Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for

Surface and Interface Engineering of FePt/C Nanocatalysts for Electro-Catalytic Methanol oxidation: Enhanced Activity and Durability

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Part I: Figures

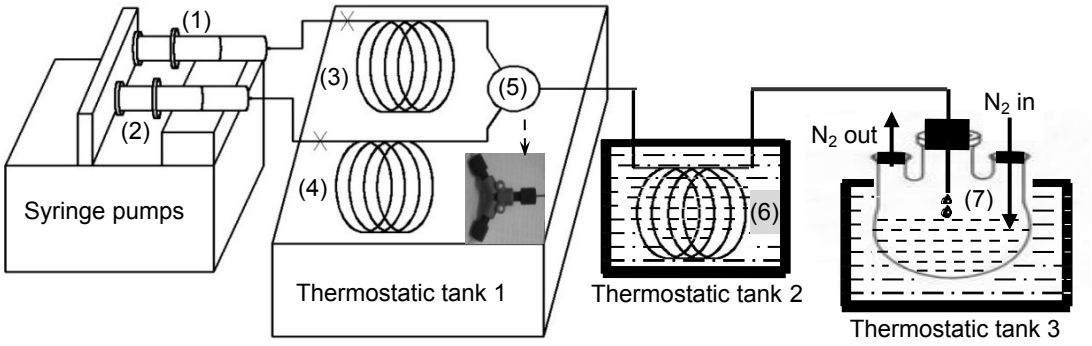

Figure S1 Experiment setup of the simple programmed microfluidic and rapid batch-cooling process：(1) and (2), syringe pumps for the reducing-agent solution and metal-salt solution; (3) and (4), microtubing coils for pre-heating reducing-agent solution and metal-salt solution with the temperature controlled by thermostatic tank 1; (5), three-way mixer for reaction between reducing-agent solution and metal-salt solution; (6), microtubing coil for nucleation and nanoparticle growth with temperature controlled by thermostatic tank 2; (7), nanoparticle receiver with temperature controlled by thermostatic tank 3, where the growth is terminated at a designed temperature (e.g., -15~10^{o}C).

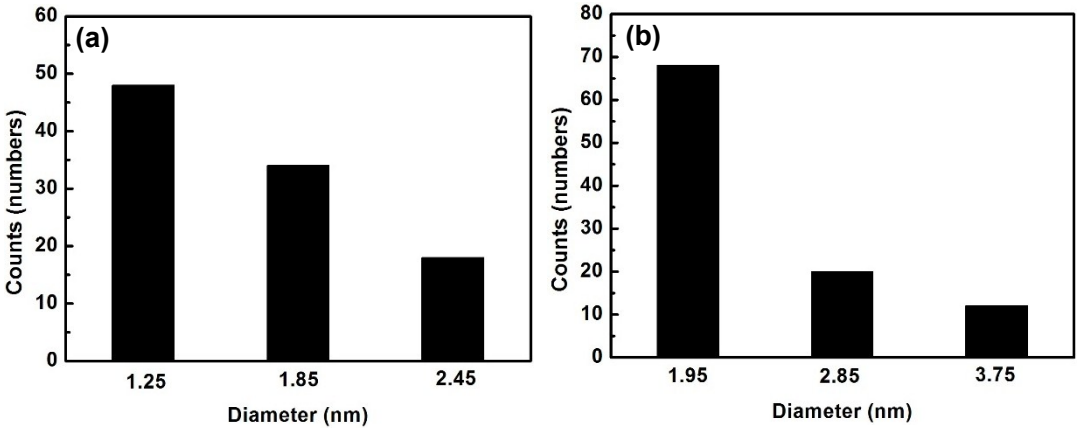

Figure S2 Size distribution of the as-synthesized NCs (a: C4) and the annealed NCs (b: C4-A).

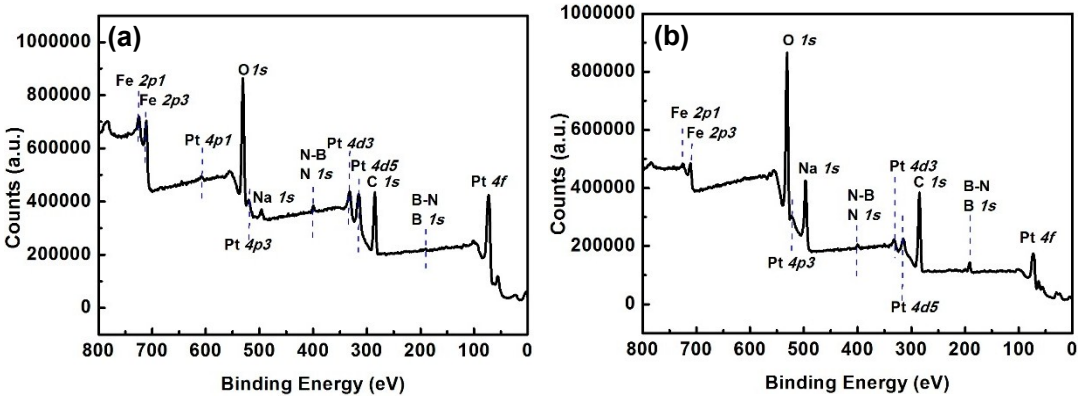

Figure S3 The full range XPS of the as-synthesized NPs (a: FePt/C3) and the annealed NPs (b: FePt/C3A), suggesting existence of Fe, Pt, N, C, O, B, Na elements.

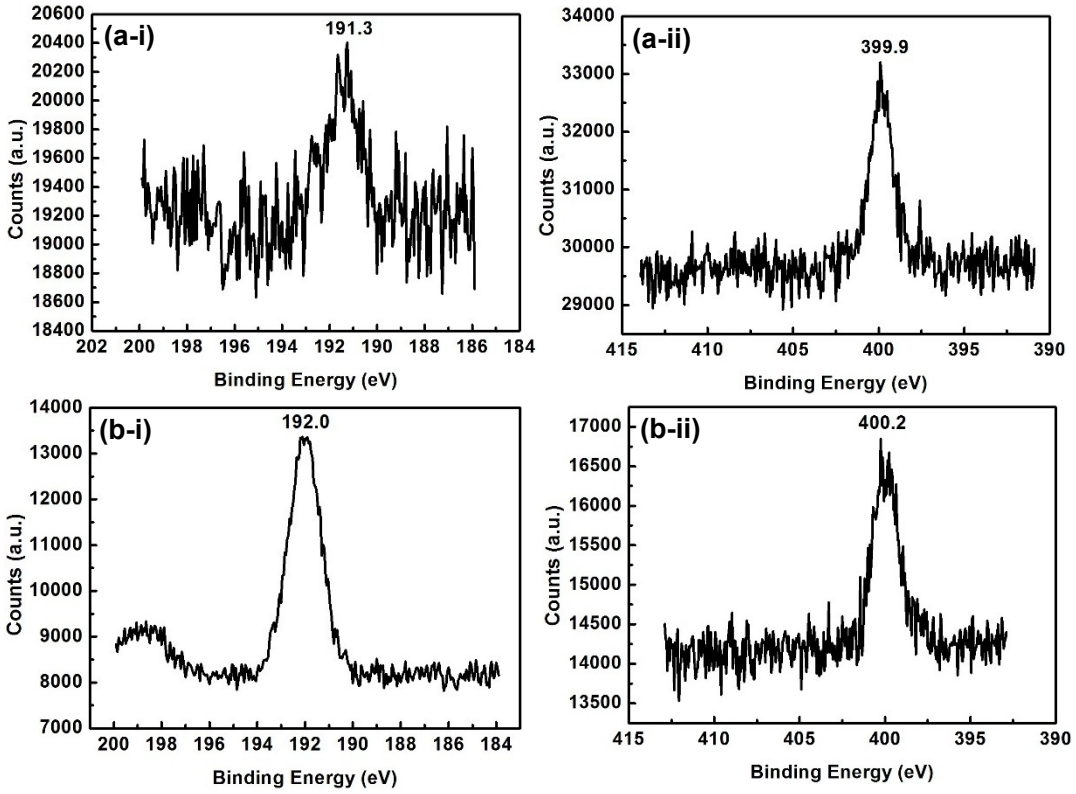

Figure S4 The high resolution XPS spectra of B (i) and N (ii) in the as-synthesized NPs (a: C4) and the annealed NPs (b: C4A).

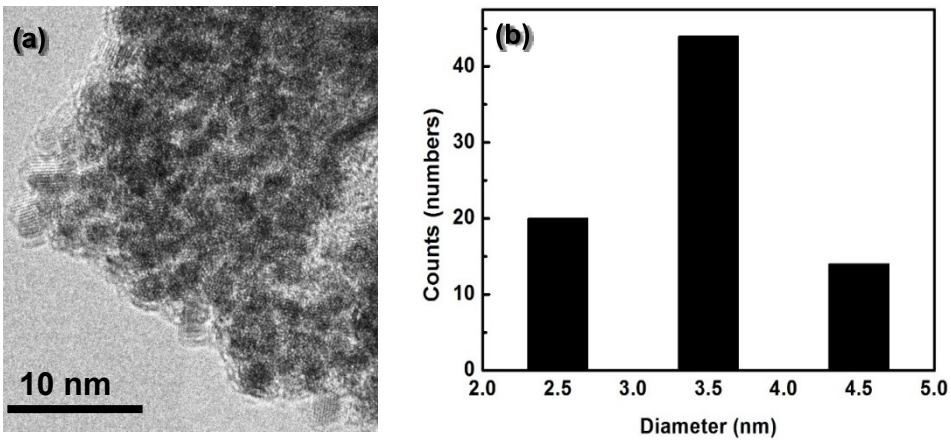

Figure S5 Wide viewed TEM images (a) and size distribution (b) of the annealed Fe-Pt/C prepared by mixing the dried Fe-Pt nanoparticles (sample: C4) with carbon black and then annealed at 350^{o}C for 2 hours under Ar flow.

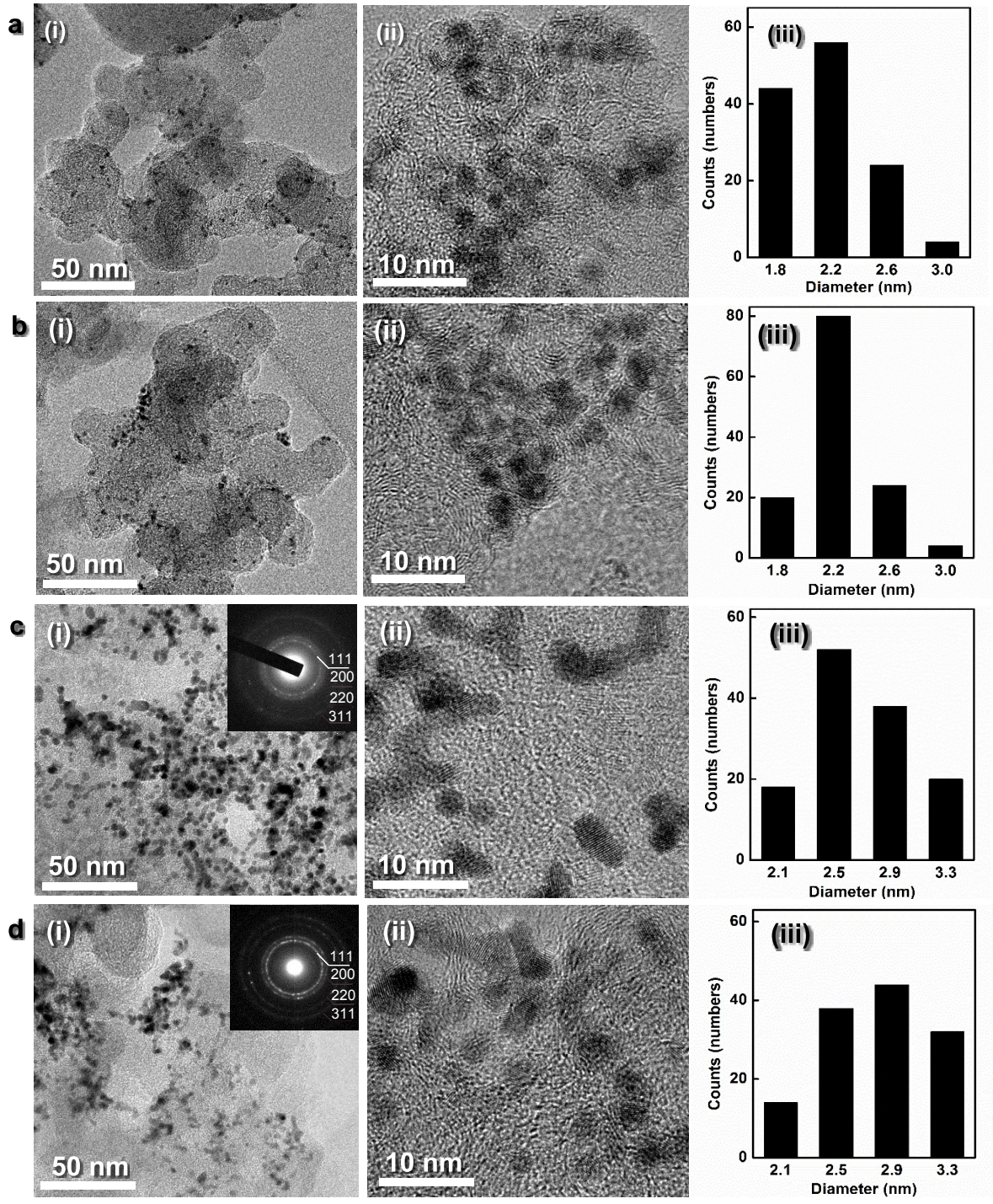

Figure S6 Wide viewed TEM images (i), high resolution TEM images (ii), the corresponding size distribution diagram (iii) of FePt NCs (Fe/Pt = 1.1/1) with *in-situ* carbon-black mixing: (a) the as-synthesized samples before catalytic CV tests (etching). (b): the annealed samples before catalytic CV testing. (c): the as-synthesized samples after catalytic CV testing. (d): the annealed samples after catalytic CV testing. The annealing condition: 350^{o}C for 2 hours under the Ar flow.

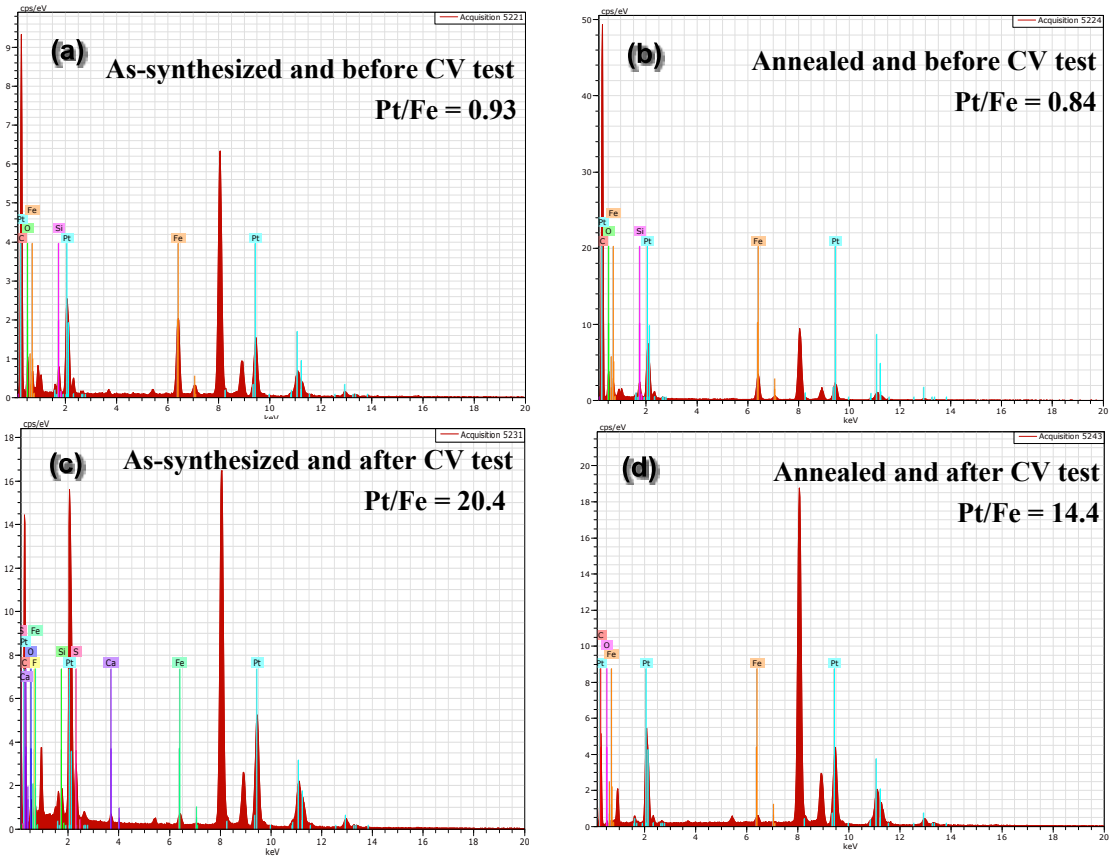

Figure S7 EDS spectra of FePt/C nanocatalysts with a designed Fe/Pt ratio of 1.1/1 prepared by in-situ carbon mixing. (a) the as-synthesized sample before CV tests (etching); (b) the annealed sample before CV tests (etching); (c) the as-synthesized sample after CV tests; (d) the annealed sample after CV tests.

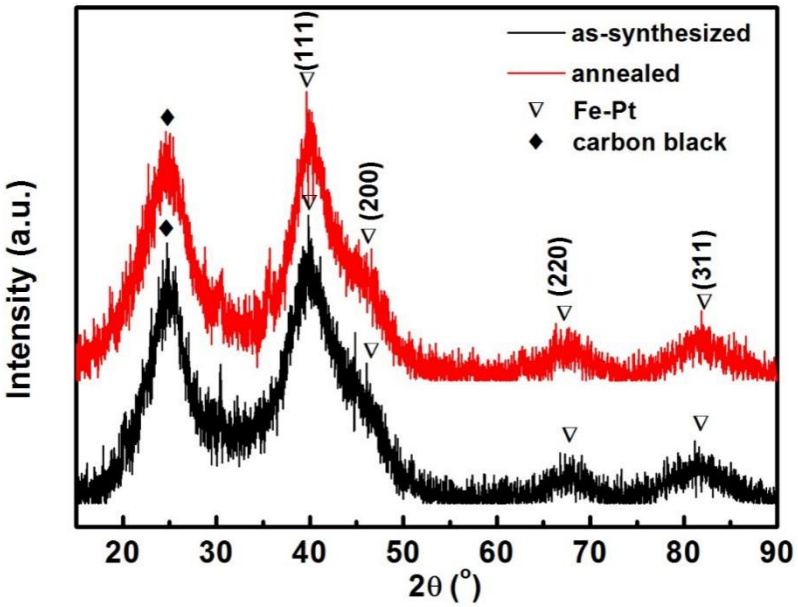

Figure S8 XRD patterns of FePt nanocrystals prepared by *in-situ* carbon mixing before any electrochemical testing for methanol oxidation reaction. Black curve: as-synthesized NCs; red curve: annealed NCs. Broad peaks at 24.7^{o} indicate that most of carbon black is amorphous carbon mixed with some low crystallinity graphite.

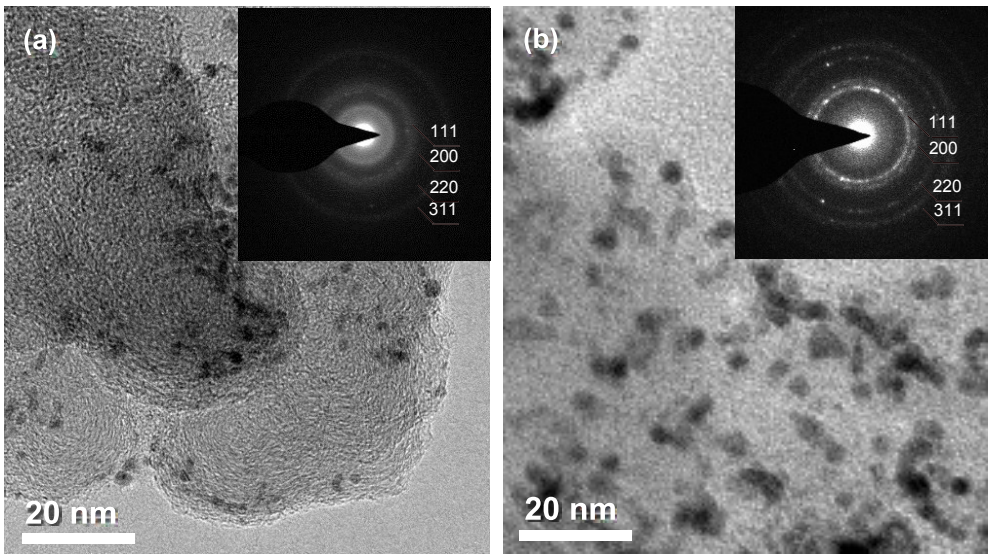

Figure S9 TEM images of the self-made Pt/C nanocatalysts (a) and the commercial Pt/C nanocatalysts (b). Insets: selected area electron diffraction (SAED).

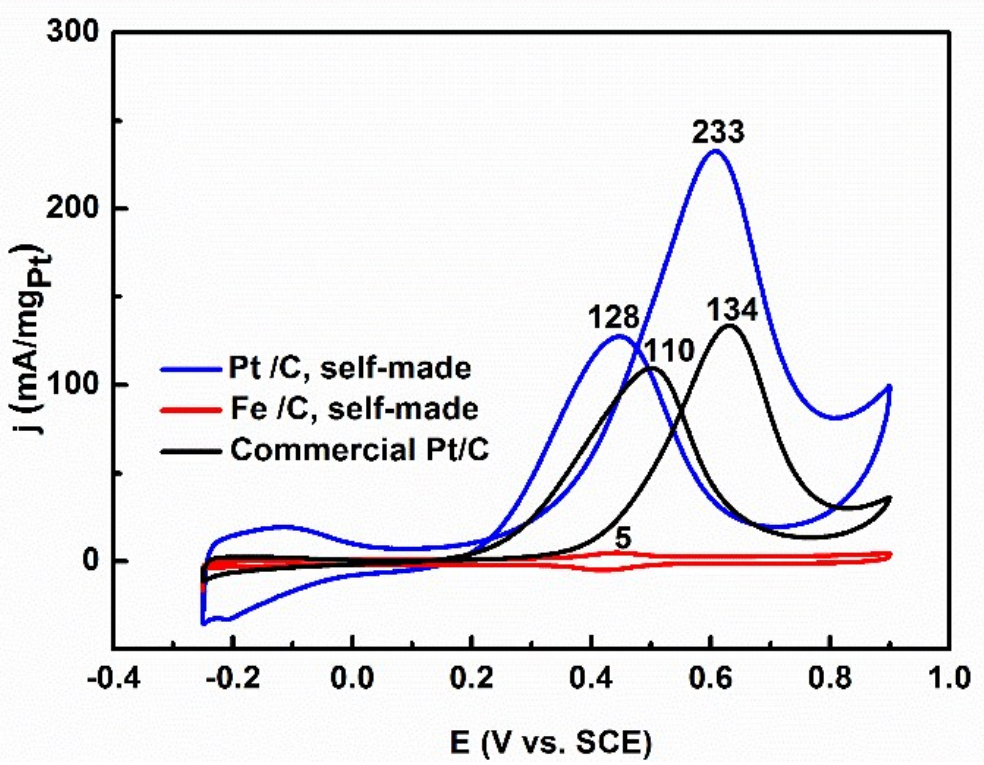

Figure S10 Mass activities of methanol oxidation reaction of self-made Pt/C and Fe/C nanocatalysts after etched in the N_2 saturated 0.1M $HClO_4$ aqueous solution by comparing with the commercial Pt/C nanocatalysts, recorded in N_2 saturated 0.1M $HClO_4$ + 0.5M CH_3OH solution. Data are calculated by the Pt content in the nanocatalyst ink determined by ICP-AES.

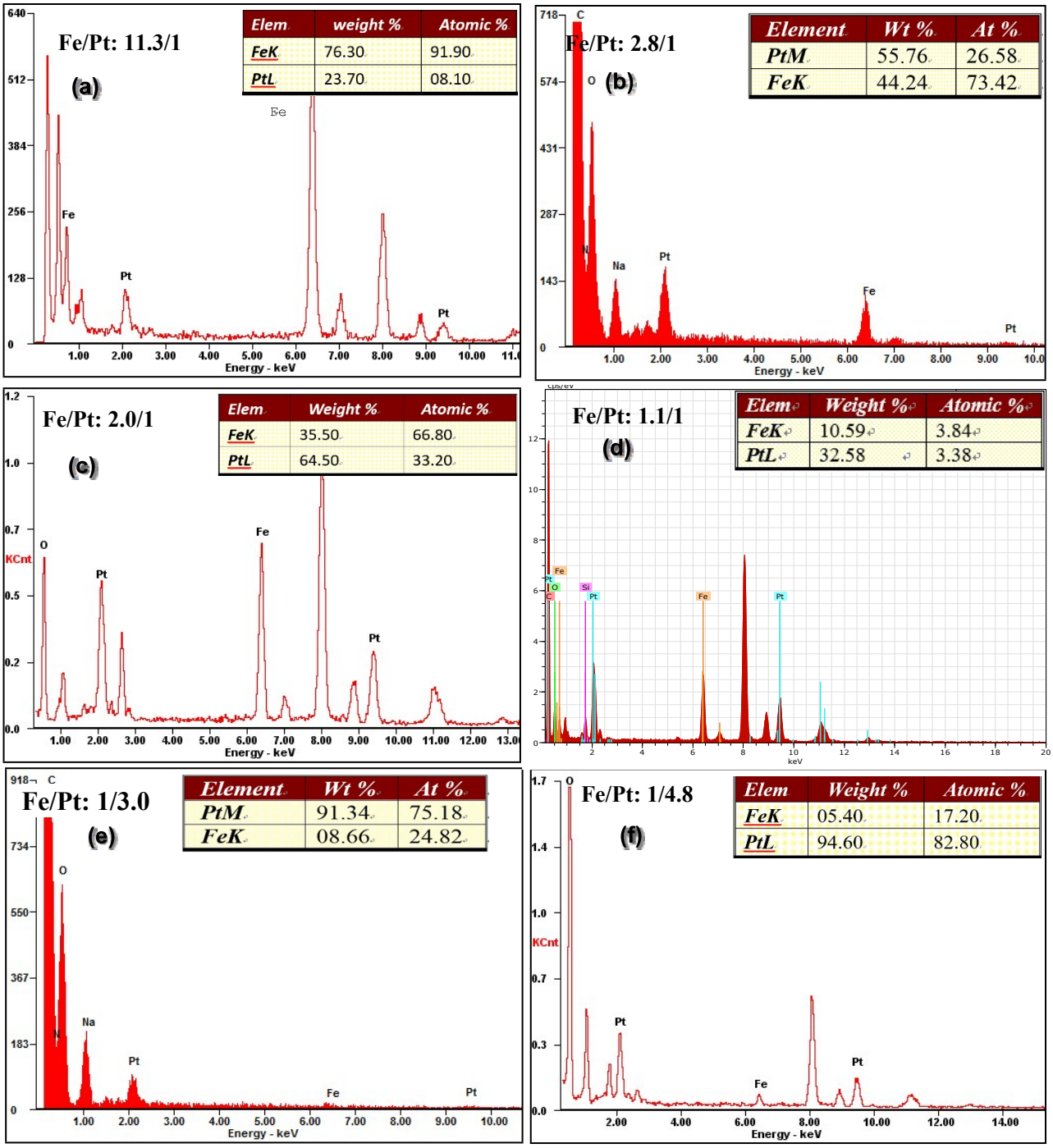

Figure S11 EDS of FePt nanocrystals with Fe/Pt ratios from: (a) 11.3/1; (b) 2.8/1; (c) 2.0/1; (d) 1.1/1; (e) 1:3.0; (f) 1:4.8.

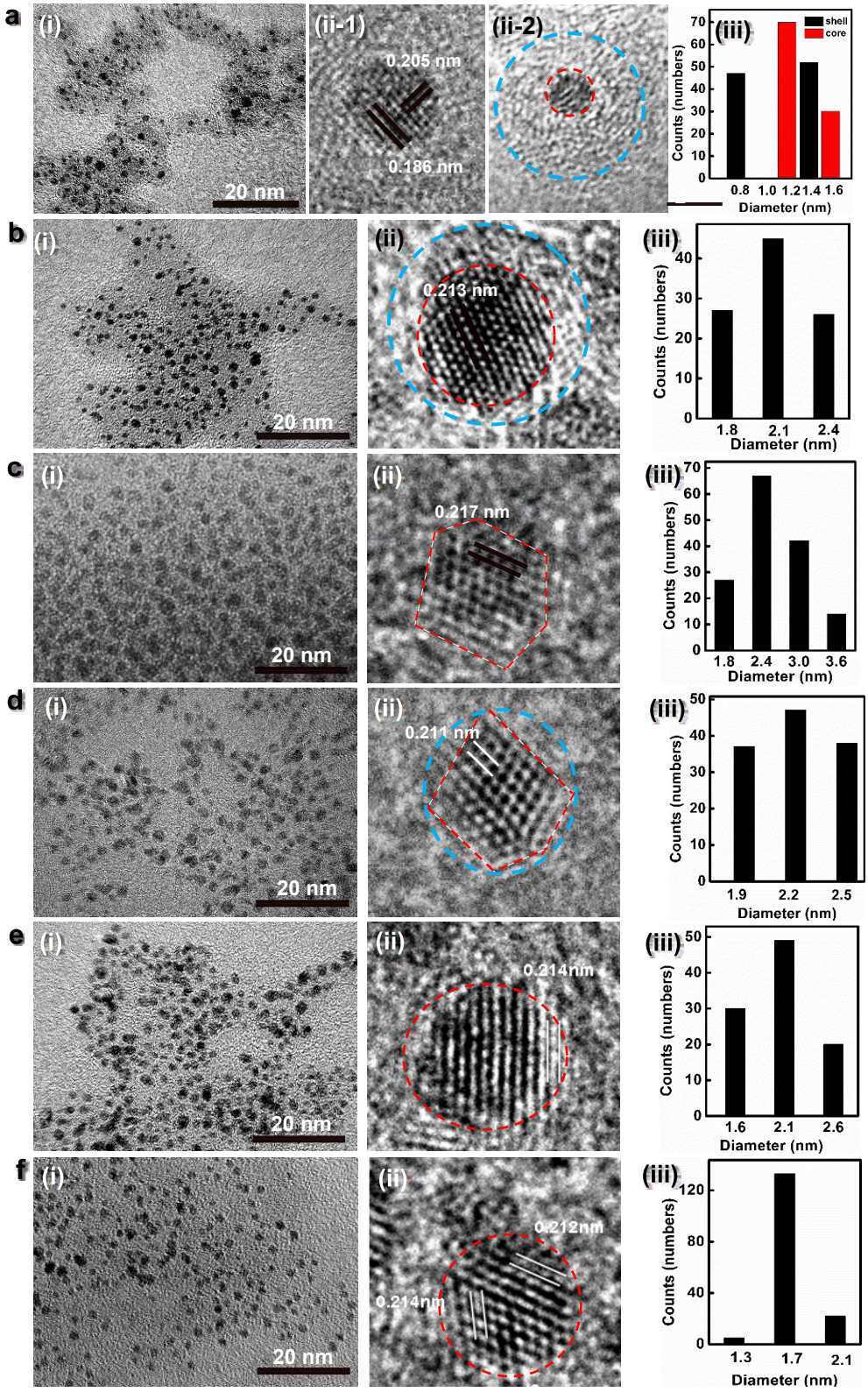

Figure S12 Wide-viewed TEM images (i), high resolution TEM images (ii) and histogram of size distribution (iii) of FePt nanocrystals with Fe/Pt ratios from: (a) 11.3/1; (b) 2.8/1; (c) 2.0/1; (d) 1.1/1; (e) 1/3.0; (f) 1/4.8 determined by energy dispersion X-ray spectrum (EDS, Figure S11).

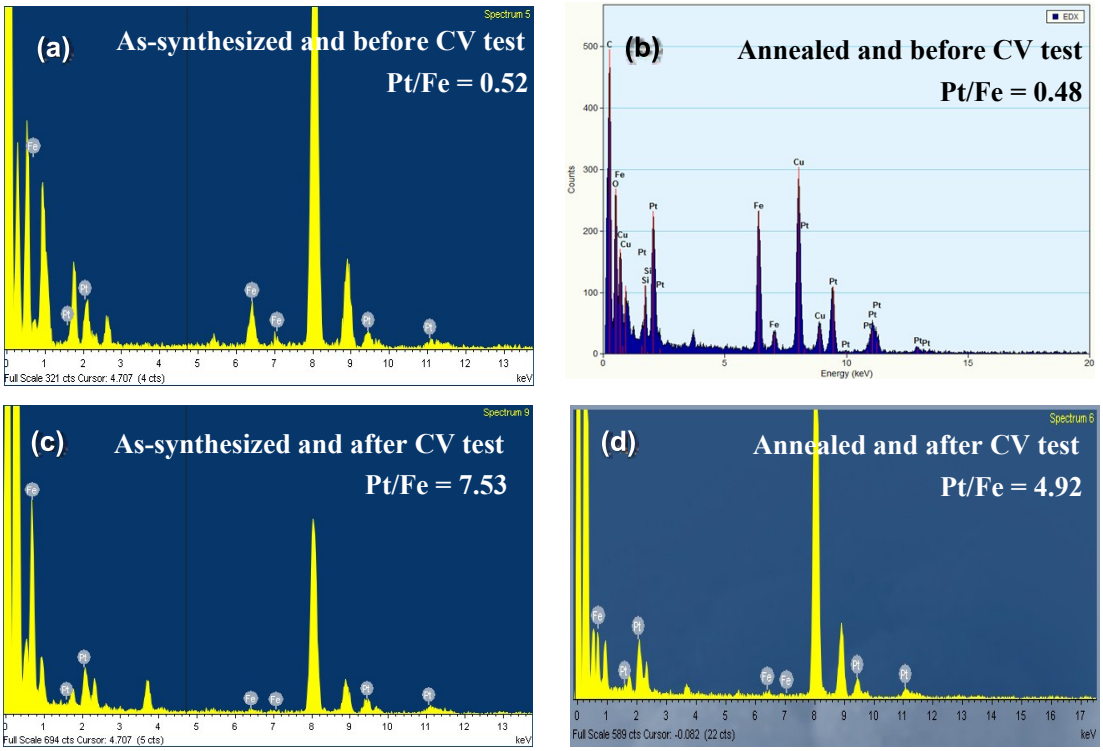

Figure S13 EDS spectra of FePt/C nanocatalysts with a Fe/Pt ratio of 2.0/1 prepared by in-situ carbon black mixing. (a) the as-synthesized sample before CV tests (etching); (b) the annealed sample before CV tests (etching); (c) the as-synthesized sample after CV tests; (d) the annealed sample after CV tests.

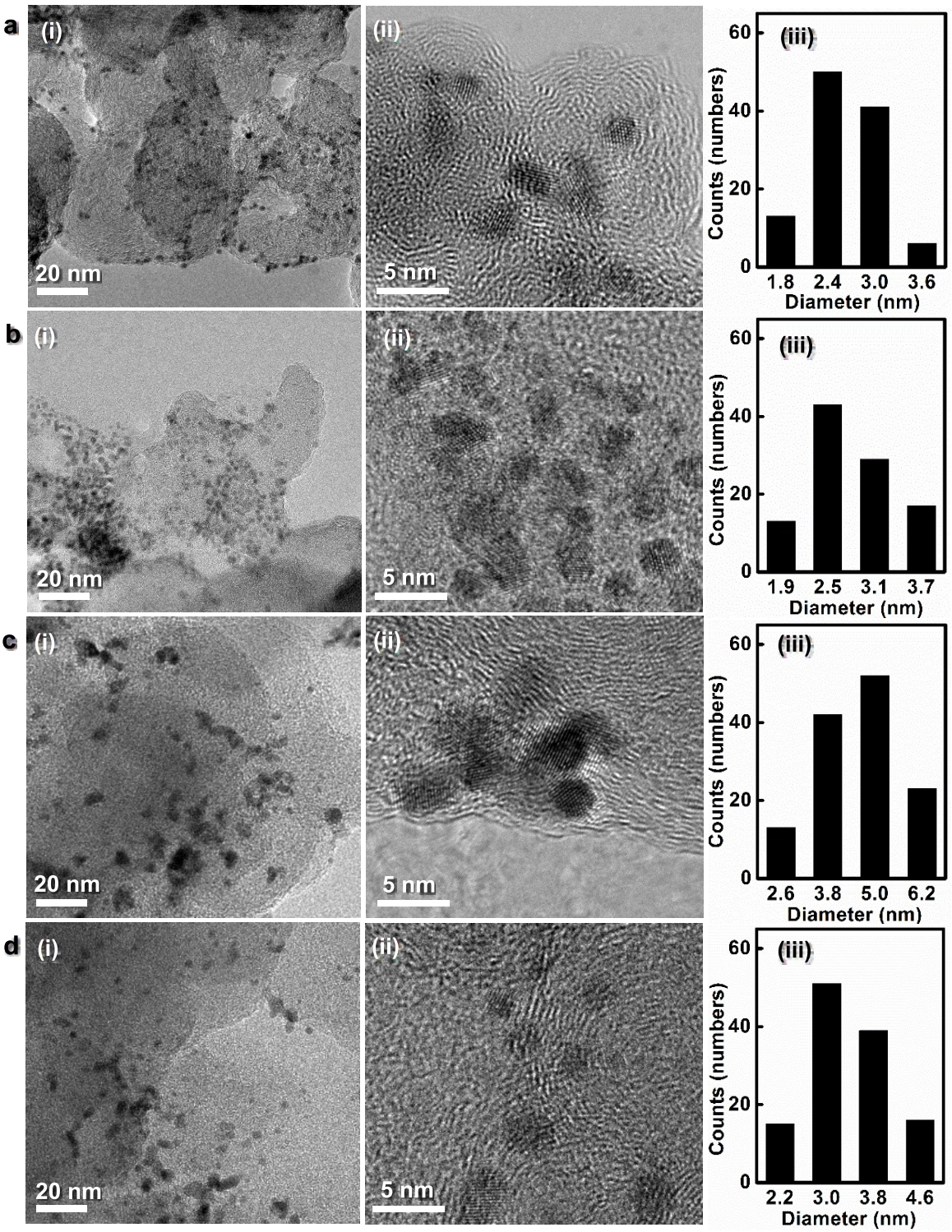

Figure S14 Wide viewed TEM images (i), high resolution TEM images (ii) and histogram of size distribution (iii) of FePt nanocrystals with Fe/Pt ratio of 2/1 prepared by in-situ carbon-black mixing: (a) non-annealed and before etching, 2.60 ± 0.43 nm; (b) annealed and before etching, 2.77 ± 0.55 nm; (c) non-annealed and after etching, 4.59 ± 1.04 nm; (d) annealed and after etching, 3.36 ± 0.71 nm.

Part II: Tables

Table S1 Synthesis conditions of FePt/C nanocomposites

Samples	Metal salts in 50mL NMP (g)[a]		Pt/Fe atom ratio[b]		Annealed or not	Carbon black mixing method [c]
	$FeCl_2 \cdot 4H_2O$	$H_2PtCl_6 \cdot 6H_2O$	designed	By EDS		
C4BE	0.1391	0.3626	1/1	0.88/1	No	Post-mixing
C4ABE	0.1391	0.3626	1/1	0.86/1	Yes	Post-mixing
C4ISBE	0.1391	0.3626	1/1	0.93/1	No	*In-situ* mixing
C4ISABE	0.1391	0.3626	1/1	0.84/1	Yes	*In-situ* mixing

[a] The corresponding reducing solution: 0.3556 g $NaBH_4$ in 50 mL NMP.

[b] Data for nanocrystals before CV tests (etching).

[c] Post-mixing: mixing the carbon black with the dried nanoparticle powder; *in-situ* mixing: mixing the carbon black powder with the nanoparticles as they are growing in the collector.

Table S2 Element distribution in the as-synthesized (C4BE) and annealed (C4ABE) FePt NCs samples by XPS, before etching

Element		C	O	N	B	Fe	Pt	Pt/Fe	Pt atom % of (Pt + Fe)
Atom %	As-synthesized	12.15	33.21	1.24	0.94	25.29	27.17	**1.07**	**51.8**
	Annealed	21.67	48.51	1.12	2.90	13.22	12.58	**0.95**	**48.8**

Table S3 Pt/Fe ratios and electro-catalytic activities of the as-synthesized and annealed samples

Sample	C4	C4A	C4IS	C4ISA	Commercial Pt/C
Method[a]	A	B	C	D	Purchased
E_{onset} (V)	0.39	0.40	0.34	0.36	0.41
E_p (V)	0.60	0.60	0.57	0.61	0.63
j_f (mA/mg-Pt)[b]	527	843	753	1232	134
j_b (mA/mg-Pt)[b]	410	697	493	961	110
j_f/j_b	1.29	1.21	1.53	1.28	1.22

[a] A: The as-synthesized Fe-Pt NCs are mixed with carbon black powder after they are dried; B: The as-synthesized Fe-Pt NCs are annealed under Ar flow for 2 hours and then mixed with carbon black powder; C: The as-synthesized Fe-Pt NCs are *in-situ* mixed with carbon black powder as they grow in the collector and then dried; D: The as-synthesized Fe-Pt NCs are *in-situ* mixed with carbon black powder as they grow in the collector, and then dried and annealed under Ar flow for 2 hours.

[b] According to the Pt contents in the catalyst ink measured by ICP-AES.

Table S4 The average sizes of the as–synthesized and the annealed Fe-Pt nanocrystals calculated from their XRD spectra with Lorentz fit and Scherrer equation

Samples	2θ (degree)	FWHM (degree)	Size from XRD (nm)	Size by TEM (nm)
C4 before etching	39.84	4.81	1.74	1.75 ± 0.38
C4A before etching	40.04	3.67	2.28	2.46 ± 0.52
C4/C, mixing NCs (C4) with carbon black and then annealing, before etching	-	-	-	3.46 ± 0.62
C4ISBE before etching	67.46	4.20	2.25	2.17 ± 0.32
C4ISABE, annealed and before etching	67.48	4.18	2.26	2.18 ± 0.26
C4IS, after etching	-	-	-	2.70 ± 0.34
C4ISA, annealed and after etching	-	-	-	2.79 ± 0.36

FWHM: Full Width at Half Maximum

Table S5 EDS results of Pt/Fe atomic ratio in $Fe_{1.1}Pt_1$ nanocrystals prepared by *in-situ* carbon black mixing.

Sample / Pt/Fe	C4ISBE, $Fe_{1.1}Pt_1$[a]	C4ISABE, $Fe_{1.1}Pt_1$[b]	C4IS, $Fe_{1.1}Pt_1$[c]	C4ISA, $Fe_{1.1}Pt_1$[d]
Atomic ratio	0.93	0.84	20.4	14.4

[a] Samples without annealing and before catalytic CV testing.
[b] Samples after annealing and before catalytic CV testing.
[c] Samples without annealing and after catalytic CV testing.
[d] Samples after annealing and catalytic CV testing.

Table S6 Measured Pt/Fe ratios and electro-catalytic activities of samples

Sample	C4	C4A	C4IS	C4ISA	C4ISBE	C4ISABE	Pt/C
Method [a]	A	B	C	D	E	F	Purchased
E_{onset} (V)	0.39	0.40	0.34	0.36	0.30	0.31	0.41
E_p (V)	0.60	0.60	0.57	0.61	0.56	0.61	0.63
j_f (mA/mg-Pt) [b]	527	843	753	1232	793	1394	134
j_b (mA/mg-Pt) [b]	410	697	493	961	445	787	110
j_f/j_b	1.29	1.21	1.53	1.28	1.78	1.77	1.22
ECSA (m^2/g)	16.9	26.5	45.4	55.4	41.8	37.3	38.6

[a] A：Data obtained by testing the FePt NCs after the CV test during which these NCs are etched in the acidic reaction solution. The as-synthesized FePt NCs are mixed with carbon black powder after they are dried; B: Data obtained by testing the FePt NCs after the CV test during which these NCs are etched in the acidic reaction solution. The as-synthesized FePt NCs are annealed under Ar flow for 2 hours and then mixed with carbon black powder; C: Data obtained by testing the FePt NCs after the CV test during which these NCs are etched in the acidic reaction solution. The as-synthesized Fe-Pt NCs are *in-situ* mixed with carbon black powder as they grow in the collector and then dried; D: Data obtained by testing the FePt NCs after the CV test during which these NCs are etched in the acidic reaction solution. The as-synthesized FePt NCs are prepared by *in-situ* mixed with carbon black powder as they grow in the collector, and then dried and annealed under Ar flow for 2 hours; E: Data obtained by directly testing the as-synthesized FePt NCs before etched in the acidic reaction solution during the CV test, which are prepared by *in-situ* mixed with carbon black powder as they grow in the collector and then dried,; F: Data obtained by directly testing the annealed FePt NCs before etched in the acidic reaction solution during the CV test, which are prepared by *in-situ* mixed with carbon black powder as they grow in the collector, and then dried and annealed under Ar flow for 2 hours.

[b] According to the Pt contents of the catalyst inks measured by ICP-AES.

Table S7 The EDS results of Pt/Fe atomic ratio in Fe_2Pt_1 nanocrystals

Sample / Pt/Fe	C3ISBE, Fe_2Pt_1[a]	C3ISABE, Fe_2Pt_1[b]	C3IS, Fe_2Pt_1[c]	C3ISA, Fe_2Pt_1[d]
Atomic ratio	0.52	0.48	7.53	4.92

[a] Samples without annealing and before catalytic testing.

[b] Samples after annealing and before catalytic testing.

[c] Samples without annealing and after catalytic testing.

[d] Samples after annealing and catalytic testing.