Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic Supplementary Information

Synthesis of size-controlled PtCu@Ru nanorattles via Pt seed-assisted formation of size-controlled removable Cu template

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Material Characterizations

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were performed on a TECNAI G2 20 S-Twin operated at 200 kV and TECNAI G2 F30 operated at 300 kV. All scanning transmission electron microscopy (STEM) images and compositional maps were acquired with the use of HAADF-STEM and energy dispersive X-ray spectrometer attached in the TECNAI G2 F30 ST. In order to visualize elemental map from our nanoparticle, the electron probe was set < 0.3nm and the camera length of STEM was selected at 120mm. The elemental maps were digitized by 25x25 pixels for 25 nm by 25 nm area and the collection time of each pixel was 0.9 second. X-ray diffraction (XRD) patterns were collected with a Rigaku Ultima III diffractometer system using a graphite-monochromatized Cu-Kα radiation at 40 kV and 40 mA. X-ray photoelectron spectroscopy were performed on a UIVAC X-Tool. The detector angle was set at 45° and incidence angle of X-ray was set at 90°.

Experimental Section

Synthesis of 6.3 nm Pt NPs

The Pt nanoparticles to be used as seeds for the synthesis of PtCu@Ru nanorattles were synthesized in the following step. Typically, $Pt(acac)_2$ (0.02 mmol, Aldrich, 97%) in oleylamine (15 mmol, Aldrich, 70%) was prepared in a 100 mL Schlenk tube. After placing the reaction mixture under vacuum at 25°C for 10 min, the reaction mixture was charged with 1 atm CO gas. Then the Schlenk tube was directly placed in oil bath, which was preheated to 200°C. After heating at the same temperature for 5 min, the reaction mixture was cooled down to room temperature. The reaction mixture, after being cooled down to room temperature and being added 20 mL toluene and 10 mL methanol, was centrifuged at 3500 rpm for 10 min. The resulting precipitates, with added methanol/toluene (v/v = 1/2 mL), were further purified by centrifugation at 3500 rpm for 5 min.

Synthesis of PtCu@Ru nanorattles:

For the synthesis of PtCu@Ru nanorattles of 15.1 nm in edge length, Pt nanoparticle solution was made by taking 2 mg of Pt NPs into 5 mL oleylamine (15 mmol, Aldrich, 70%). 1 mL of Pt nanoparticle solution was added to a mixture of $Cu(OAc)_2$ (0.02 mmol, Aldrich, 98%), $Ru(acac)_3$ (0.02 mmol, STREM Chemicals, 99%) and CTAB (0.02 mmol, Aldrich, 99%) with 4 mL oleylamine (12 mmol, Aldrich, 70%) in a 100 mL Schlenk tube. For 13.4 nm PtCu@Ru nanorattles, all conditions were same with above condition except 0.8 mg Pt NPs (2 mL of Pt nanoparticle solution) were used. For 16.7 nm and 19.8 nm, the size of PtCu@Ru nanorattles was tuned by adding different amount of Cu precursor and CTAB (cetyltrimethylammonium bromide) while the amount of Pt and Ru is fixed in each Schlenk tube. The synthetic conditions are summarized in the table below.

size	synthesized Pt nanoparticles	$Cu(OAc)_2$	$Ru(acac)_3$	CTAB	oleylamine
13.1 nm	0.8 mg	0.02 mmol	0.02 mmol	0.02 mmol	15 mmol
15.1 nm	0.4 mg	0.02 mmol	0.02 mmol	0.02 mmol	15 mmol
16.7 nm	0.4 mg	0.03 mmol	0.02 mmol	0.03 mmol	15 mmol
19.8 nm	0.4 mg	0.04 mmol	0.02 mmol	0.04 mmol	15 mmol

After placing the reaction mixture under vacuum at 25°C for 10 min, the reaction mixture was charged with 1 atm CO gas. Then the schlenk tube was directly placed in a hot oil bath, which was preheated to 280°C. After heating at the same temperature for 30 min, the reaction mixture was cooled down to room temperature. The reaction mixture, after being cooled down to room temperature and being added 20 mL toluene and 10 mL methanol, was centrifuged at 3500 rpm for 10 min. The resulting precipitates, with added methanol/toluene (v/v = 1/2 mL), were further purified by centrifugation at 3500 rpm for 5 min.

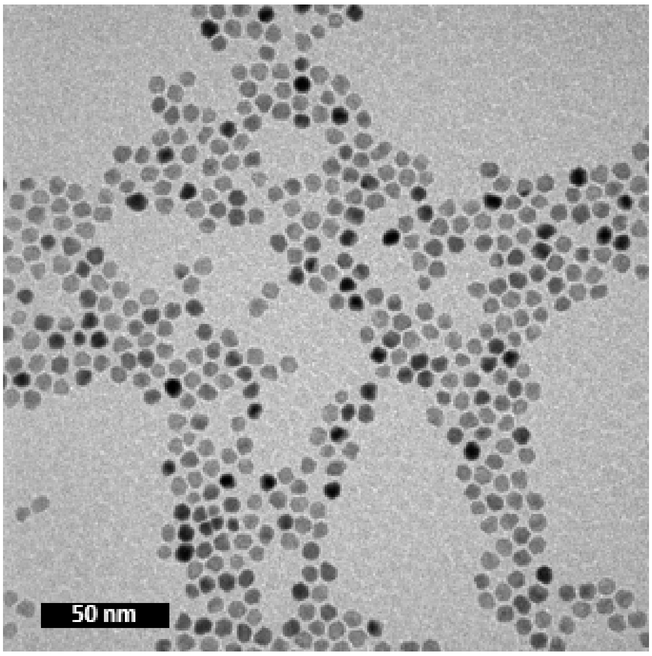


Fig. S1 Synthesized Pt nanoparticles. The average size is 6.3 ± 0.8 nm.

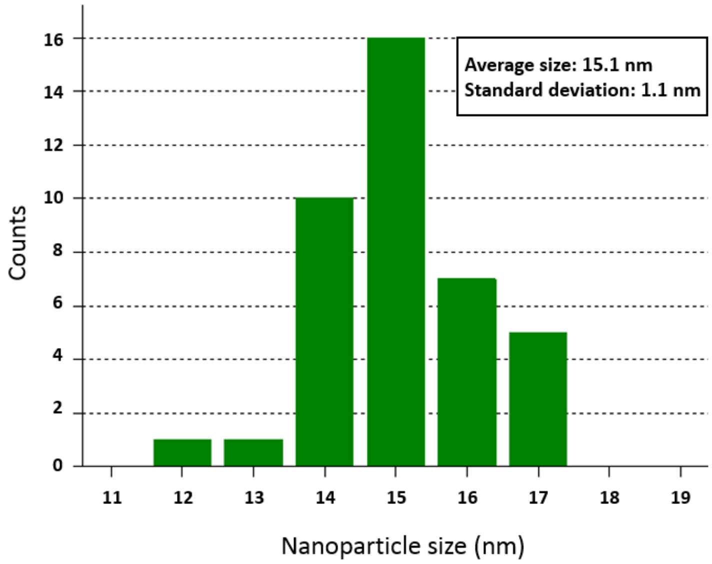


Fig. S2 Size distribution of 15.1 ± 1.1 nm PtCu@Ru.

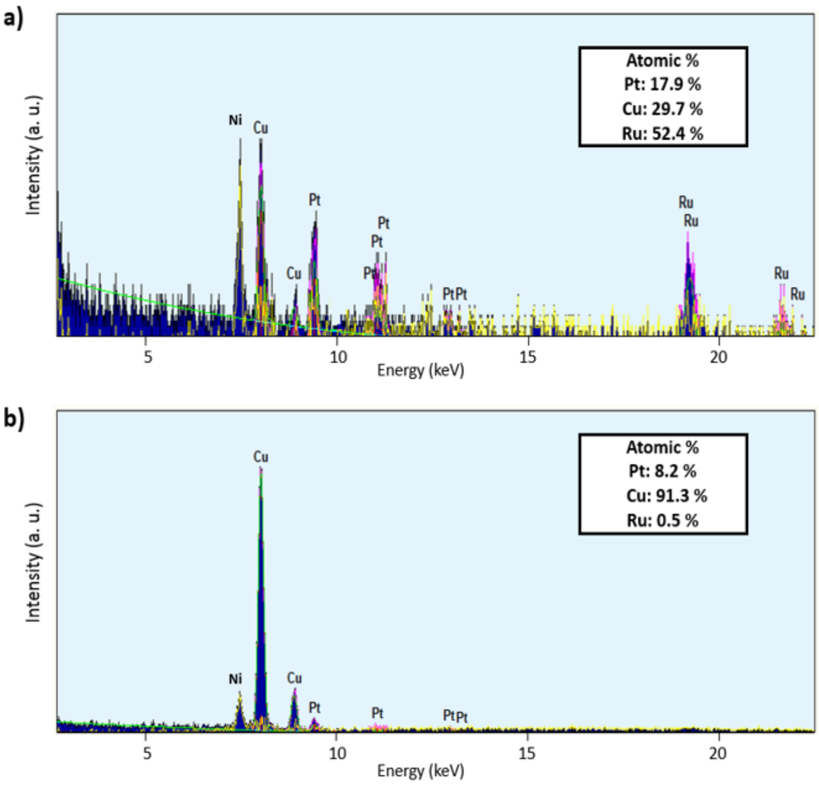


Fig. S3 Elemental mapping analysis by energy dispersive X-ray spectroscopy for a) PtCu@Ru nanorattles in Fig. 1e and b) Pt@Cu core-shell nanoparticle in Fig. 2b. Samples were prepared on a nickel grid.

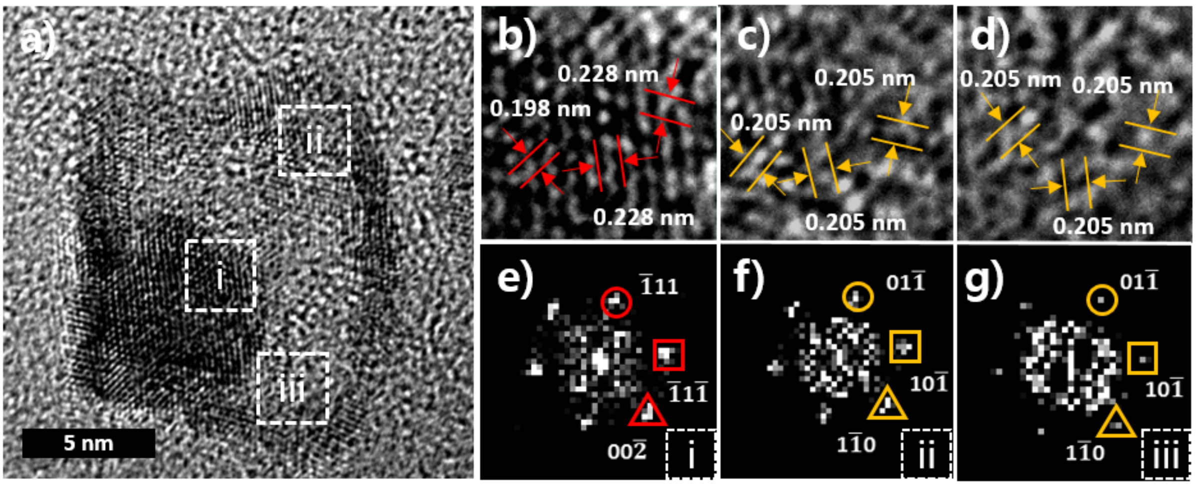


Fig. S4 a) High resolution TEM image of the PtCu@Ru nanocrystals. b-d) HR-TEM images and e-g) FFT patterns of several different positions within a PtCu@Ru nanocrystal in a). The FFT patterns with zone axis of [110] are observed in region i), and zone axis of [111] is observed in region ii) and iii). This reveals a *fcc* Pt structure for region i), and *hcp* Ru structure for region ii) and iii), confirming the nanorattle structure.

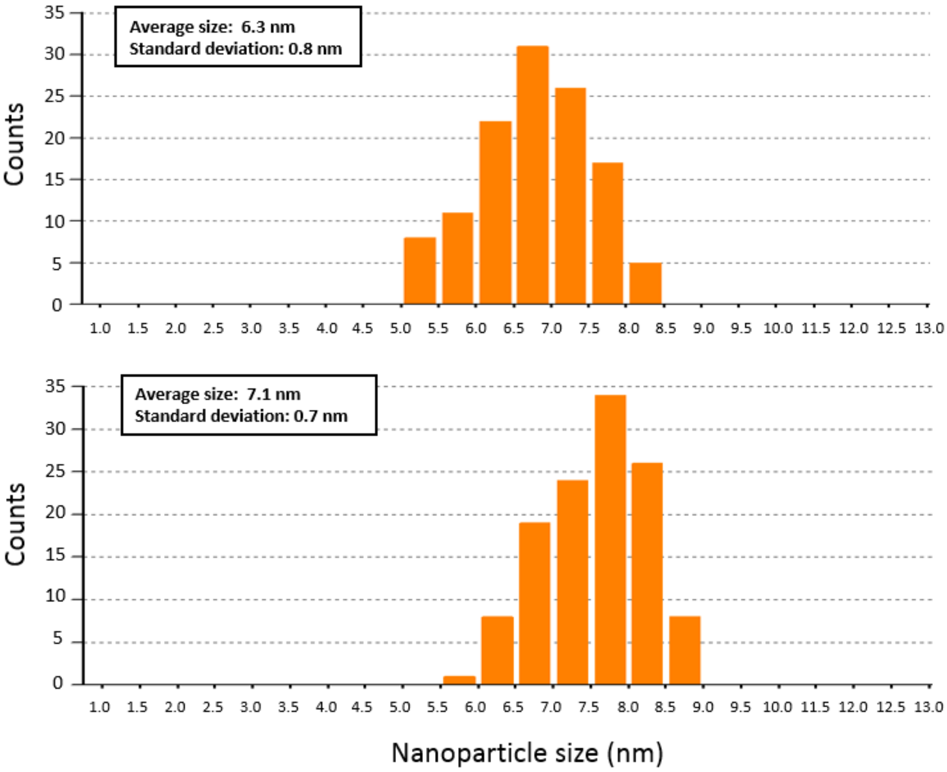


Fig. S5 Size distribution of synthesized Pt NPs (Top) and Pt core in the PtCu@Ru nanorattles (Down).

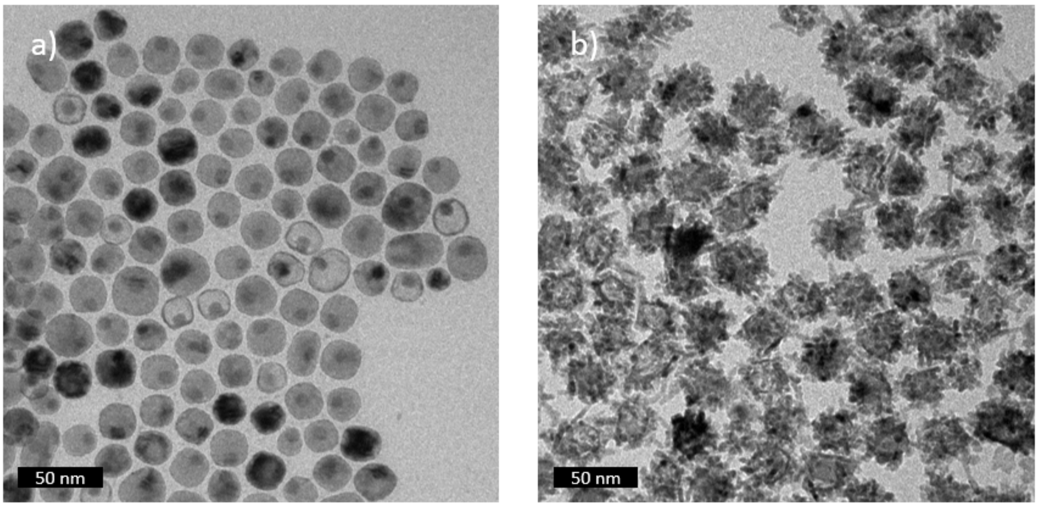


Fig. S6 PtCu@Ru NPs synthesized a) under Ar condition or b) under CO without CTAB.

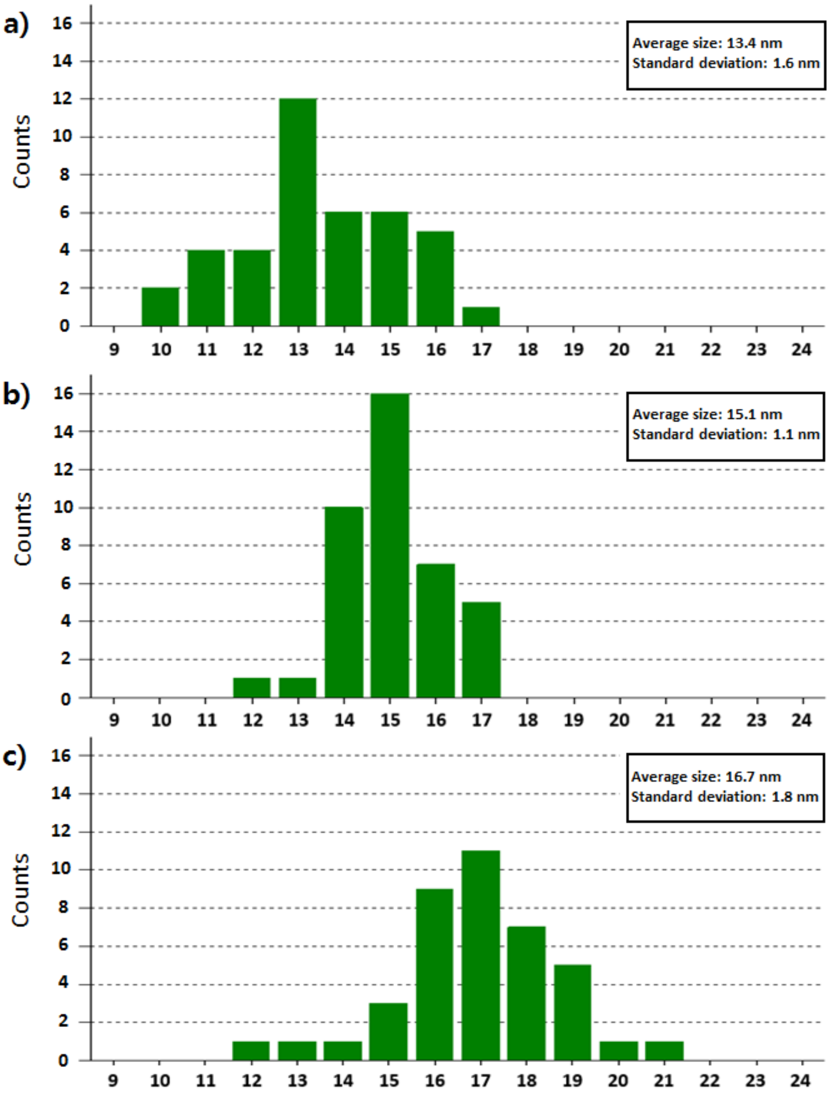
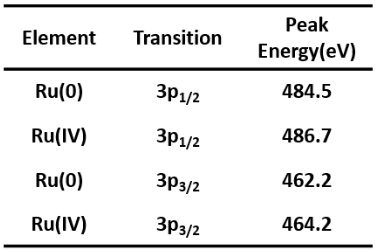


Fig. S7 Size distributions for PtCu@Ru nanorattles.



Element	Transition	Peak Energy(eV)
Ru(0)	$3p_{1/2}$	484.5
Ru(IV)	$3p_{1/2}$	486.7
Ru(0)	$3p_{3/2}$	462.2
Ru(IV)	$3p_{3/2}$	464.2

Fig. S8. Reference binding energies (BE) of the Ru 3p used for analyzing XPS spectra. [1]

Reference

1 K. C. Park, I. Y. Jang, W. Wongwiriyapan, S. Morimoto, Y. J. Kim, Y. C. Jung, T. Toya, M. Endo, *J. Mater. Chem.*, 2010, **20**, 5345