and Cu elements for sample after heating Pd@HKUST-1 in vacuum. (e) and (f) line analysis for red line in (d) 1 and 2, respectively.