Supporting Information

Facile synthesis of Ru-decorated Pt cubes and icosahedra as highly active electrocatalysts for methanol oxidation

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Calculations the number of Ru atomic ad-layers in a simple core-shell model.

The edge length (a_1) of the PtRu cube is 12.7 nm. Suppose the edge length of the Pt cube is a_0. The volume of Pt cube is V_{Pt} a_0^3 , while the volume of PtRu cube is $V_{PtRu} = a_1^3 = (12.7)^3$ nm^3 . Suppose Pt and Ru share a same lattice spacing. The atomic percent of Pt in cubes is $N_{Pt}/N \approx V_{Pt}/V_{PtRu} = a_0^3/a_1^3 = 88\%$ (Table S1). So, a_0 can be calculated as 12.17 nm and the thickness of Ru ad-layers is $l = (a_1 - a_0)/2 = 0.265$ nm which is corresponded to about one and a half layers of (200) planes of *fcc* Ru.

Similarly, the atomic percent of Pt in icosahedra is $N_{Pt}/N \approx V_{Pt}/V_{PtRu} = d_0^3/d_1^3 = 85\%$ (Table S1). The size of Pt icosahedra (d_0) is calculated as 11.37 nm considering the size of PtRu icosahedra ($d_1 = 12$ nm). Thus, the thickness of Ru as-layers is $l = (d_1 - d_0)/2 = 0.316$ nm, which is corresponded to about one and a half layers of (0002) planes of *hcp* Ru.

Table S1. ICP-AES, XPS data and ECSA of the Ru decorated Pt bimetallic cubes and icosahedra as well as Pt_7Ru nanoparticles and the commercial Pt/C (ETEK).

samples	$n_{Pt}:n_{Ru}$[1]	Pt/Ru atomic ratio[2]	composition	Pt/Ru atomic ratio (surface)[3]	ECSA(m^2/g_{pt})[4]
Cubes	2:3	7.8:1	$Pt_{88}Ru_{12}$	0.76:1	11.2
Icosahedra	2:3	5.8:1	$Pt_{85}Ru_{15}$	0.71:1	9.8
Pt_7Ru/C	7:1	6.9:1	$Pt_{87}Ru_{13}$	/	30.1
Pt/C	/	/	/	/	68

1: Molar ratio between the Pt and Ru salt precursors.

2. The Pt/Ru atomic ratio was calculated from inductively coupled plasma atomic emission spectrometry (ICP-AES).

3. The Pt/Ru atomic ratio was calculated from X-ray photoelectron spectroscopy (XPS).

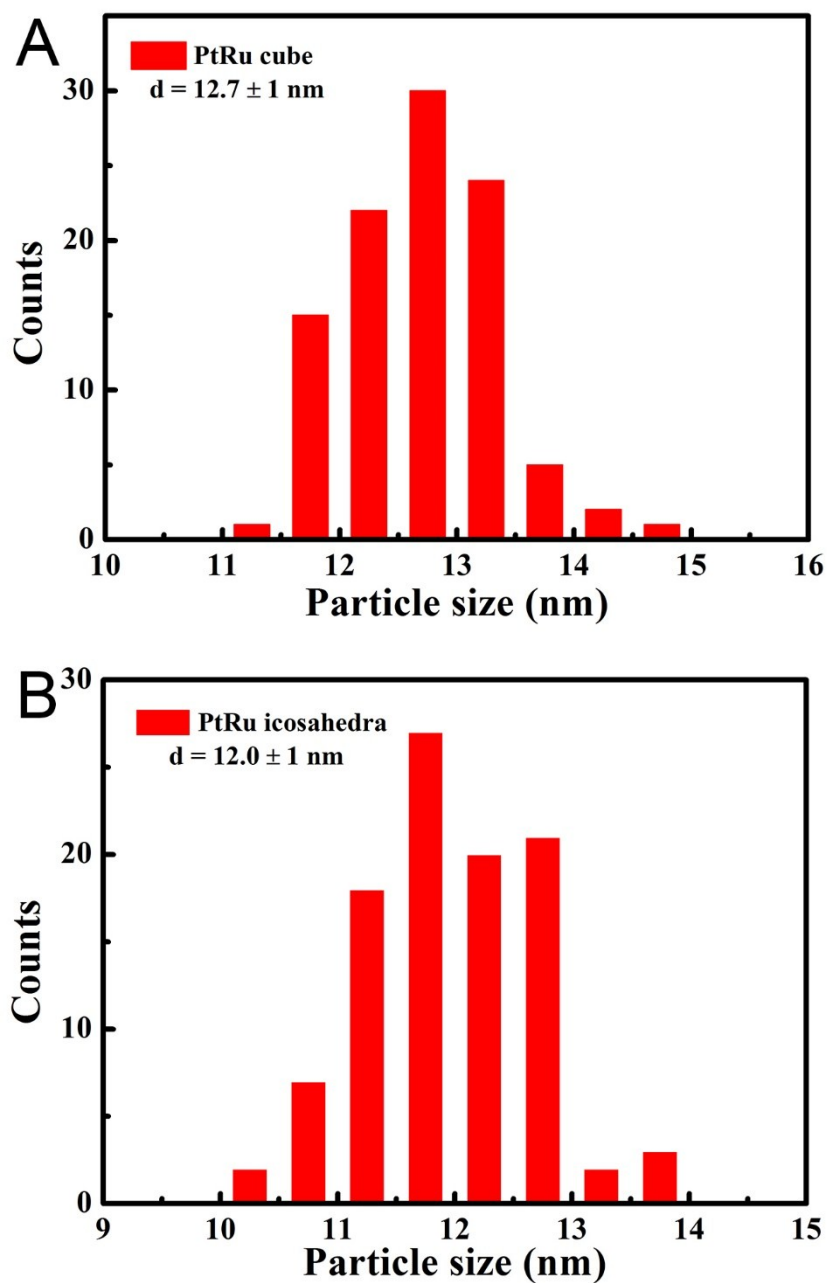4: The ECSA was calculated from CV curves in Figure S11-12.

Figure S1. Size distribution of (A) Ru decorated Pt bimetallic cubes and (B) Ru decorated Pt bimetallic icosahedra.
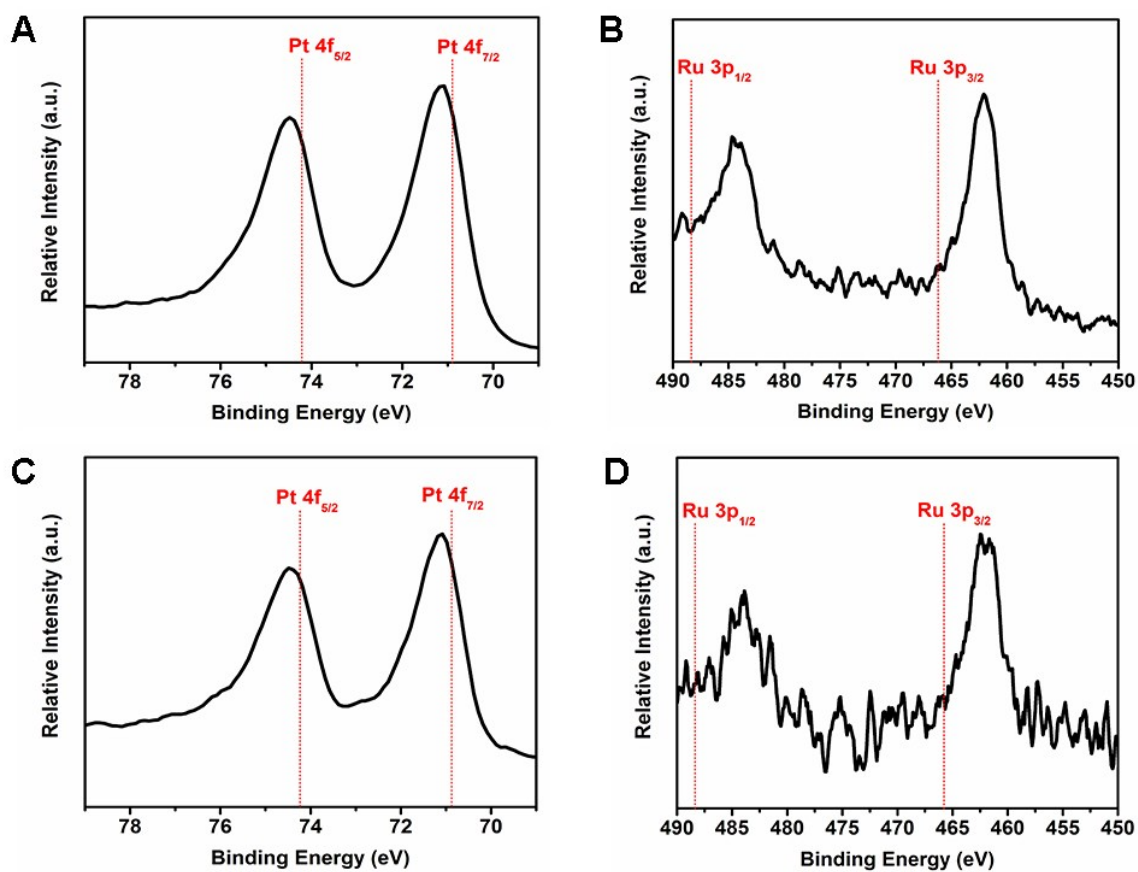
Figure S2. X-Ray photoelectron spectra (XPS) of Pt 4f orbits and Ru 3p orbits for nanocrystals with cubic (A, B) and icosahedral (C, D) shape.
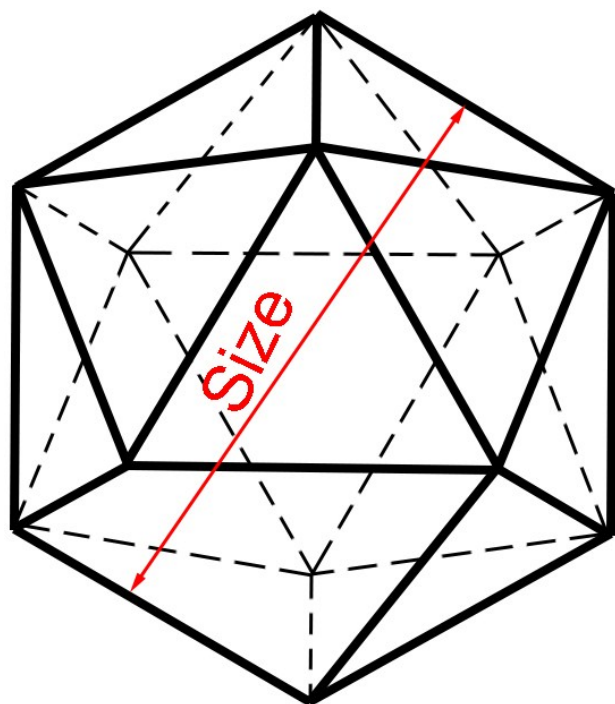
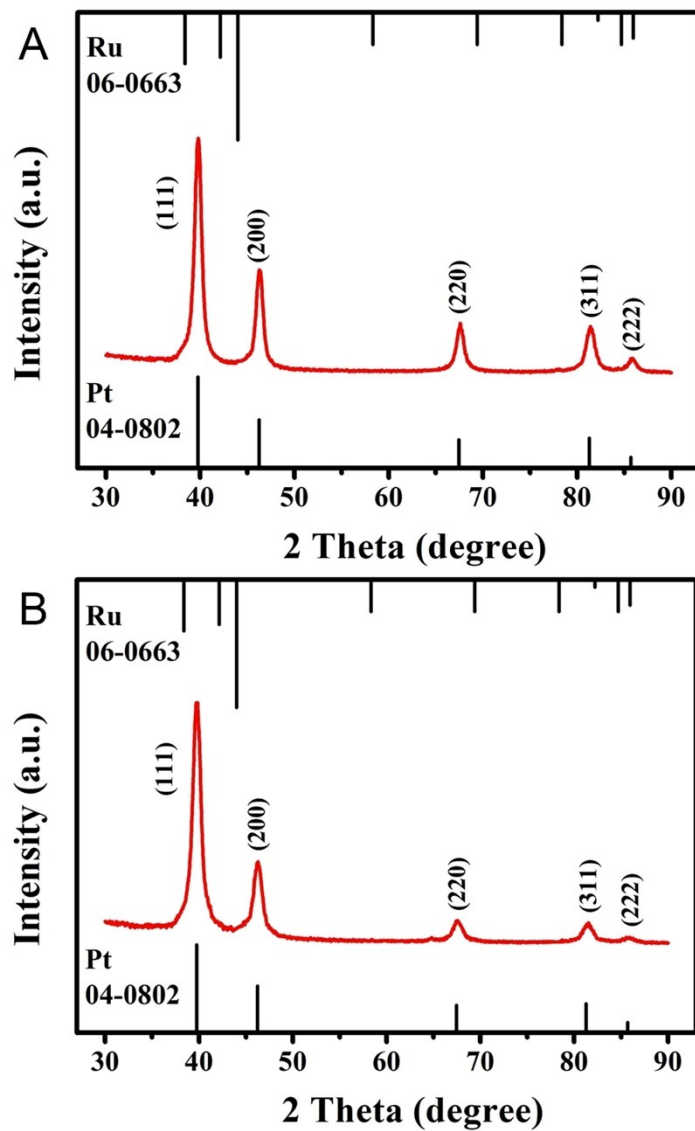**Figure S3.** Schematic illustration the definition of size for a Ru decorated Pt icosahedron.

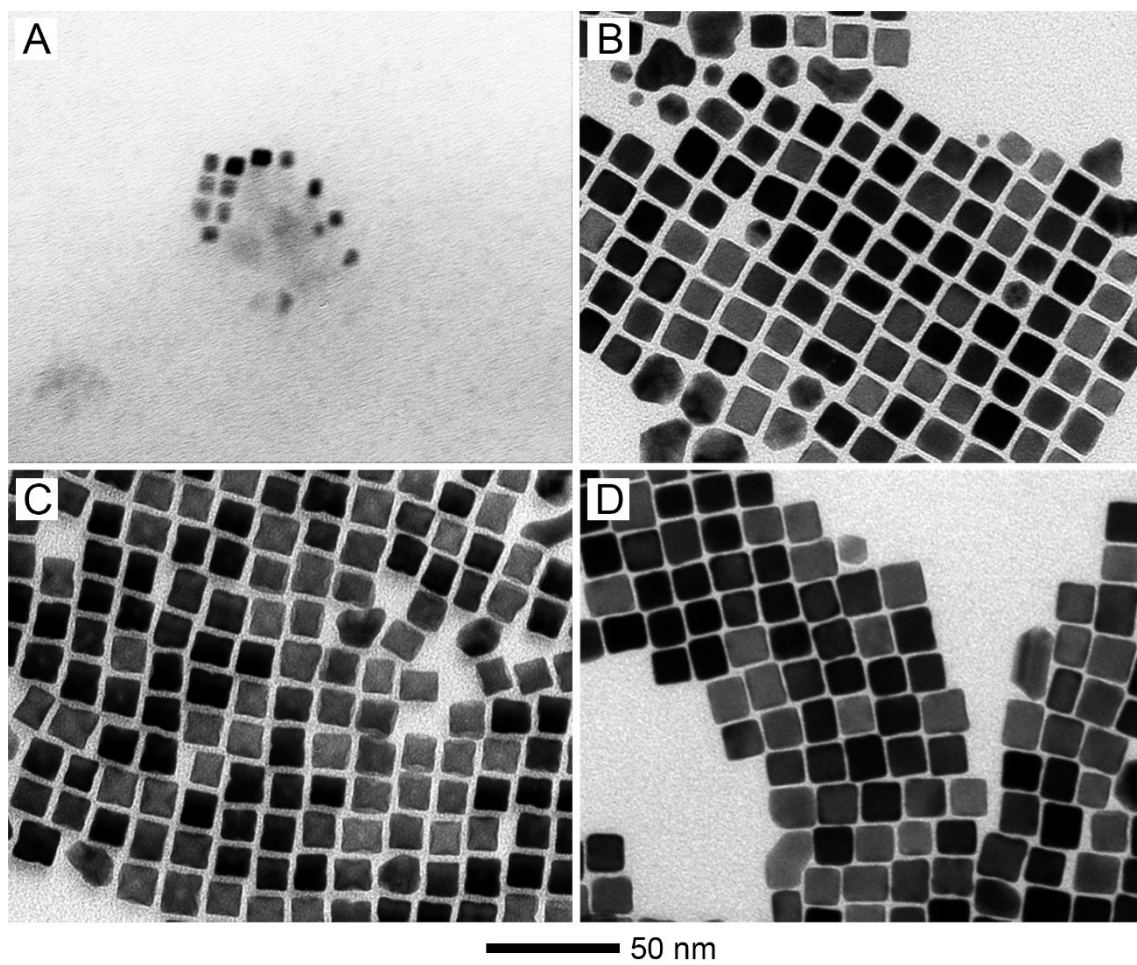**Figure S4.** XRD patterns of nanocrystals with a shape of cube (A) and icosahedron (B).

Figure S5. TEM images of the Pt-Ru nanocrystals prepared using the standard procedure for the cubes, except for different periods of time: (A) 5, (B) 10, (C) 30, and (D) 60 min.
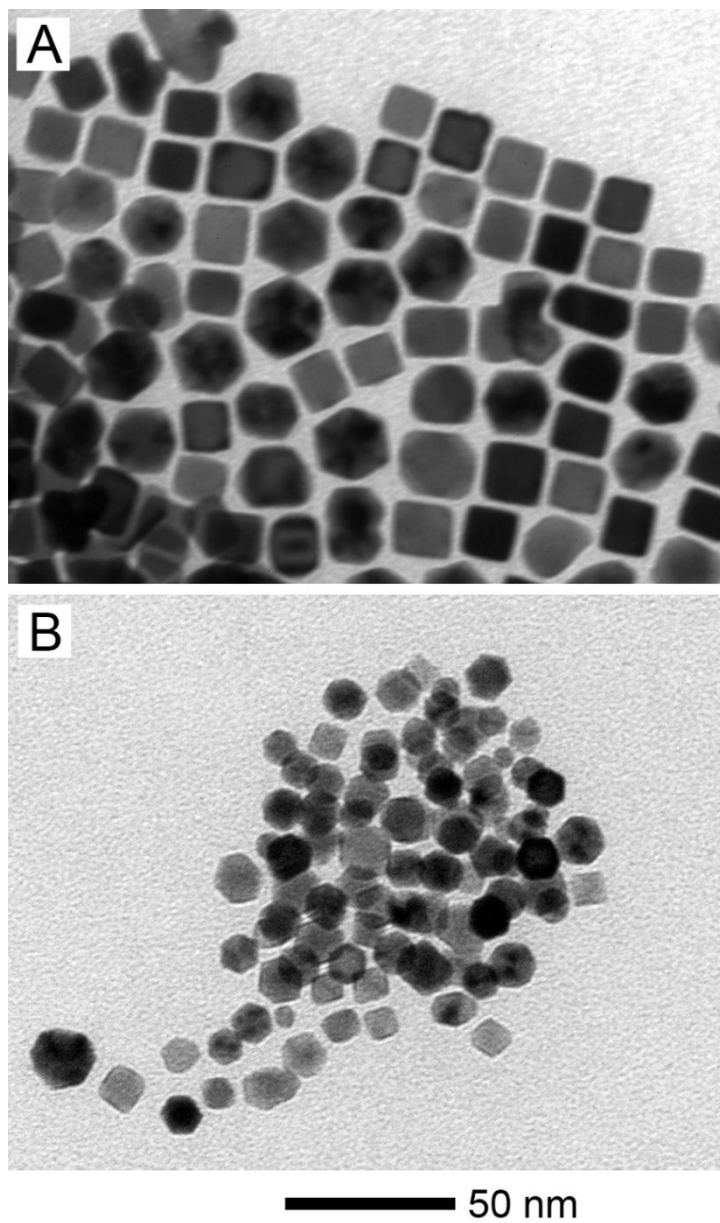
Figure S6. TEM images of Pt-Ru nanocrystals that were obtained using the standard procedure for the cubes, except for different Pt/Ru molar ratios: (A) 1:1 and (B) 3:2.
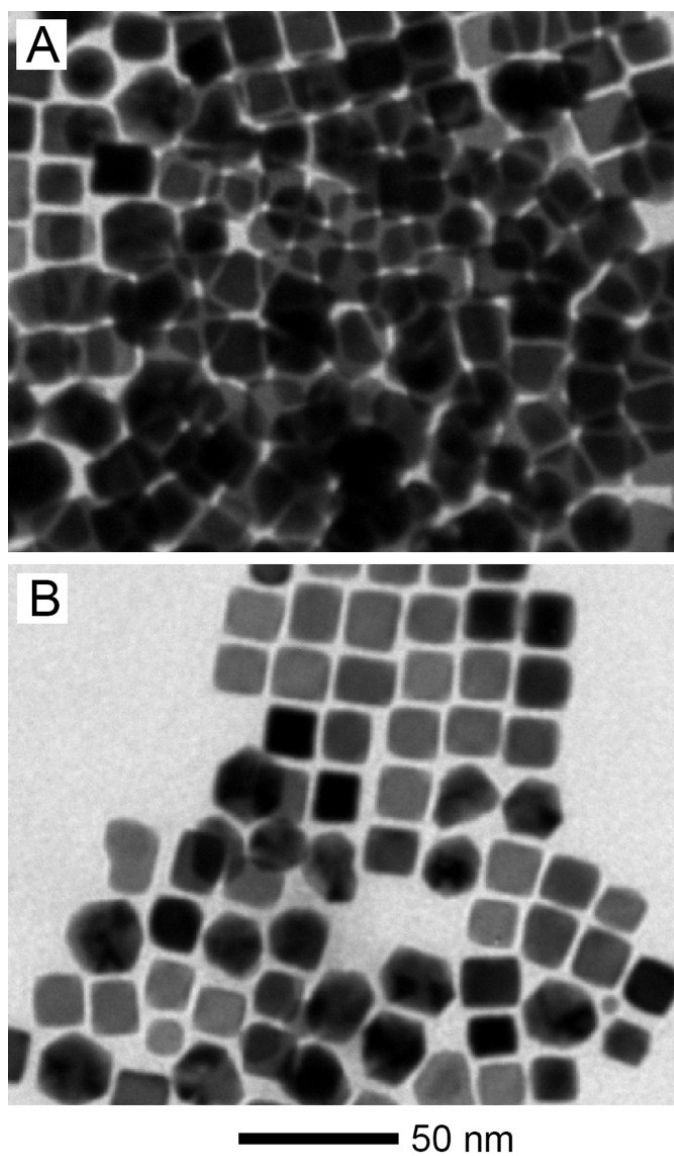
Figure S7. TEM images of the Pt-Ru nanocrystals prepared using the standard procedures for the cubes, except for different amount of TOPO: (A) 55 and (B) 220 mg.
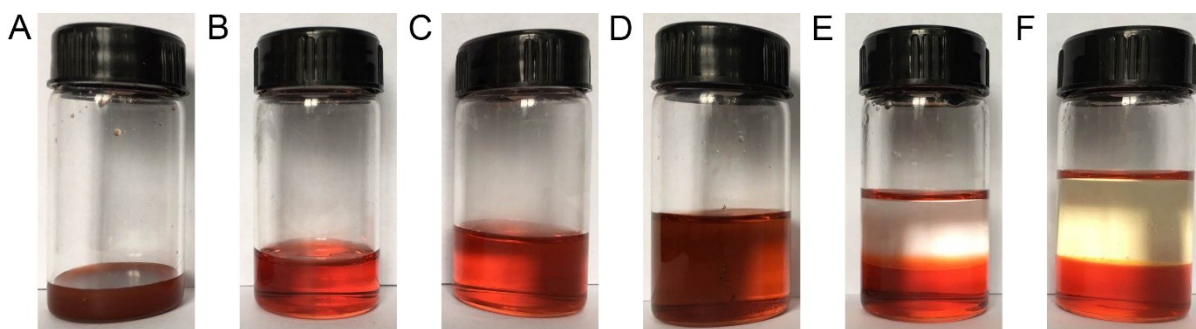
Figure S8. Photographs of the stock solutions prepared by dissolving Pt and Ru salt precursor into different solvents: (A) OAm, (B) DMF, (C) OAm + DMF, (D) OAm + hexadecane, (E) DMF+hexadecane, (F) OAm + DMF +hexadecane. The Pt and Ru salt precursors in DMF show a wine red color, but such precursors in OAm have a dark red color. From Figure S8F, DMF has a higher solubility to the precursors than OAm. DMF and OAm can be miscible in a mixture (Figure S8C). However, the addition of hexadecane in the mixture facilitates the formation of two phase solution (i.e., one phase contains OAm and hexadecane and the other consists of DMF). DMF containing the Pt and Ru precursors was observed to stay in the bottom layer of the vial, as shown in Figure S8F.
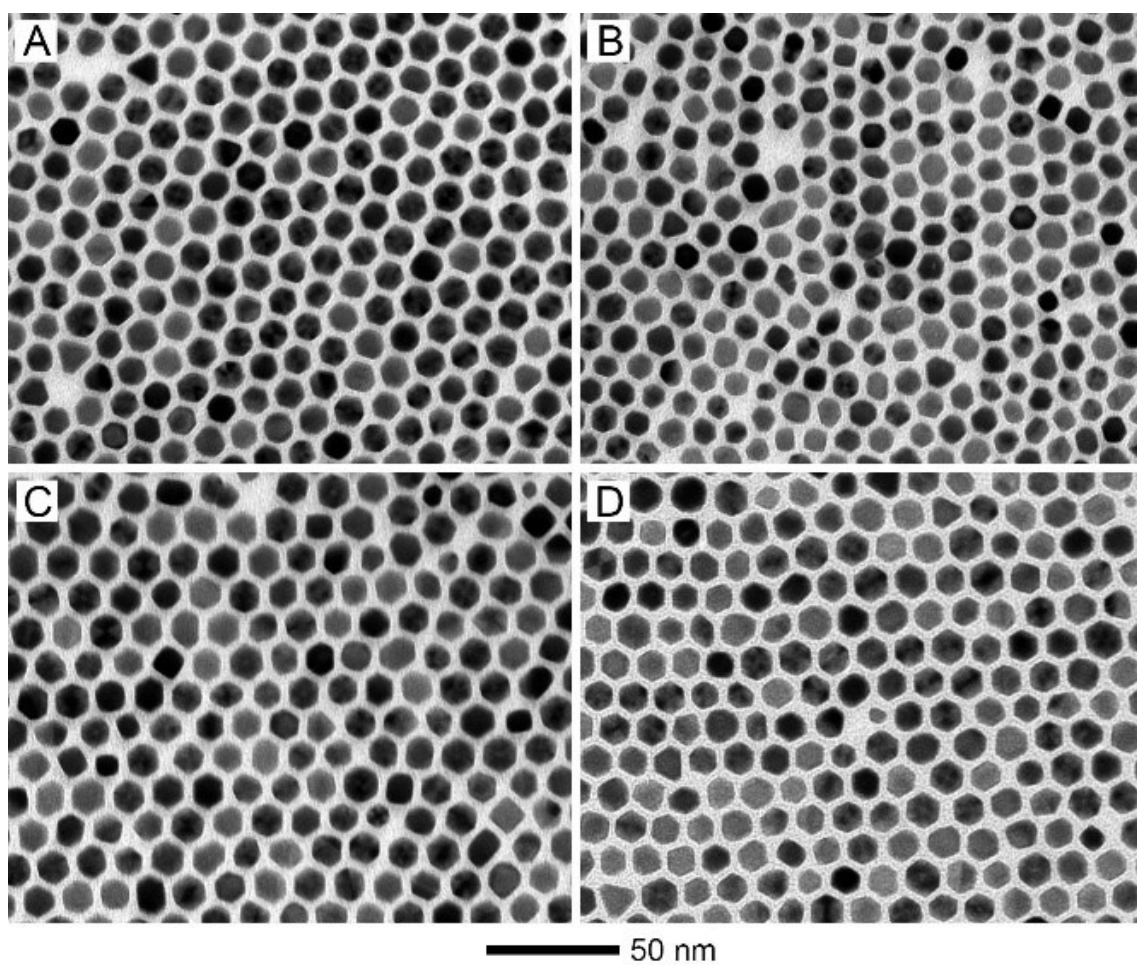
Figure S9. TEM images of the Pt-Ru bimetallic nanocrystals prepared using the standard procedure for the icosahedra, except for different periods of time: (A) 10, (B) 30, (C) 60 and (D) 120 min.
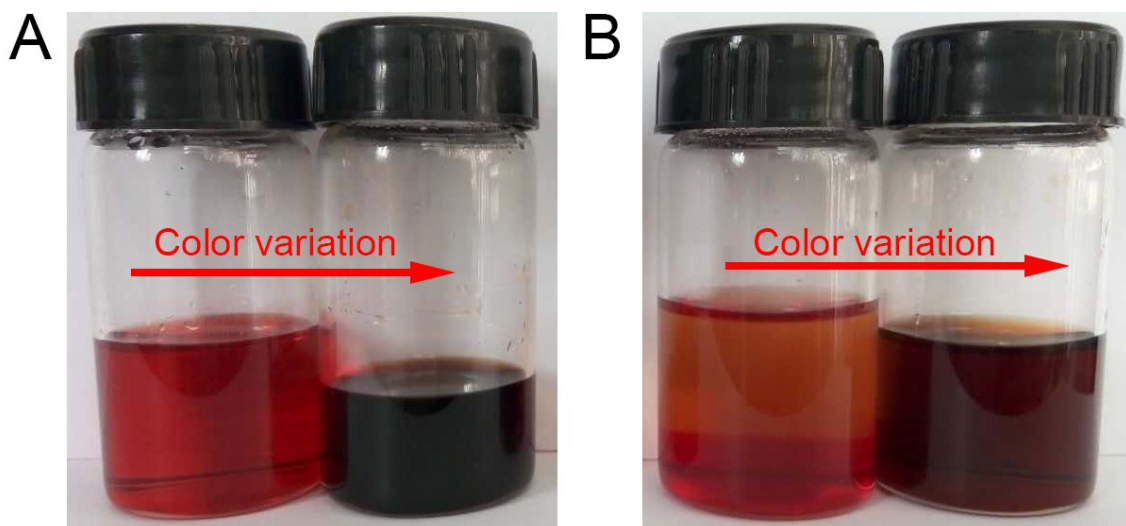
Figure S10. Photographs showing the color variation of the different stock solution at 220 °C for 5 min for the synthesis of (A) Ru decorated Pt cubes and (B) Ru decorated Pt icosahedra.
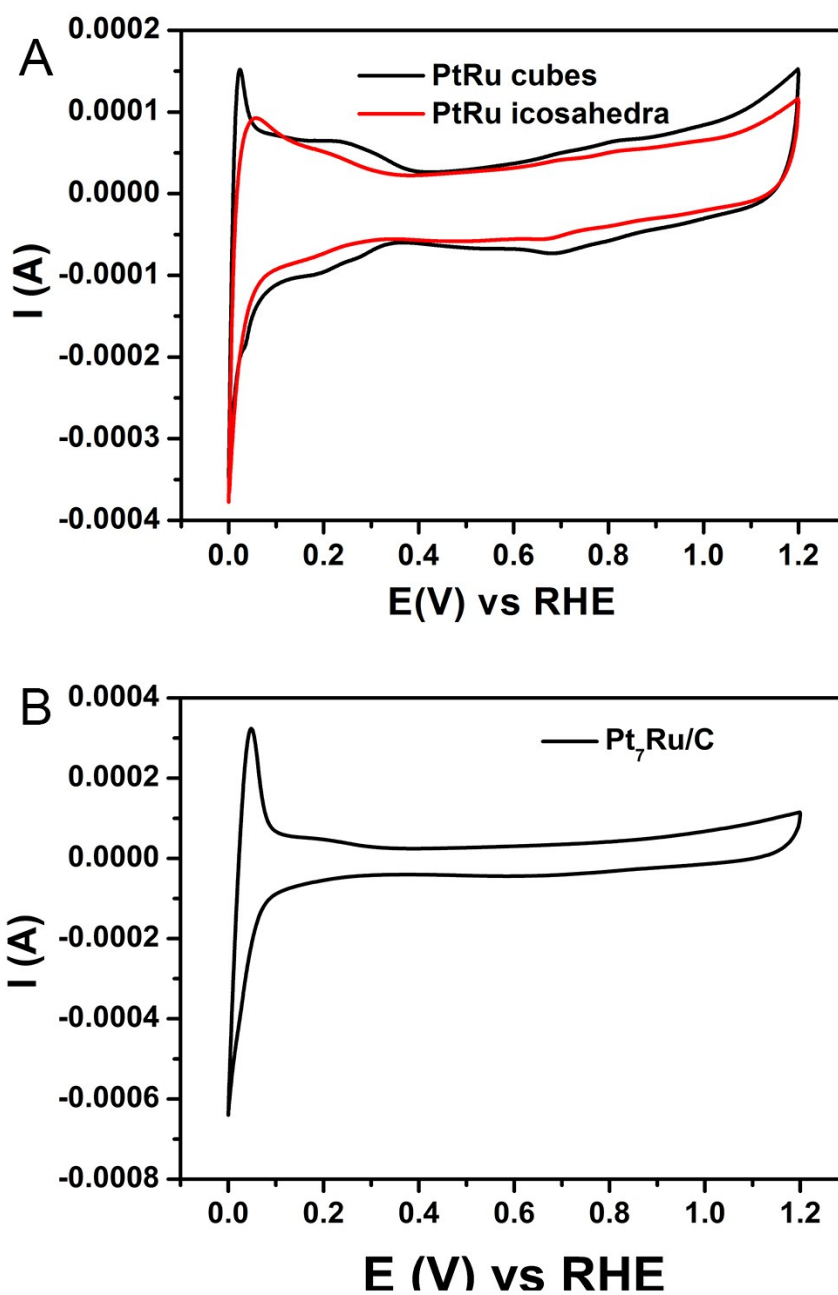
Figure S11. Cyclic voltammograms (CVs) of (A) Ru decorated Pt cubes and icosahedra and (B) Pt_7Ru/C in an Ar-saturated 0.1 M $HClO_4$ solution at a sweep rate of 50 mV/s.
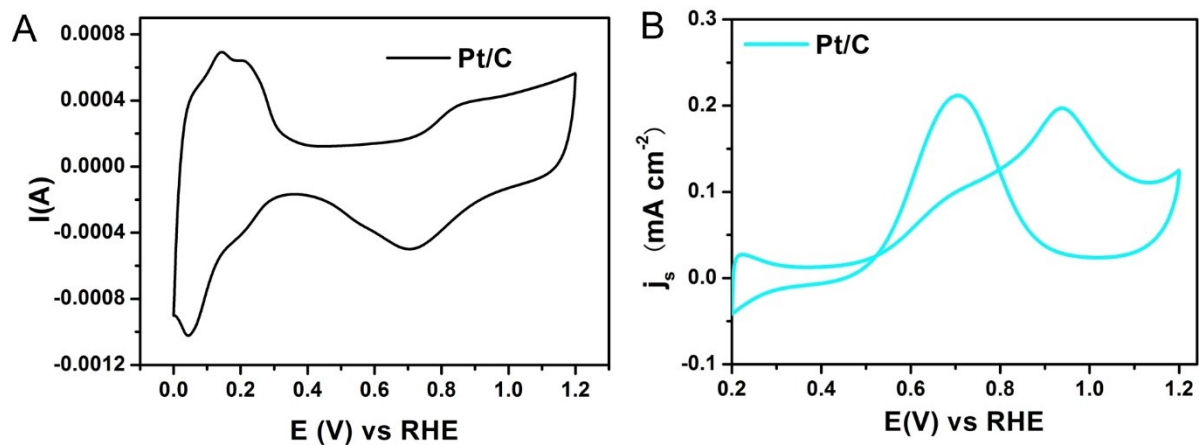
Figure S12. (A) Cyclic voltammograms (CVs) and (B) specific activity of the commercial Pt/C in Ar-saturated 0. 5 M H_2SO_4 and 0.5 M MeOH solution at a sweep rate of 50 mV/s.
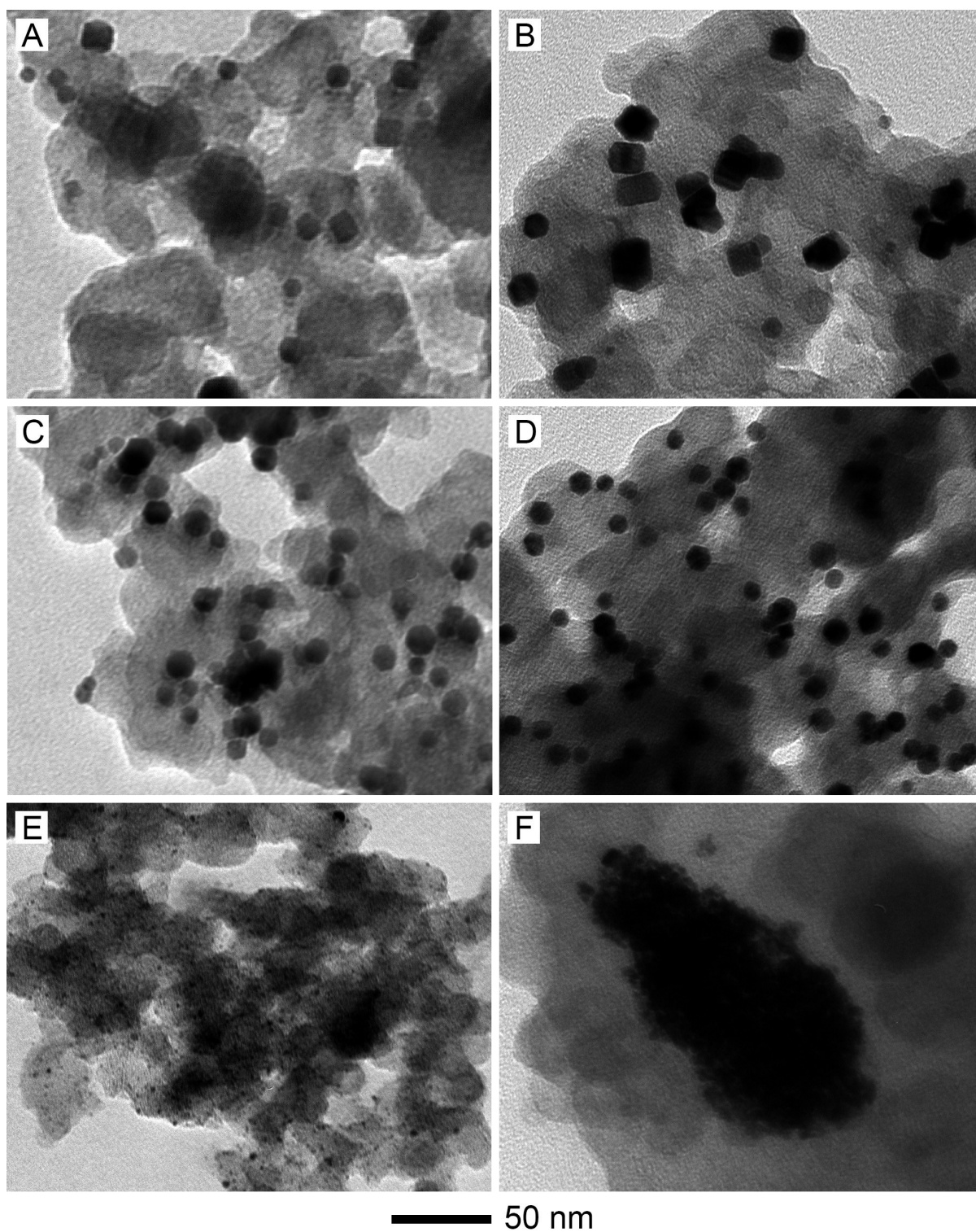
Figure S13. TEM images of PtRu nanocrystals with (A, B) cubic and (C, D) icosahedral shapes and (E, F) Pt$_7$Ru catalysts before and after electrochemical measurements.