Electronic Supplementary Information (ESI) for

Formation mechanism of bimetallic PtRu alloy nanoparticles in solvothermal synthesis†

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1. Experimental

For the preparation of bimetallic PtRu nanoparticles, ruthenium acetylacetonate ($Ru(acac)_3$) and platinum acetylacetonate ($Pt(acac)_2$) were used as precursors, and ethanol was used as both solvent and reducing agent. A relatively high concentration of precursor solution improves the quality of diffraction data. As a result, ethanol solutions of 0.25 M $Ru(acac)_3$ and 0.25 M $Pt(acac)_2$ were prepared. The above two solutions were mixed with the volume ratio of 1:1.

A custom-designed high-pressure flow cell with a sapphire capillary was used for the real-time probing of synchrotron radiation powder X-ray diffraction (SR-PXRD).[1] After injecting the precursor solution, the sapphire capillary is sealed, pressurized and subsequently heated to the targeted temperature using a HPLC pump and a hot air flow, respectively. The experiment was performed at a temperature of 200 °C and under a

pressure of 25 MPa. The *in situ* SR-PXRD data were measured at beam line I711, at MAX-lab, Sweden, using monochromatic X-rays with a wavelength of 1.0009 Å. The data was collected on a Mar 165 CCD detector. The measurements were performed with a time resolution of 5 s between each frame, of which 1 s was the detector readout.

2. Rietveld refinements

The raw data images were integrated using FIT2D,[2] which reduces the data to standard 1 D PXRD data. The time-resolved SR-PXRD data were Rietveld refined using the FullProf program[3]. In order to carry out precise size analysis, the data were corrected for instrumental broadening using a LaB6 standard (NIST SRM 660a). **Fig. S1** is a typical refinement of *in situ* SR-PXRD data with observed, calculated and difference patterns for PtRu nanoparticles at the reaction time of 10 min showing a good agreement with the observed pattern. **Table S1** displays selected refinement parameters for the in situ PXRD data at the reaction time of 10 s, 15 s, 2 min and 10 min, respectively.

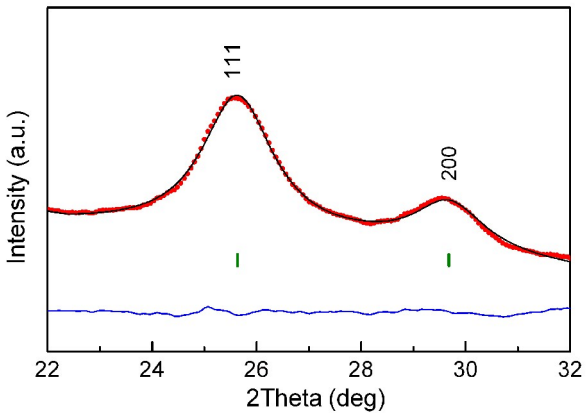

Fig. S1 Observed (red), calculated (black), and difference (blue) patterns of selected *in situ* SR-PXRD data at the reaction time of 10 min.

Table S1. Refined parameters of the SR-PXRD data at reaction time of 10 s, 15 s, 2 min and 10 min. The data in the range of $22° < 2\theta < 32°$ are included in the refinement.

Reaction time	10 s	15 s	2 min	10 min
Data points	595	595	595	595
Reflections	2	2	2	2
R_{WP} (%)	3.76	2.36	3.03	2.36
R_I (%)	0.639	1.02	1.99	1.75
R_F (%)	0.392	0.658	1.36	1.05
a (Å)	3.9304(2)	3.9312(2)	3.8978(2)	3.9084(2)
Particle size (nm)	4.1(1)	4.9(1)	3.2(1)	3.0(1)

3. Two step mechanism fit of the scale factor

It was proposed a two-step mechanism for transition-metal nanocluster formation, including nucleation (A → B, rate constant k_1) and autocatalytic growth (A + B → 2B, rate constant k_2), in which A represents the precursor and B represents the growing nanocluster.[4,5] The rate constants k_1 is inversely proportional to the length of the induction period during which the nucleation occurs and k_2 is proportional to the normalized slope of the linear part of the curve after the induction period.

$$[A]_t = \frac{\frac{k_1}{k_2} + [A]_0}{1 + \frac{k_1}{k_2[A]_0} * \exp(k_1 + k_2[A]_0)t} \quad \text{(S1)}$$

In the present study, however, the scale factor (α) of PtRu nanoparticles is obtained. Here, by assuming $[A]_t = 1 - \alpha$ and $[A]_0 = 1$, as shown in **Fig. S2**, a reasonable fit of kinetic curve with $k_1 = 2.2(5)$ min^{-1} and $k_2 = 0.7(2)$ min^{-1} is obtained for the two-step mechanism.

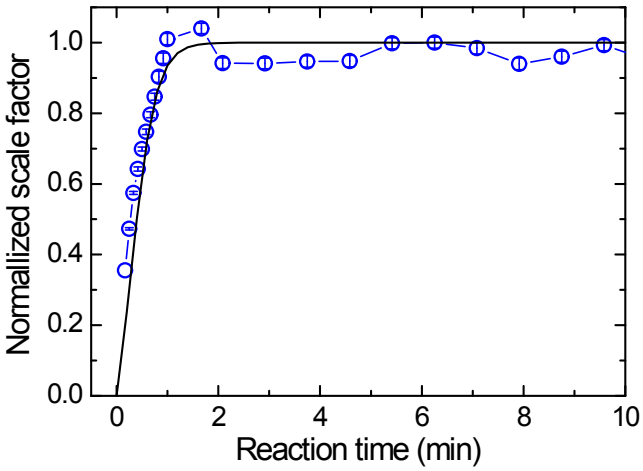

Fig. S2 Time evolution of normalized scale factor and the fit using two-step mechanism to the formation curve.

References

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