Electronic Supplementary Information

One pot synthesis of hollow Cu-doped Ru octahedral nanocage via *in situ* generated metastable Cu nanoparticle 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. Elemental mapping and energy dispersive X-ray spectra (EDX) were obtained with a FEI Titan Cubed 60-300 with Chemi-STEM technology and a JEOL ARM200F Cs STEM. 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.

Experimental Section

Preparation of hollow Ru octahedral nanocages

A slurry of $Ru(acac)_3$ (0.02 mmol, STREM Chemicals, 99 %), $Cu(OAc)_2$ (0.02 mmol, Aldrich, 98 %), and CTAB (0.02 mmol, Aldrich, 99 %) in oleylamine (15 mmol, Aldrich, 70 %) was prepared in a 100 mL Schlenk tube. After placing the solution under vacuum at 25 ^oC for 10 min, the solution was charged with 1 atm CO. Then the Schlenk tube was directly placed in a hot oil bath, which was preheated to 300 ^oC. 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, after removing the supernatant, were further purified 2 times by washing with methanol/toluene (v/v = 1/2 mL) and then by centrifugation at 3500 rpm for 5 min.

Preparation of hollow urchin shaped Ru nanostructures and Cu@Ru core-shell nanostructures

A slurry of $Ru(acac)_3$ (0.02 mmol, STREM Chemicals, 99 %), $Cu(OAc)_2$ (0.02 mmol, Aldrich, 98 %) in oleylamine (15 mmol, Aldrich, 70 %) was prepared in a 100 mL Schlenk tube. After placing the solution under vacuum at 25 ^oC for 10 min, the solution was charged with 1 atm CO. Then the Schlenk tube was directly placed in a hot oil bath, which was preheated to 300 ^oC. 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, after removing the supernatant, were further purified 2 times by washing with methanol/toluene (v/v = 1/2 mL) and then by centrifugation at 3500 rpm for 5 min.

Electrochemical measurement of hollow Ru octahedral nanocages

Indium–tin oxide (ITO) electrodes were obtained from Corning (Daegu, Korea) and pretreated by dipping in 1 M HCl for 10 min. To prepare Ru nanoparticle-modified electrodes, 70 μL of a toluene solution containing 100 μg/mL Ru nanoparticle was dropped onto ITO electrodes (1 cm × 2 cm). Afterward, the electrodes were dried at 80 °C for 30 min. Electrochemical measurements were carried out using CHI 617 (CH Instruments, Inc., Austin, TX, USA). A Teflon electrochemical cell was assembled with an ITO working electrode, an Ag/AgCl (3 M NaCl) reference electrode, and a Pt counter electrode. The exposed electrode area was 0.28 cm^2.

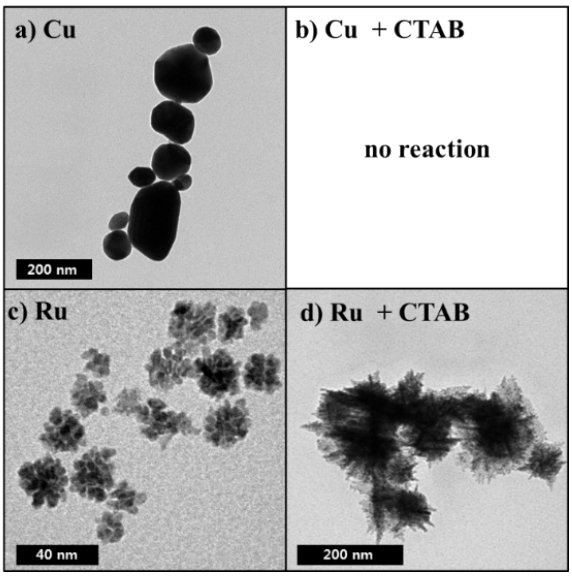


Fig. S1 TEM images of synthesized nanoparticles in oleylamine at 300 °C: a) Cu nanoparticles obtained from $Cu(OAc)_2$ in the absence of CTAB; b) no nanoparticles were obtained from $Cu(OAc)_2$ and CTAB; c) Dendritic Ru nanoparticles from $Ru(acac)_3$ in the absence of CTAB; d) Ru nanoparticles obtained from $Ru(acac)_3$ and CTAB.

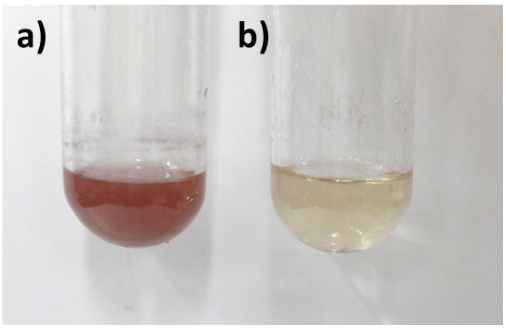


Fig. S2 a) Synthesized Cu nanoparticles in oleylamine and b) dissolution of Cu nanoparticles by reacting with CTAB at high temperature of 300 °C.

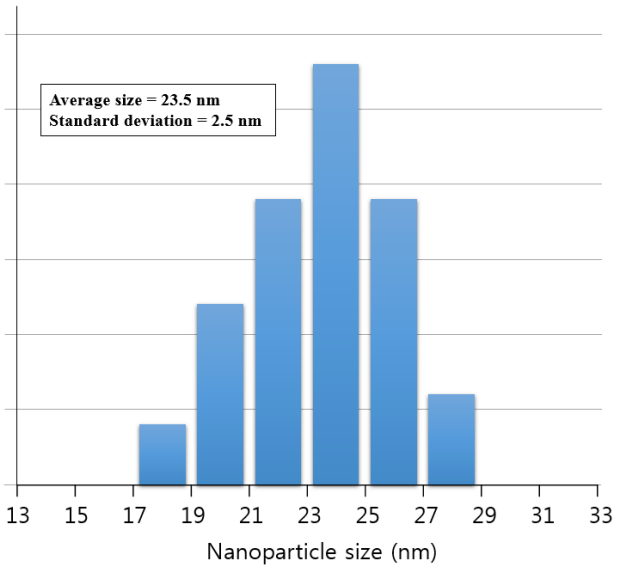


Fig. S3 Size distribution of hollow Ru nanocages in Figure 1. The size is defined as distance from diagonal corner to corner of an octahedron.

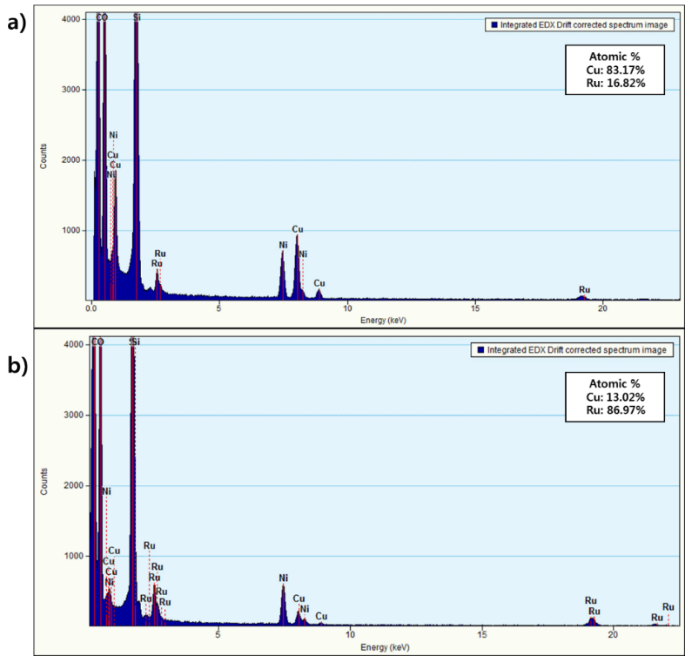


Fig. S4 Elemental mapping analysis by Energy Dispersive X-ray spectroscopy for a) RuCu alloy nanoparticles in Figure 2b and b) hollow Cu-doped Ru nanocages in Figure 2d. Samples were prepared on a nickel grid.

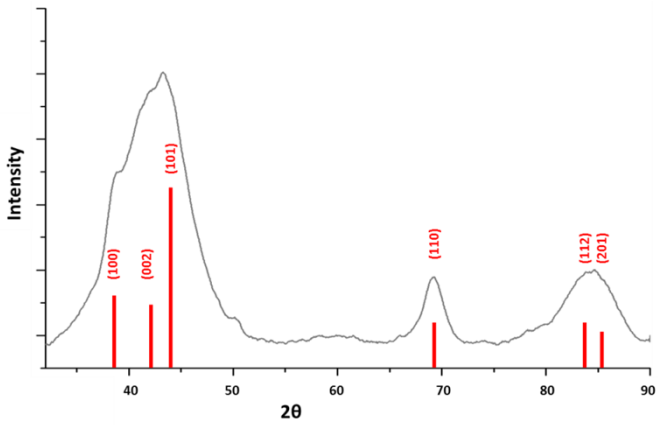


Fig. S5 XRD pattern of Cu-doped Ru nanocages in Figure 1. Red lines indicate the Ru hcp structure. (JCPDS Powder Diffraction File no. 06-0663)

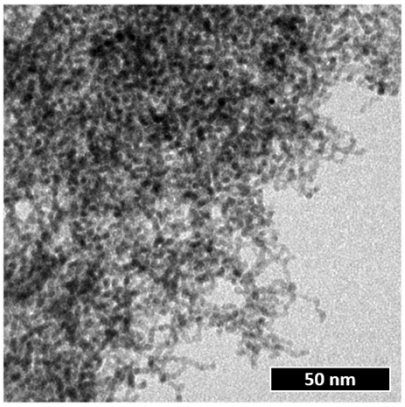


Fig. S6 Synthesized nanoparticles at Ar condition instead of CO. Worm-like nanoparticles are synthesized under CO condition.

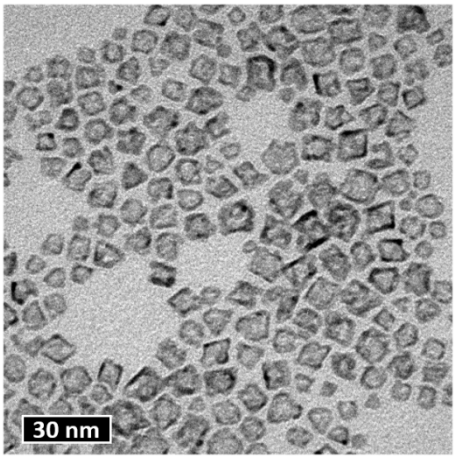


Fig. S7 Octahedron-like nanocages prepared from co-decomposition of CuBr and $Ru(acac)_3$ precursors in the absence of CTAB.

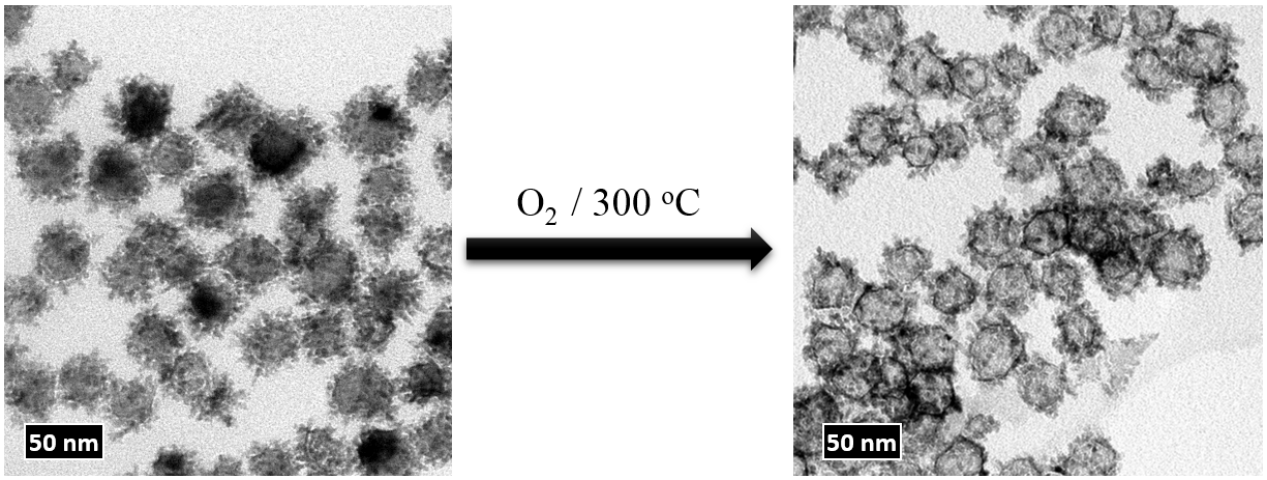


Fig. S8 Core leaching of Cu@Ru core-shell nanoparticle in Figure 3 by the action of oxygen etchant.

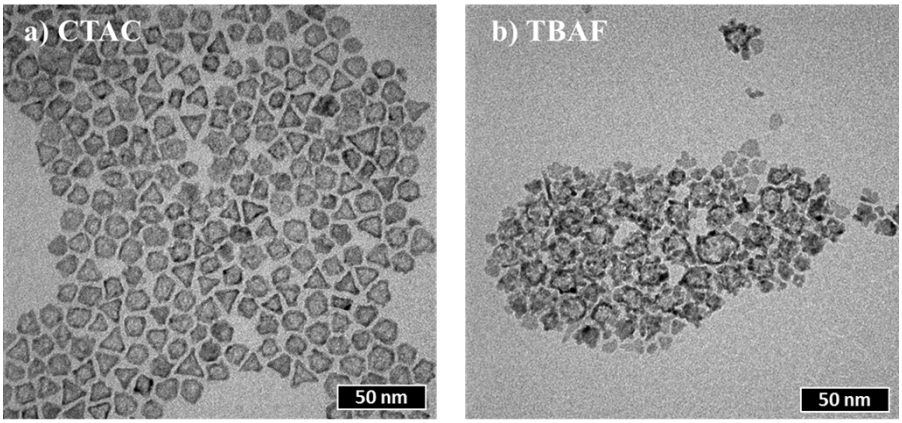


Fig. S9 a) RuCu nanoparticles synthesized with CTAC. Triangular plate and pseudo-octahedral shape are observed. B) RuCu nanoparticles synthesized with TBAF (Tetrabutylammonium fluoride). Morphology of nanoparticles is not well-defined in these cases.

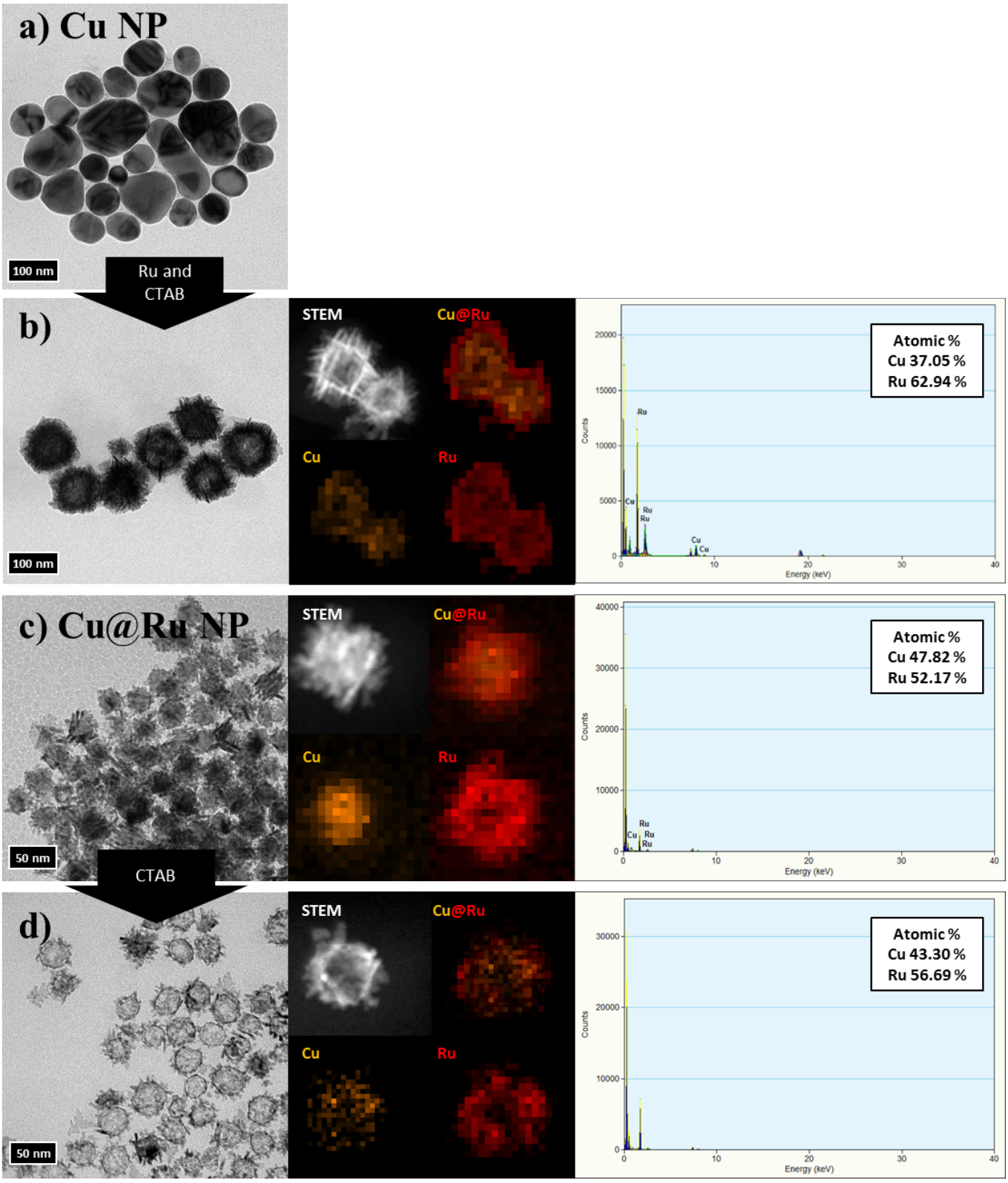
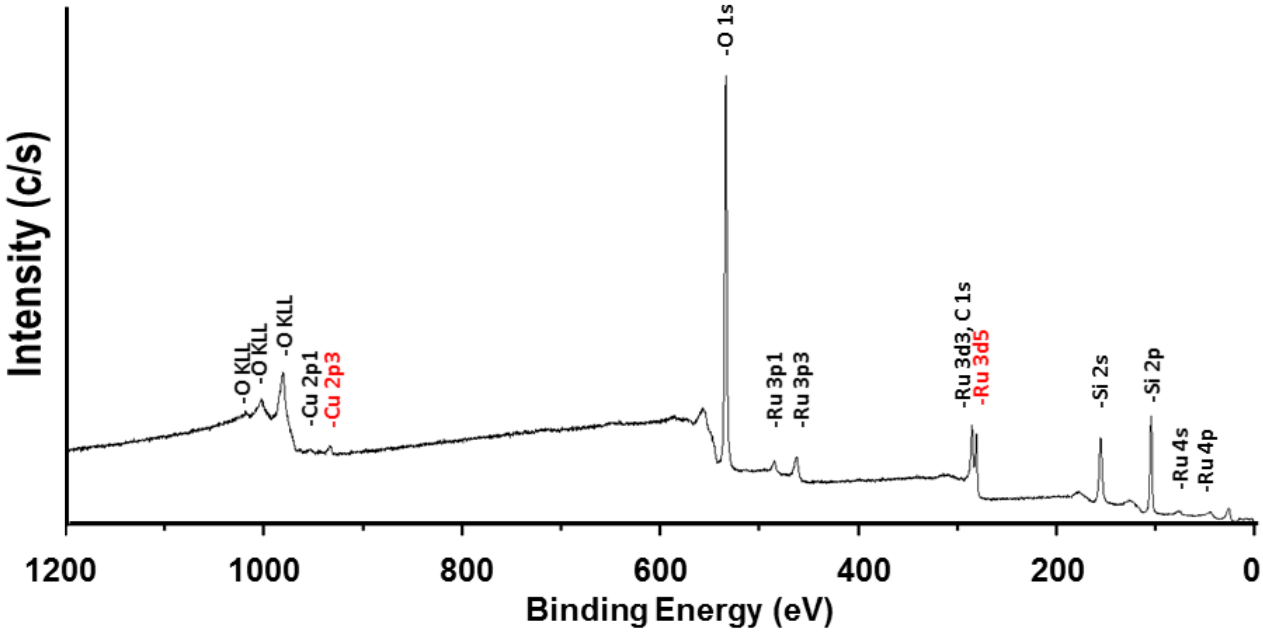


Fig. S10 a) Pre-synthesized Cu nanoparticles. b) Pre-synthesized Cu nanoparticles were treated with Ru precursor and CTAB at 300 ^{o}C.

c) Cu@Ru core-shell nanoparticles. d) Cu@Ru core-shell nanoparticles were treated with CTAB at 300 ^{o}C.



Element	Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV-cts/s)
Cu(0)	$2p_{3/2}$	932.63	1.76	4085
Cu(I)	$2p_{3/2}$	932.18	1.31	443
Cu(II)	$2p_{3/2}$	933.76	2.14	2141

Element	Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV-cts/s)
Ru(0)	$3d_{5/2}$	280.10	1.142	9153
Ru(IV)	$3d_{5/2}$	280.90	1.242	9802

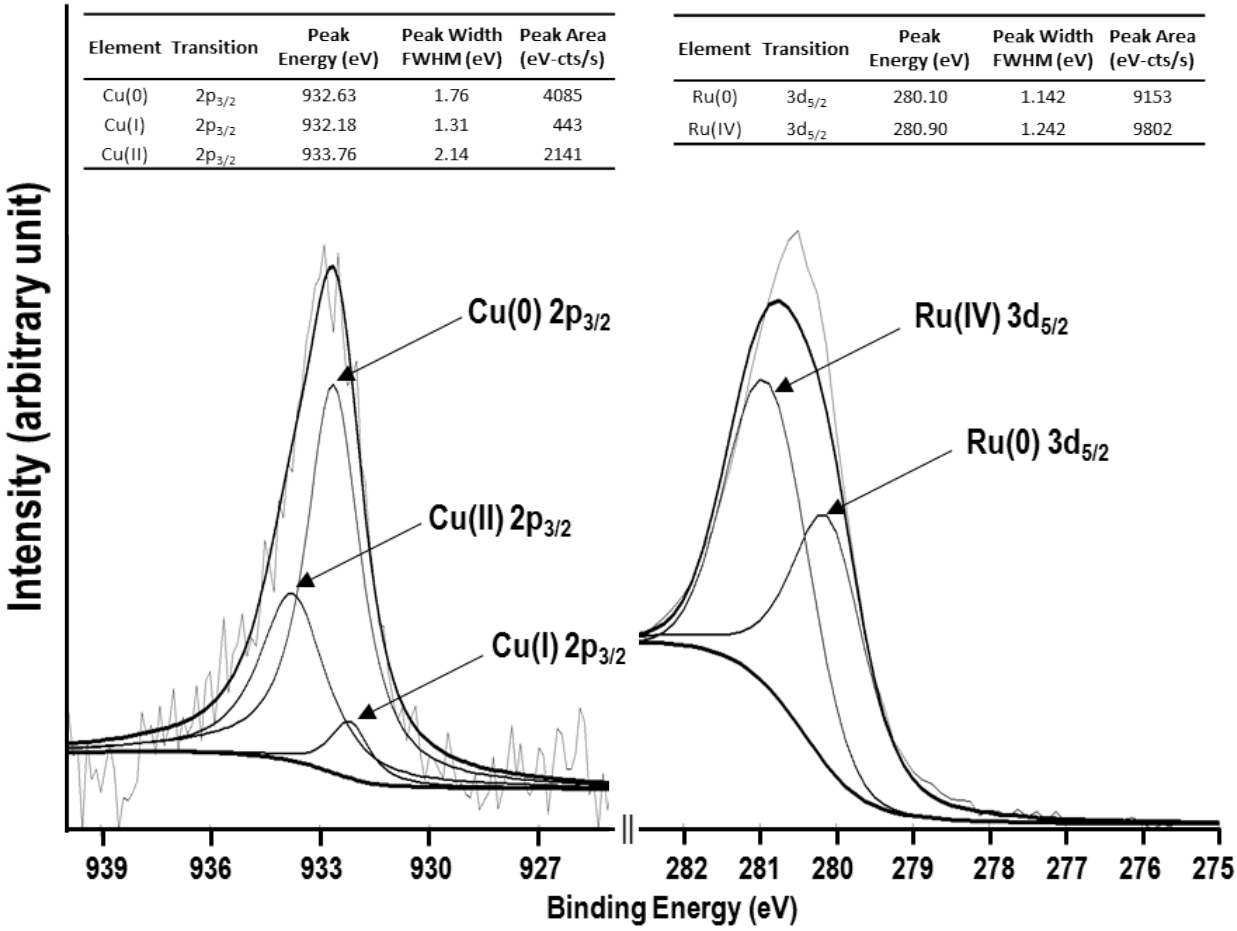


Fig. S11 X-ray Photoelectron Spectra (XPS) of Cu-doped Ru octahedral nanocages. Partial oxidation of Ru and Cu is observed. It is found that Ru in nanocage exists both as 48.3 % Ru(0) and 51.7 % Ru(IV). Cu was found as 61.3 % Cu(0), 6.6 % Cu(I), and 32.1 % Cu(II).

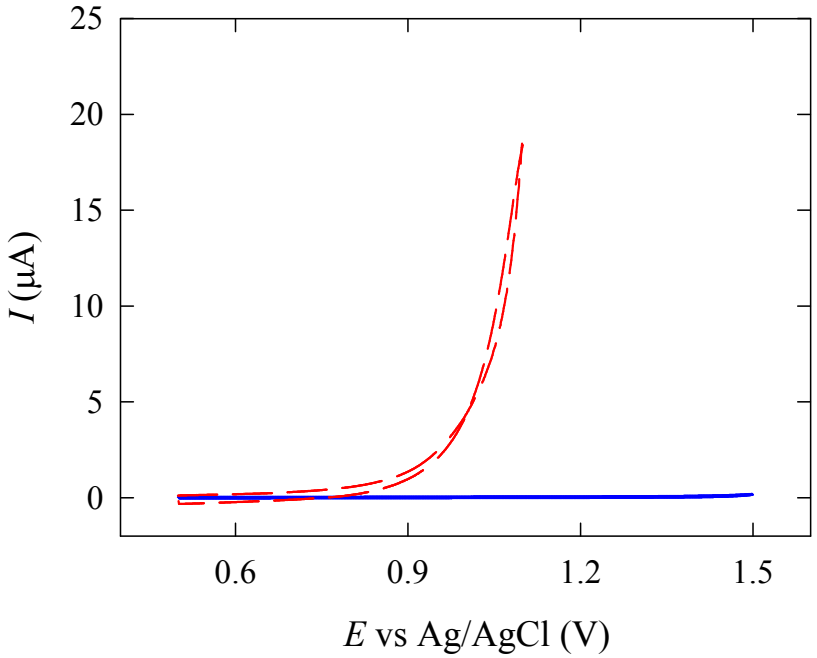


Fig. S12 Cyclic voltammograms measured (at a scan rate of 10mV/s) in 0.1 M $HClO_4$ at a bare ITO electrode and a Ru nanocage-modified ITO electrode.