

## Electronic Supplementary Information

Formation of double layer hollow nanostars of Pd/CuIr by utilizing a Kirkendall effect and a facile Cu atom movement along twinning boundaries and their usage as efficient water splitting catalysts

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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-K $\alpha$  radiation at 40 kV and 40 mA.

## **Experimental Section**

### ***Preparation of Pd nanocrystals***

A slurry of Pd(acac)<sub>2</sub> (0.164 mmol, Aldrich 90%), TOP (0.5 mL, Trioctylphosphine, Aldrich 90%) in oleylamine (15 mmol, Aldrich 70 %) was prepared in a 100 mL Schlenk tube. After placing the reaction mixture under vacuum at room temperature for 10 min, the color of the reaction mixture changed orange in 1 min. And reaction mixture was charged with 1 atm Ar. Then the Schlenk tube was directly placed in a hot oil bath, which was slowly heated to 250°C. After heating at the 250°C for 30 min, the reaction mixture was cooled down to room temperature, washed several times with toluene and methanol, followed by centrifugal separation.

### ***Preparation of Pd@CuIr nanostars***

In a typical synthesis of Pd@CuIr nanoparticles, A slurry of 0.1 mg of the 5 nm Pd sphere seed, Ir(acac)<sub>3</sub> (0.02 mmol, STREM 98 %), Cu(OAc)<sub>2</sub> (0.029 mmol, Aldrich 98 %), and CTAC (cetyltrimethylammoniumchloride) (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°C for 1 hour, 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 280°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.

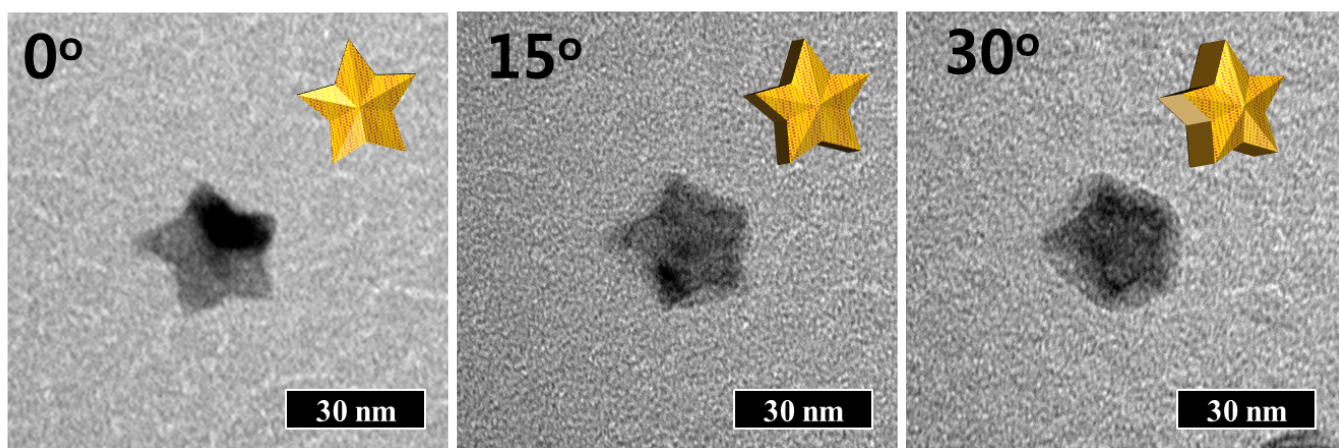
### ***Preparation of hollow nanostars***

After placing the Pd@CuIr nanostar reaction mixture under vacuum at 90°C for 30 min, the reaction mixture was charged with 1 atm O<sub>2</sub>. Then the Schlenk tube was directly placed in a hot oil bath, which was preheated to 200°C. After heating at the same temperature for 1 hour, the reaction mixture was cooled down to room temperature, washed several times with toluene and methanol, followed by centrifugal separation.

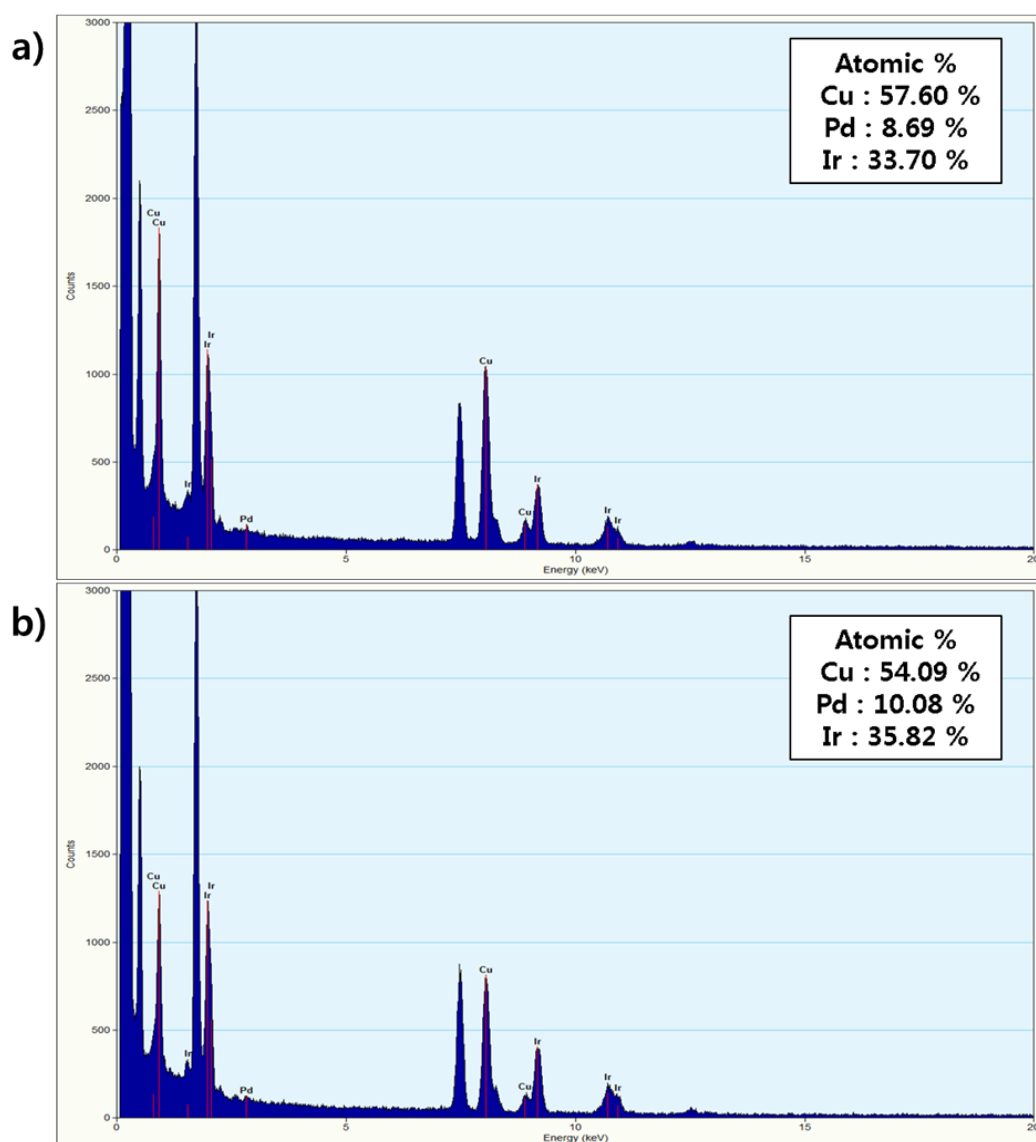
### ***Electrochemical measurement***

Before measuring electrocatalytic activity of nanoparticles, nanoparticles were treated with acetic acid to remove organic ligands. The synthesized nanoparticles were put into conical 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 centrifugation and dried in oven for 24 hours.

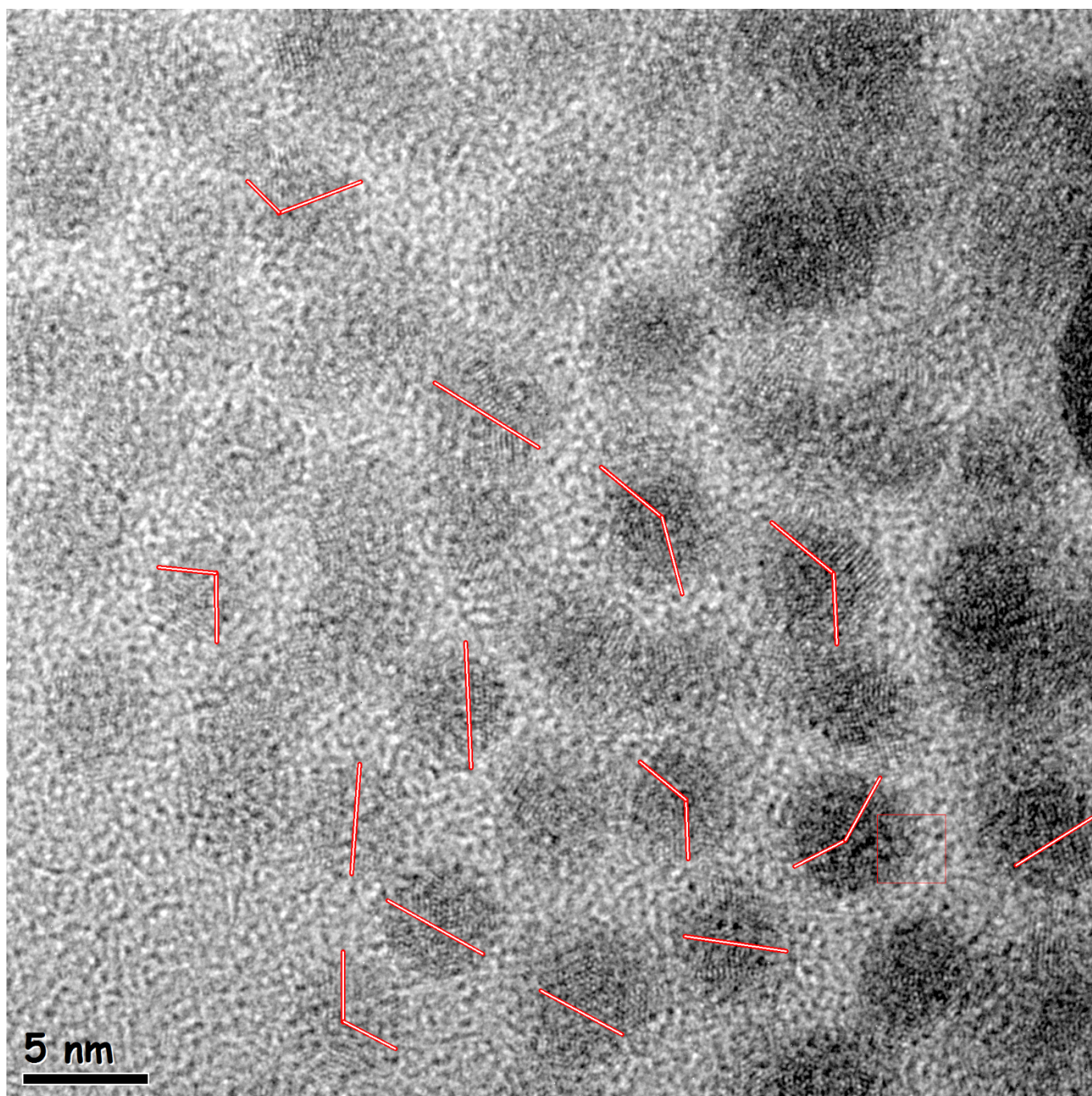
Indium–tin oxide (ITO) electrodes were obtained from Corning (Daegu, Korea) and pretreated by dipping in 1 M HCl for 10 min. To prepare two kinds of Ir nanoparticle (Pd@CuIr and Hollow-PdCuIr)-modified electrodes, 70  $\mu$ L of an ethanol solution containing 100  $\mu$ g/mL each nanoparticle was dropped onto ITO electrodes (1 cm  $\times$  2 cm). Afterward, the electrodes were dried at 80°C for 10 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<sup>2</sup>.



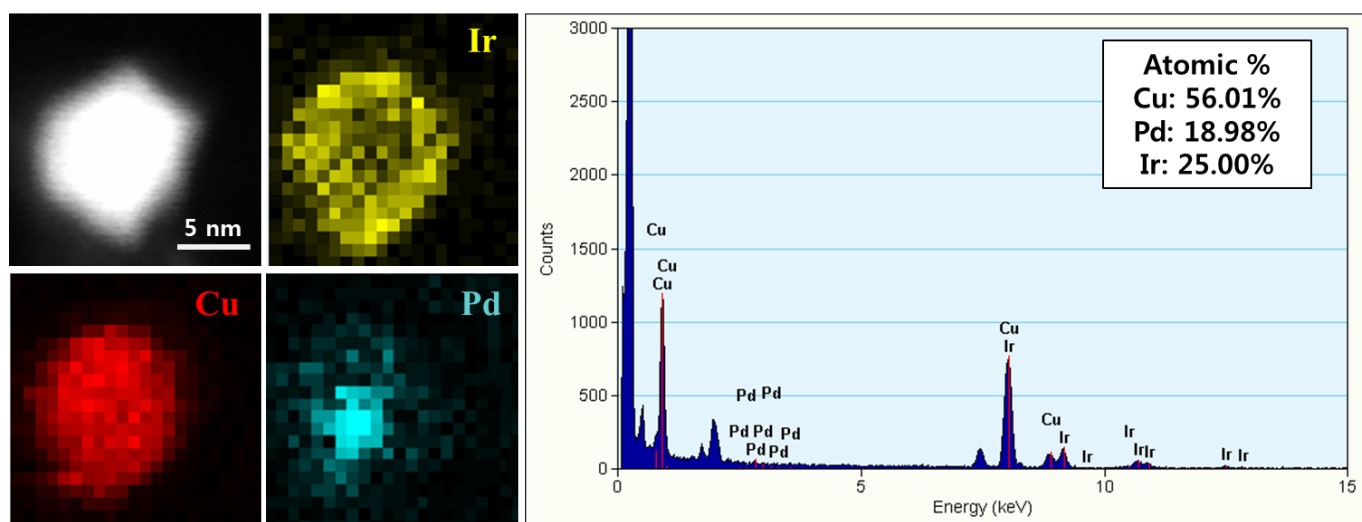
**Fig. S1** TEM images of Pd@CuIr nanostar in Fig 1 viewed from different grid tilting angles.



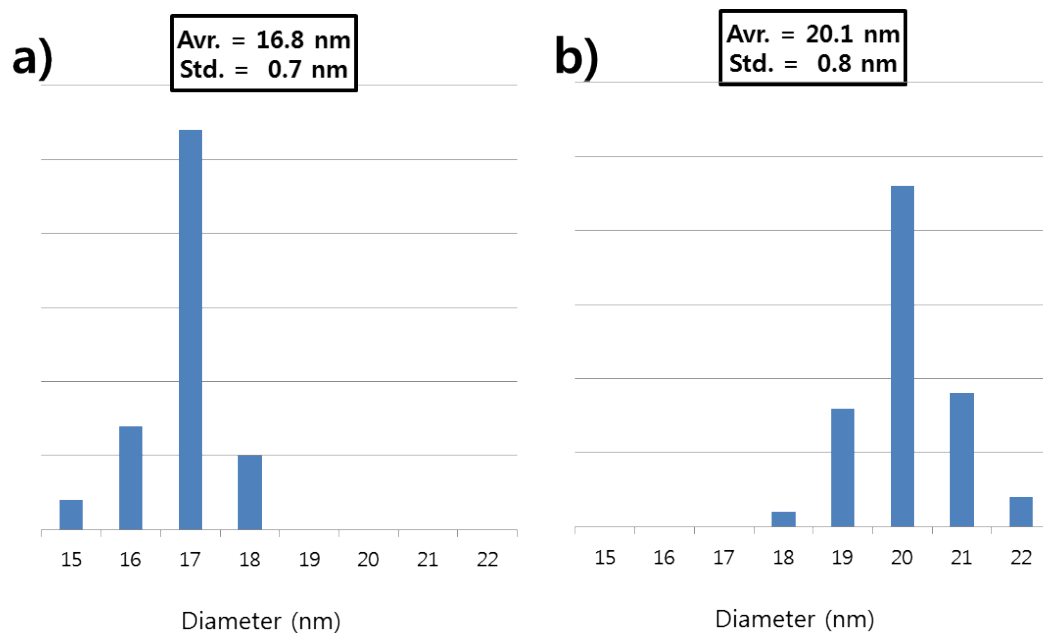
**Fig. S2** Elemental mapping analysis by Energy Dispersive X-ray spectroscopy for nanostars. a) Pd@CuIr nanostars in Fig. 1. b) hollow nanostars in Fig. 3. Samples were prepared on a nickel grid.



**Fig. S3** HRTEM image of polycrystalline Pd seed nanoparticle. Grain boundaries of Pd nanoparticles were determined by FFT pattern analysis.

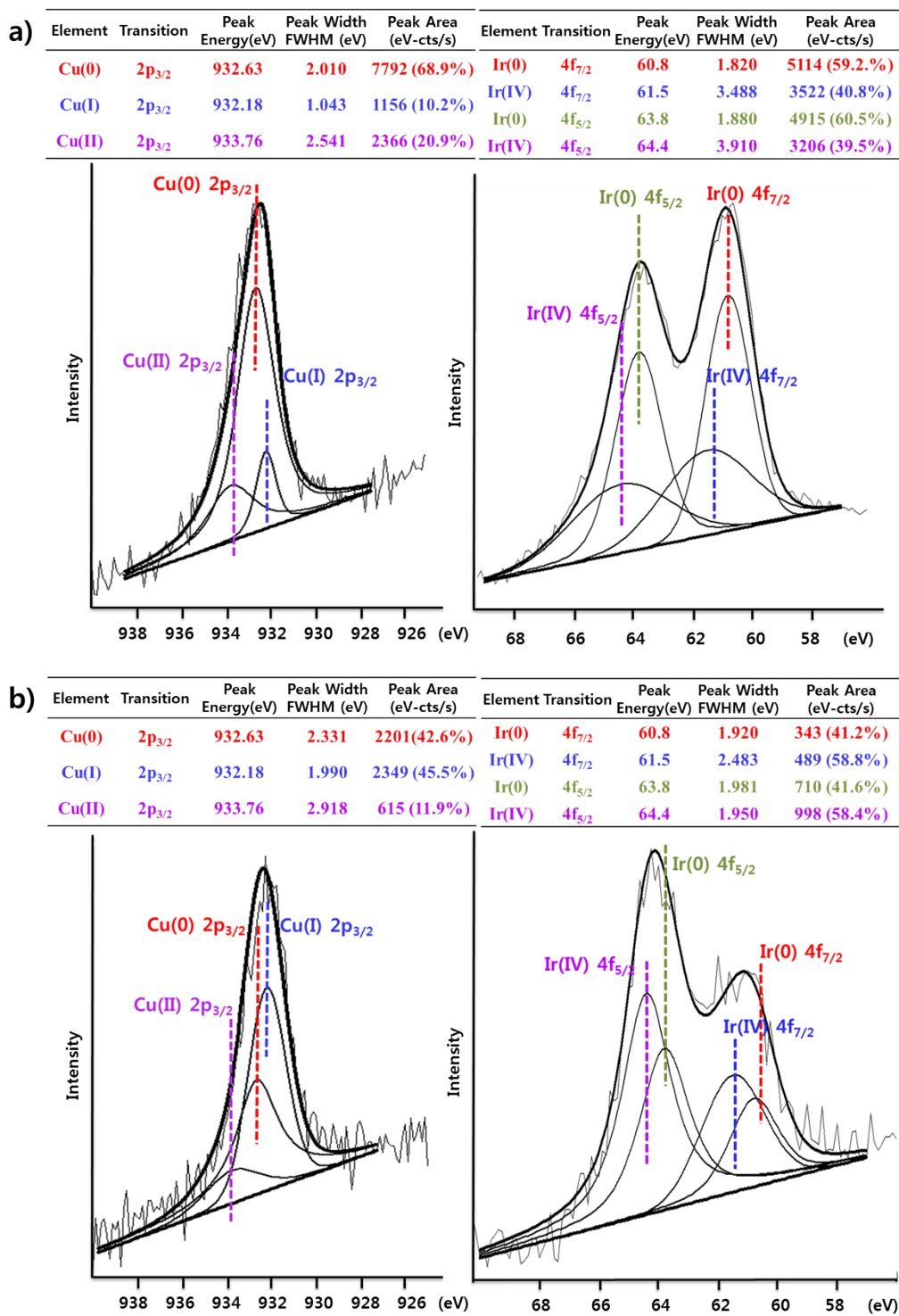


**Fig. S4** Elemental mapping analysis data of 5 min sample in Fig 2c along with its elemental analysis.

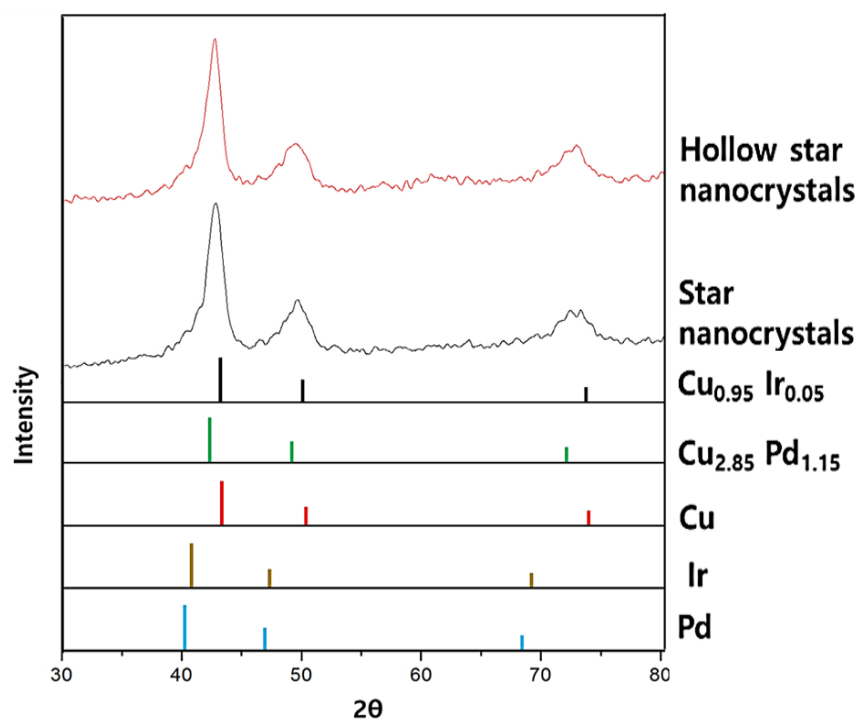


**Fig. S5** Size distribution of a) Pd@CuIr nanostars and b) hollow double layer Pd/CuIr nanostars





**Fig. S6** X-ray photoelectron spectra of a) Pd@CuIr nanostars and b) hollow double layer Pd/CuIr nanostars



**Fig. S7** XRD pattern of Pd, Ir, Cu,  $\text{Cu}_{2.85}\text{Pd}_{1.15}$ ,  $\text{Cu}_{0.95}\text{Ir}_{0.05}$ , Pd@CuIr nanostars, and hollow double layer Pd/CuIr nanostars