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Electronic Supplementary Information

Rational Syntheses of Core-Shell Fe@(PtRu) Nanoparticle Electrocatalysts for Methanol Oxidation Reaction with Complete Suppression of CO-Poisoning and Highly Enhanced Activity

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Table S1. Composition of commercial Pt and PtRu, and Loading amounts of reagents for Fe@(PtRu) samples and Fe@Pt and their ICP-AES analysis data.

Sample (Atomic ratio)	Loading amount (mmole) acac-complexes of			Carbon support (mg)	Amount of element (wt.%) (ICP-AES)			Total metal content (wt.%)
	Pt^{II}	Ru^{III}	Fe^{III}		Pt	Ru	Fe	
Pt/C	-	-	-	-				37.7
$Fe_{0.42}@Pt_{0.58}$	0.12	-	0.08	65.3	21	-	4.4	25.4
PtRu	-	-	-	-	20	10	-	30.0
$(PtRu)_{0.5}$	0.1	0.1	-	68.6	13.8	7.6	-	21.4
$Fe_{0.30}@(PtRu)_{0.35}$	0.1	0.1	0.068	76.7	13.9	7.2	4.0	25.1
$Fe_{0.34}@(PtRu)_{0.33}$	0.1	0.1	0.077	79.3	15.3	8.1	4.7	28.1
$Fe_{0.38}@(PtRu)_{0.31}$	0.1	0.1	0.084	80.7	14.3	7.4	5.3	27.0
$Fe_{0.44}@(PtRu)_{0.28}$	0.1	0.1	0.1	81.9	13.7	7.1	6.1	26.9

Calculations of shell thickness on a sphere core-shell NP

Atomic volumes (V_a, cm^3/mol): Pt, 9.1; Ru, 8.3; Fe, 7.1

In the formula $Fe_x@(PtRu)_{(1-x)/2}$

On the x = 0.30 ($Fe_{0.30}@(PtRu)_{0.35}$) sample:

- Average diameter of the NPs is d = 2.1 nm (from TEM)
  - Radius of a NP (r) = 1/2 × d = 1.05 nm
  - Volume of a NP (V_{NP}) = $4\pi r^3/3$ = 4.85 nm^3
  - Volume fraction of Fe (Vf_{Fe}) = 0.30 V_a(Fe)/(0.30 V_a(Fe) + 0.35 (V_a(Pt) + V_a(Ru)) = 0.259 ……(1)
  - Volume of the Fe core in the NP (V_{Fe}) = $Vf_{Fe} \times V_{NP}$ = 1.25 nm^3
  - Radius of Fe core (R_{Fe}) = $(3/4\pi \times V_{Fe})^{1/3}$ = 0.66 nm

Thickness of (PtRu)-shell = 1.05 – 0.66= **0.39 nm**

On the x = 0.44 ($Fe_{0.44}@(PtRu)_{0.28}$) sample:

- Average diameter of the NPs is d = 2.3 nm (from TEM)
  - Radius of a NP (r) = 1/2 × d = 1.15 nm
  - Volume of a NP (V_{NP}) = $4\pi r^3/3$ = 6.37 nm^3
  - Volume fraction of Fe (Vf_{Fe}) = 0.44 V_a(Fe)/(0.44 V_a(Fe) + 0.28 (V_a(Pt) + V_a(Ru)) = 0.391
  - Volume of the Fe core in the NP (V_{Fe}) = $Vf_{Fe} \times V_{NP}$ = 2.49 nm^3
  - Radius of Fe core (R_{Fe}) = $(3/4\pi \times V_{Fe})^{1/3}$ = 0.84 nm

Thickness of (PtRu)-shell = 1.15 – 0.84 = **0.31 nm**

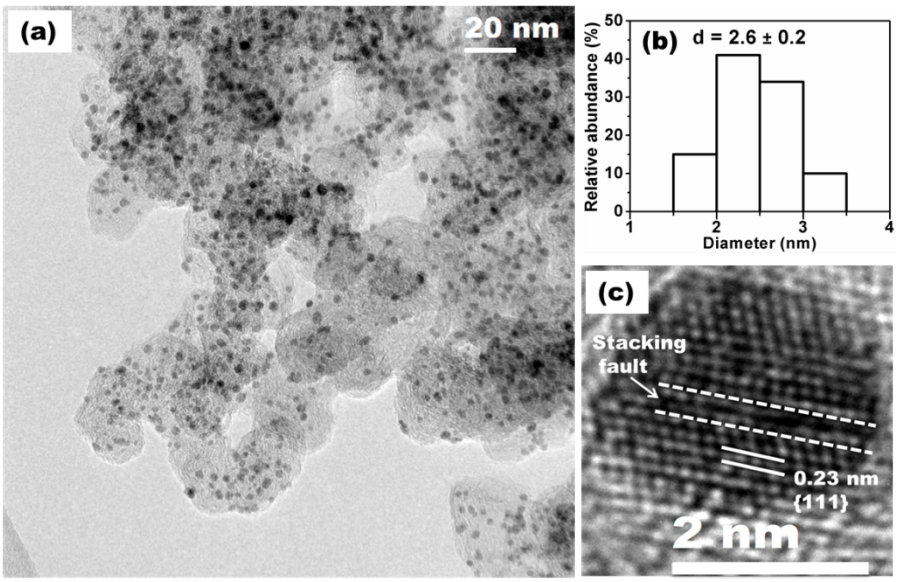

Fig. S1 (a) TEM image, (b) particle size distribution plot (by counting 200 NPs), and (c) HRTEM image of $(PtRu)_{0.5}$.

Table S2. Summary of XPS analyses on PtRu, $(PtRu)_{0.5}$, $Fe_{0.30}@(PtRu)_{0.35}$, and $Fe_{0.44}@(PtRu)_{0.28}$.

Sample	BE (ΔBE with respect to Pt or Ru in $(PtRu)_{0.5}$) (eV)		
	Pt $4f_{7/2}$	Pt $4f_{5/2}$	Ru $3d_{5/2}$
PtRu	71.26	74.51	280.20
$(PtRu)_{0.5}$	71.28	74.45	280.26
$Fe_{0.30}@(PtRu)_{0.35}$	71.43 (+0.15)	74.67 (+0.22)	280.49 (+0.23)
$Fe_{0.44}@(PtRu)_{0.28}$	71.47 (+0.19)	74.72 (+0.27)	280.52 (+0.26)

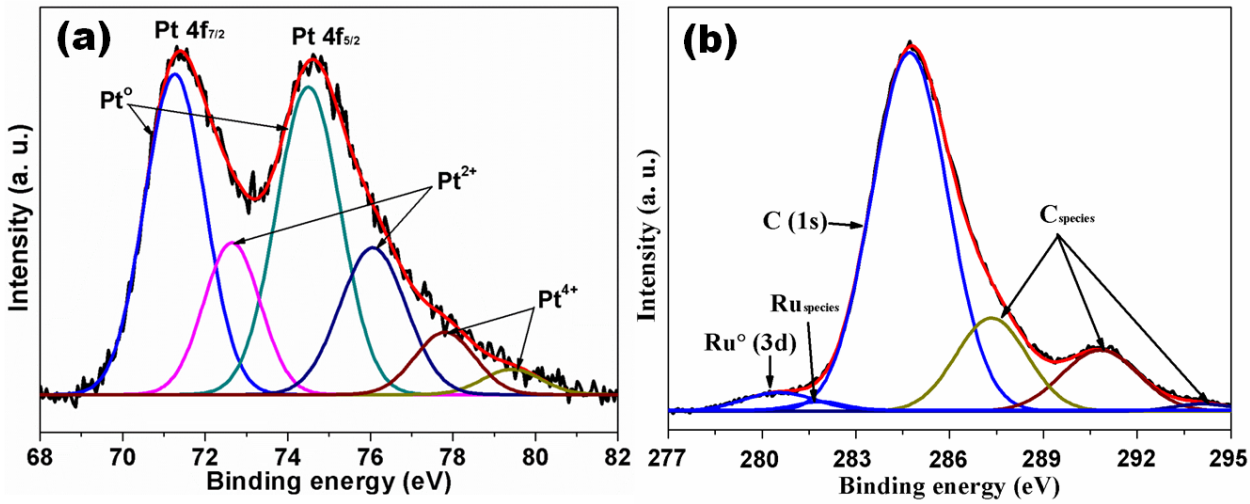

Fig. S2 XPS spectra on (a) Pt 4f region and (b) Ru 3d region of PtRu sample.

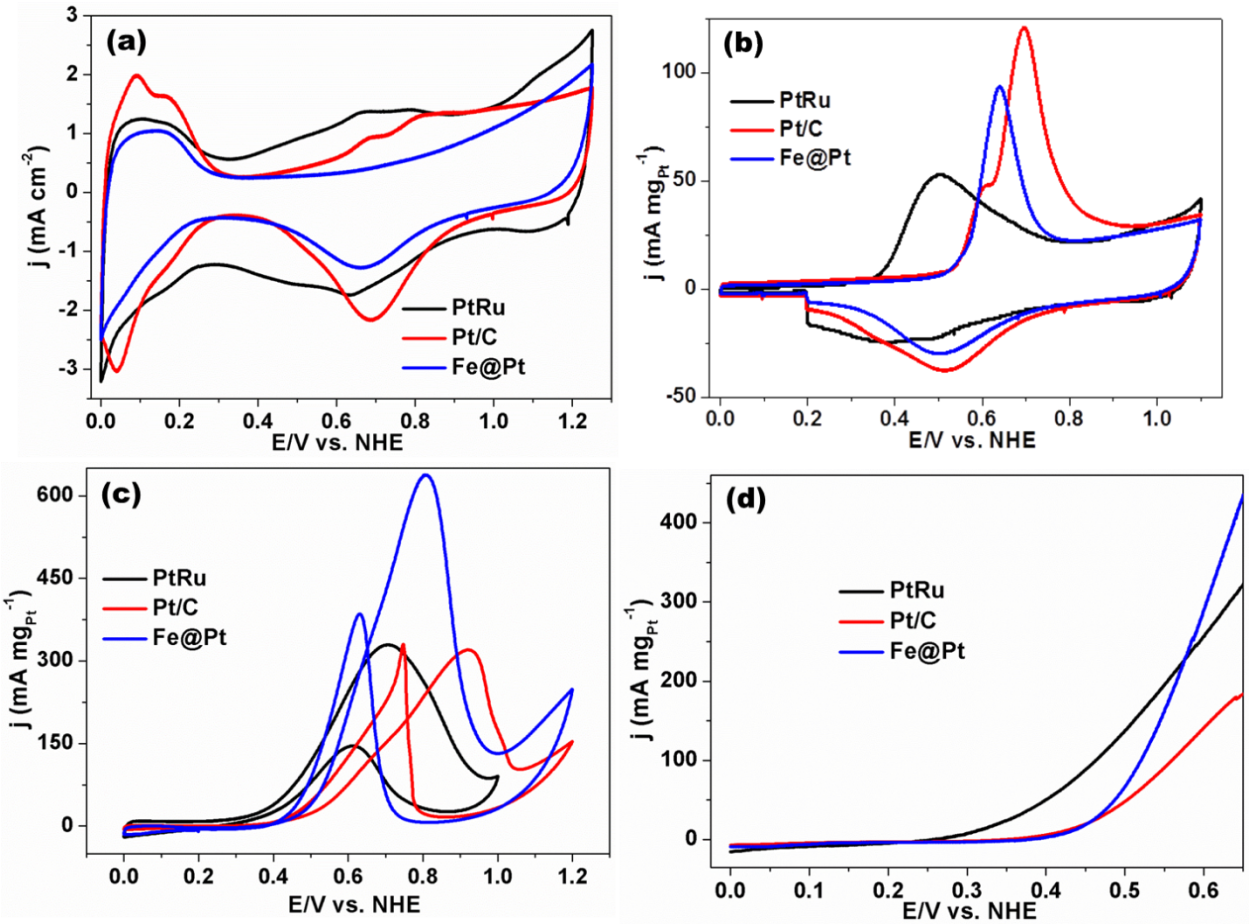

Fig. S3 Comparison of electrochemical data of PtRu, Pt/C, and Fe@Pt: (a) CV, (b) CO-stripping curve, (c) CV of MOR, and (d) LSVs of MOR.

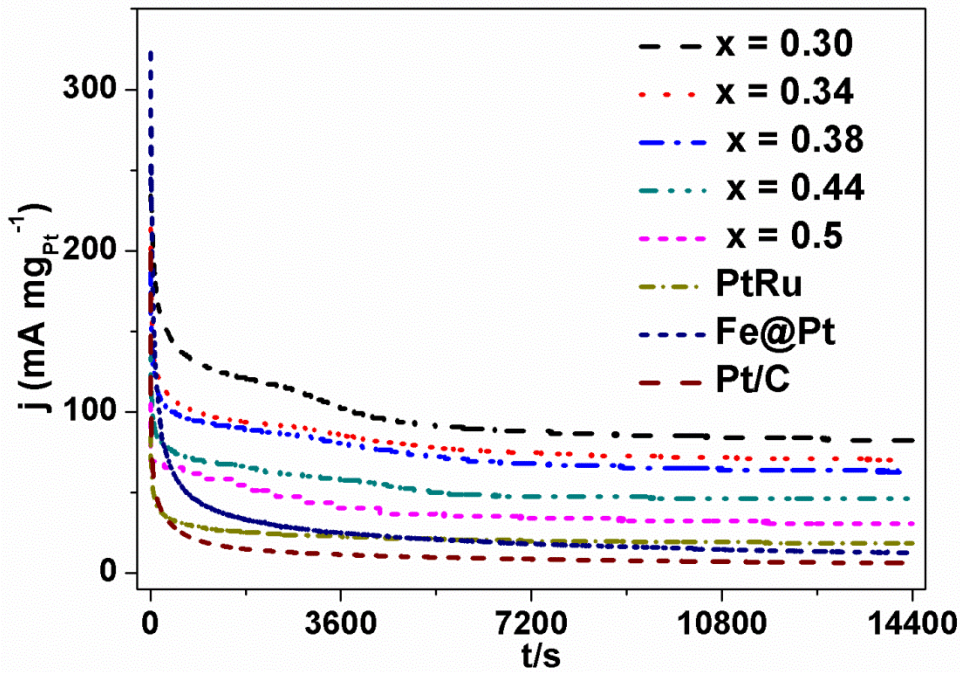

Fig. S4 Chronoamperometric curves of x = 0.0, 0.30, 0.34, 0.38, and 0.44 samples, PtRu, Fe@Pt, and Pt/C at applied potential of 0.65 V.

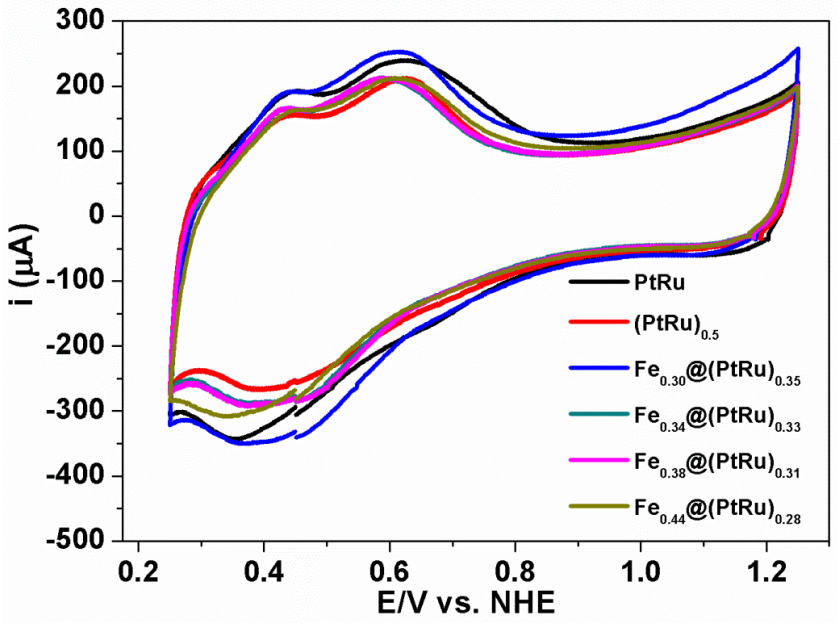

Fig. S5 CV curves of Cu-stripping measurements on $Fe_x@(PtRu)_{(1-x)/2}$ (x = 0, 0.30, 0.34, 0.38, 0.44) and PtRu samples measured in 0.1 $HClO_4$ aqueous solution containing 1 M $CuSO_4$.

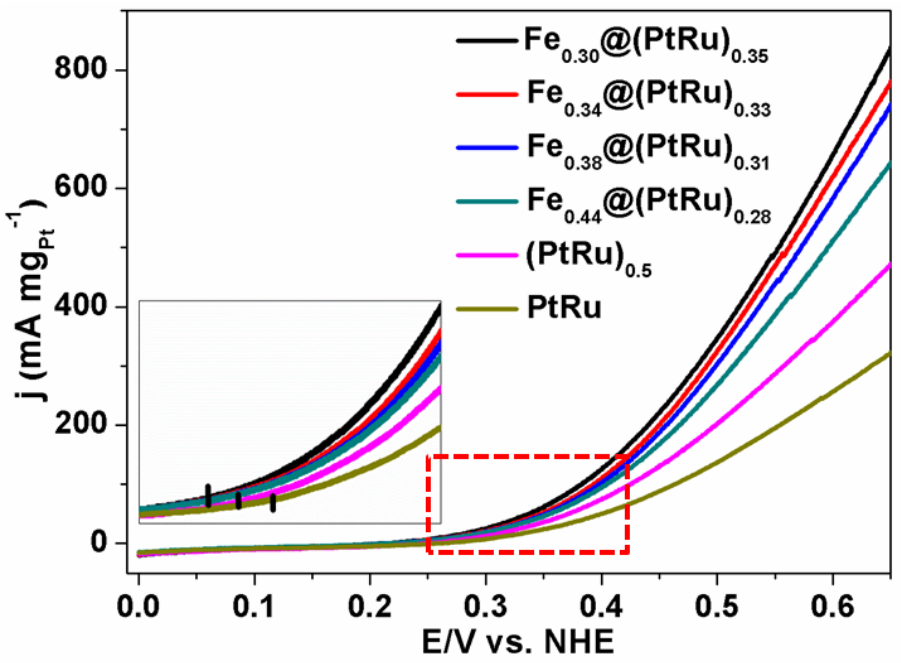

Fig. S6 LSVs of $Fe_x@(PtRu)_{(1-x)/2}$ (x = 0.0, 0.30, 0.34, 0.38, 0.44) and PtRu samples measured in an electrolyte of 0.1 $HClO_4$ containing 1 M CH_3OH. Inset shows onset potentials of MOR on all catalysts.