Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic Supplementary Information

One pot synthesis of octahedral {111}CuIr gradient alloy nanocrystals with Cu-rich core and Ir-rich surface and their usage as efficient water splitting catalyst

Donghwan Yoon [a], Sulgi Bang [a], Jongsik Park [a], Jongchan Kim [b], Hionsuck Baik [c],
Haesik Yang [b*], and Kwangyeol Lee [a*†]

[a] Department of Chemistry and Research Institute for Natural Sciences, Korea University, Seoul 136-701 (Korea)

[b] Department of Chemistry and Chemistry Institute of Functional Materials, Pusan University, Busan 609-735 (Korea)

[c] Korea Basic Science Institute (KBSI), Seoul 136-713 (Korea)

*Corresponding authors: kylee1@korea.ac.kr (K. Lee), hyang@pusan.ac.kr (H. Yang)

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 CuIr octahedral nanocrystals

In a typical synthesis of CuIr nanoparticles, A slurry of $Ir(acac)_3$ (0.02 mmol, STREM 98 %), $Cu(OAc)_2$ (0.02 mmol, Aldrich 98 %), and CTAC (Cetyltrimethylammonium chloride) (0.02 mmol, Aldrich 98 %) in oleylamine (15 mmol, Aldrich 70 %) was prepared in a 100 mL Schlenk tube. After placing the reaction mixture under vacuum at 90 ^{o}C for 1 h, the reaction mixture was charged with 1 atm CO. Then the Schlenk tube was directly placed in a hot oil bath, which was preheated to 300^{o}C. After heating at the same temperature for 15 min, the reaction mixture was cooled down to room temperature, washed several times with toluene and methanol, followed by centrifugal separation.

Electrochemical measurement

Before measuring electrocatalytic activity of nanoparticles, nanoparticles were treated with acetic acid to remove organic ligands. The synthesized nanoparticles were put into cornical tube with 2 ml toluene, 7 ml ethanol and 1 ml acetic acid and stirred for 24 hours. After acetic acid treatment, the nanoparticles were separated and washed by centrifuger and dryed in oven for 24 hours.

Indium–tin oxide (ITO) electrodes were obtained from Corning (Daegu, Korea) and pretreated by dipping in 1 M HCl for 10 min (M. Choi, K. Jo, H. Yang, Bull. Korean Chem. Soc. 2013, 34, 421-425). To prepare nanoparticle-modified electrodes, 70 μL of a ethanol solution containing 100 μg/mL nanoparticle was dropped onto ITO electrodes (1 cm × 2 cm). Subsequently, 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 (exposed area = 0.28 cm^2), an Ag/AgCl (3 M NaCl) reference electrode, and a Pt counter electrode

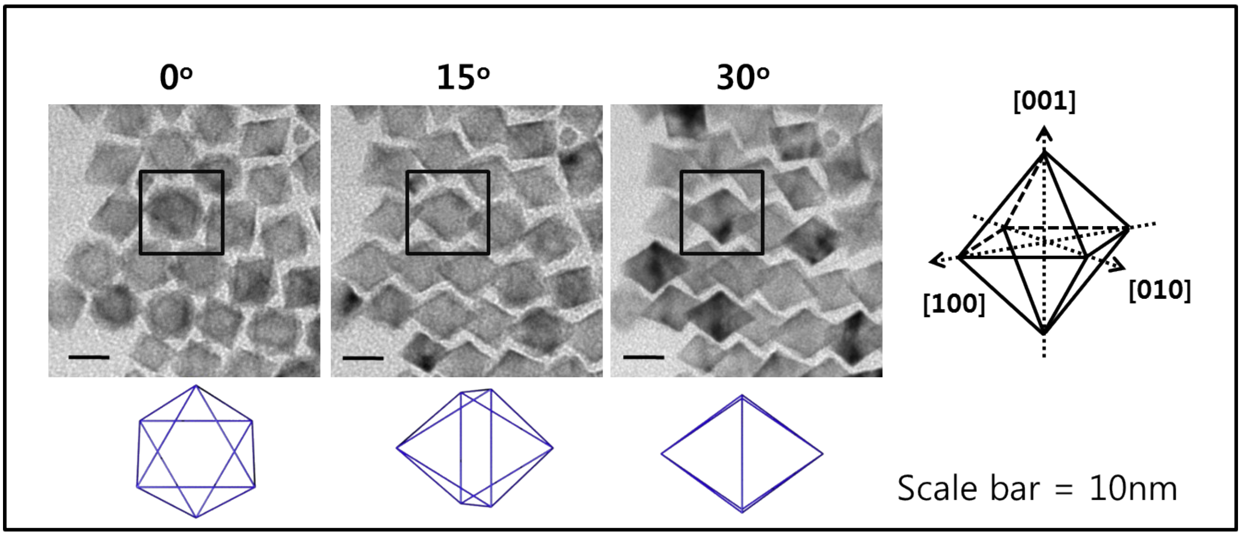

Fig. S1 TEM images of octahedral CuIr nanocrystals at various grid tilting angles. The angle between [111] and [110] is about 35°, thus confirming the octahedral structure.

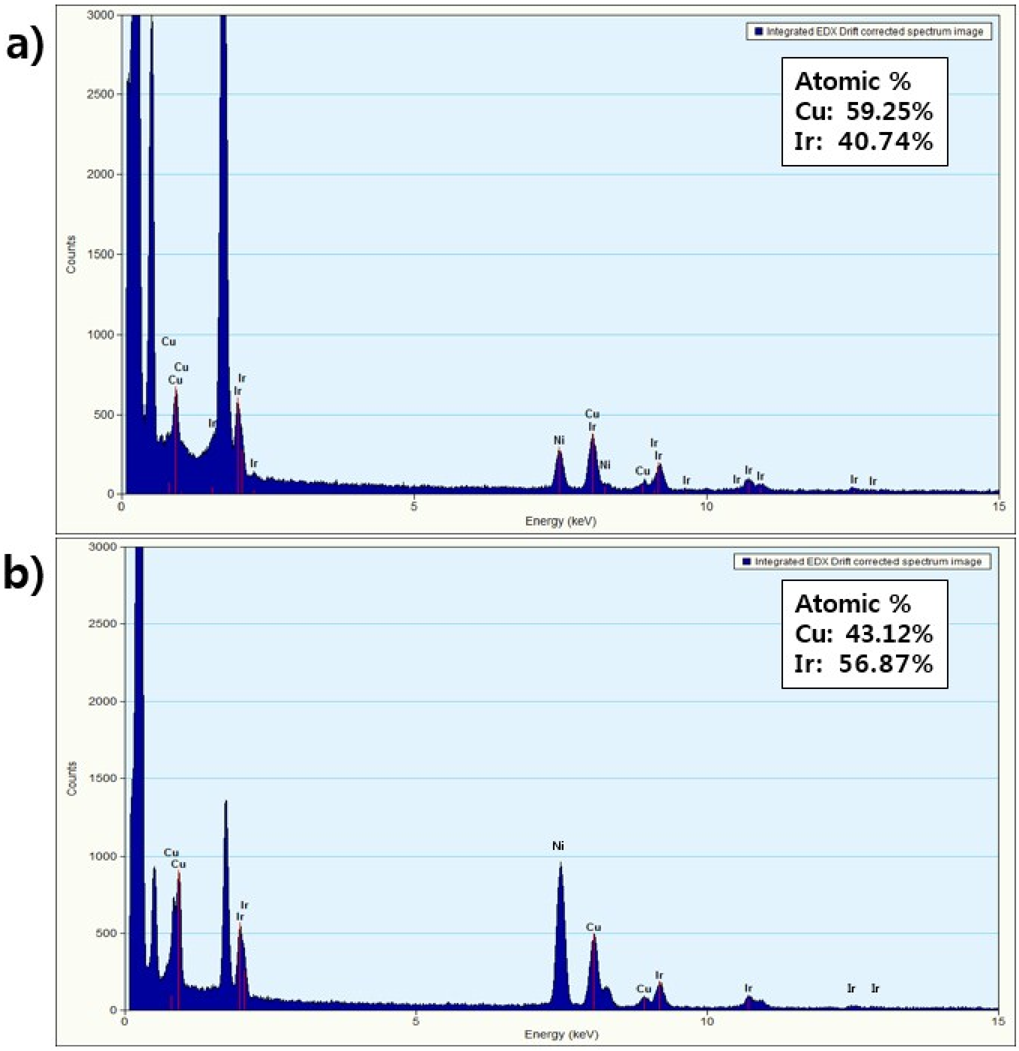

Fig. S2 Elemental mapping analysis by Energy Dispersive X-ray spectroscopy for reaction intermediate nanocrystals. a) Sample obtained at 3min in Figure 2, b) Sample obtained at 15min in Figure 2. Samples were prepared on a nickel grid

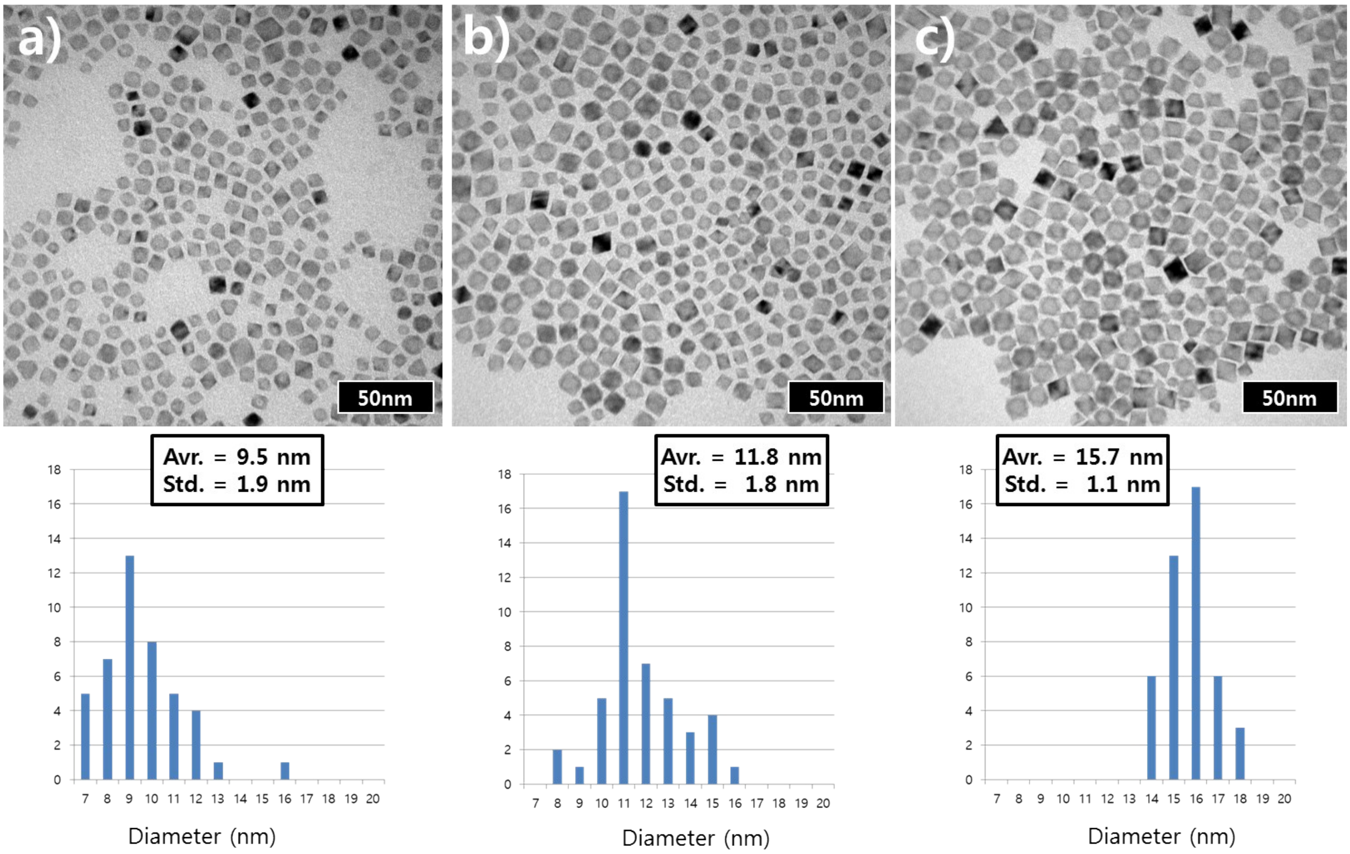

Fig. S3 Size distribution of reaction intermediate nanocrystals obtained at a) 3 min, b) 5min, and c) 15min sample

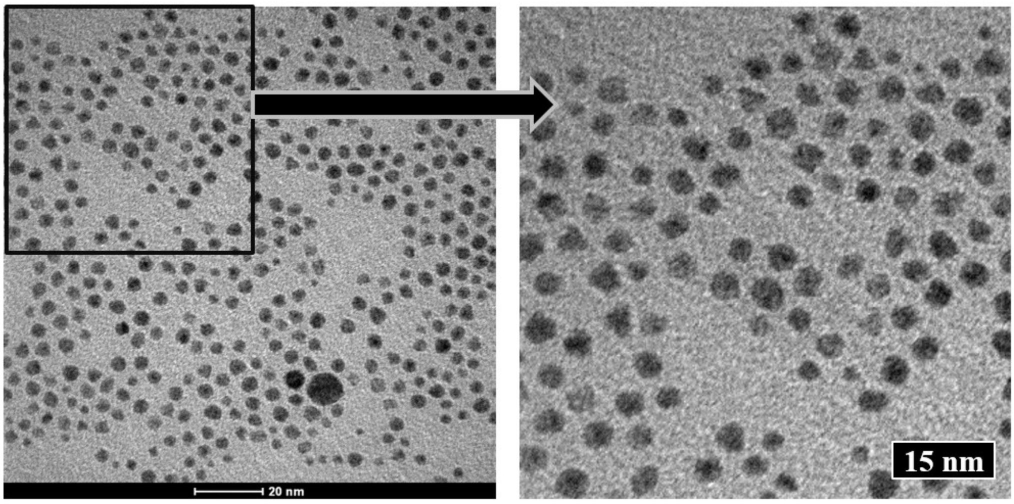

Fig. S4 Nanoparticles synthesized under Ar gas instead of CO gas.

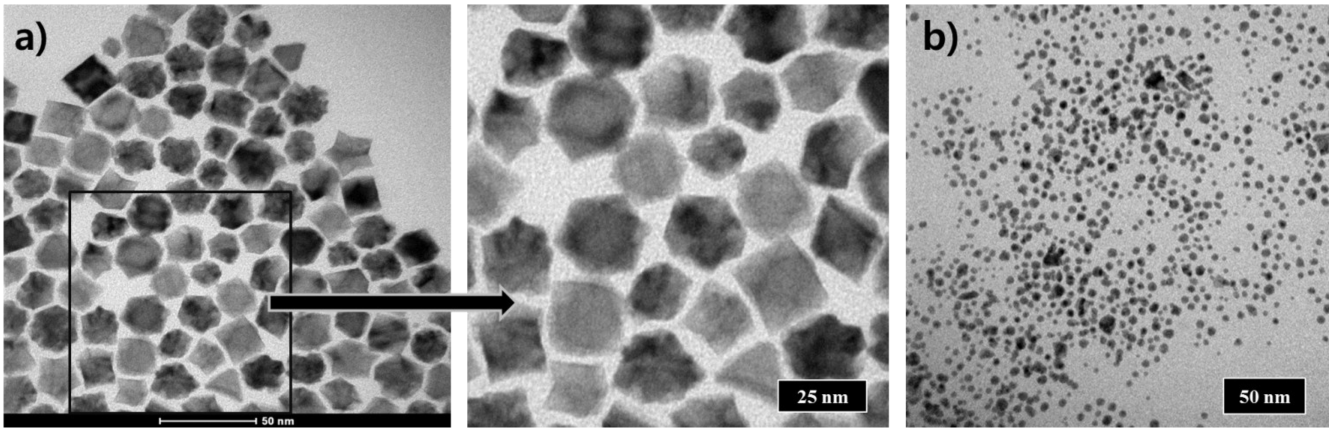

Fig. S5 a) Nanoparticles synthesized with CTAB (cetyltrimethylammonium bromide) instead of CTAC (cetyltrimethylammonium chloride). b) Small spherical Ir nanocrystals used for comparing OER activity.