Supporting Information

Tailoring the morphology of Pt_3Cu_1 nanocrystals supported on graphene nanoplates for ethanol oxidation

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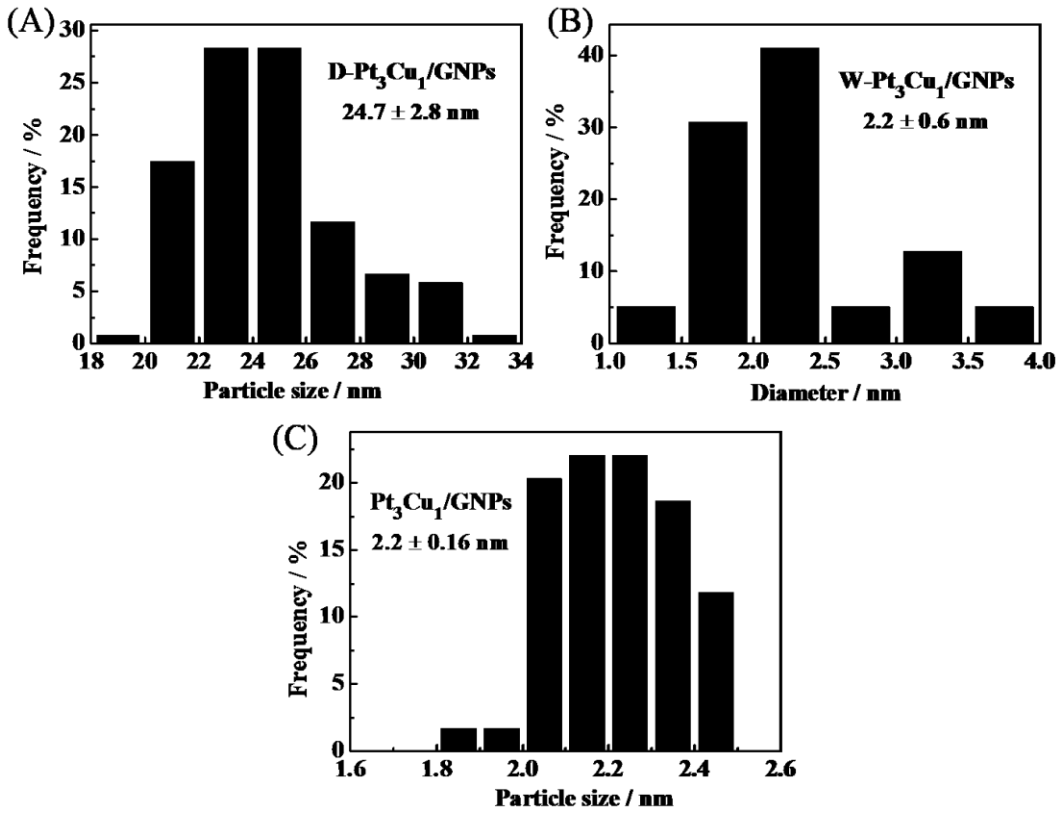

Figure S1 (A) Sizes distributions of D-Pt_3Cu_1/GNPs; (B) Diameter distributions of W-Pt_3Cu_1/GNPs; (C) Sizes distributions of Pt_3Cu_1/GNPs.

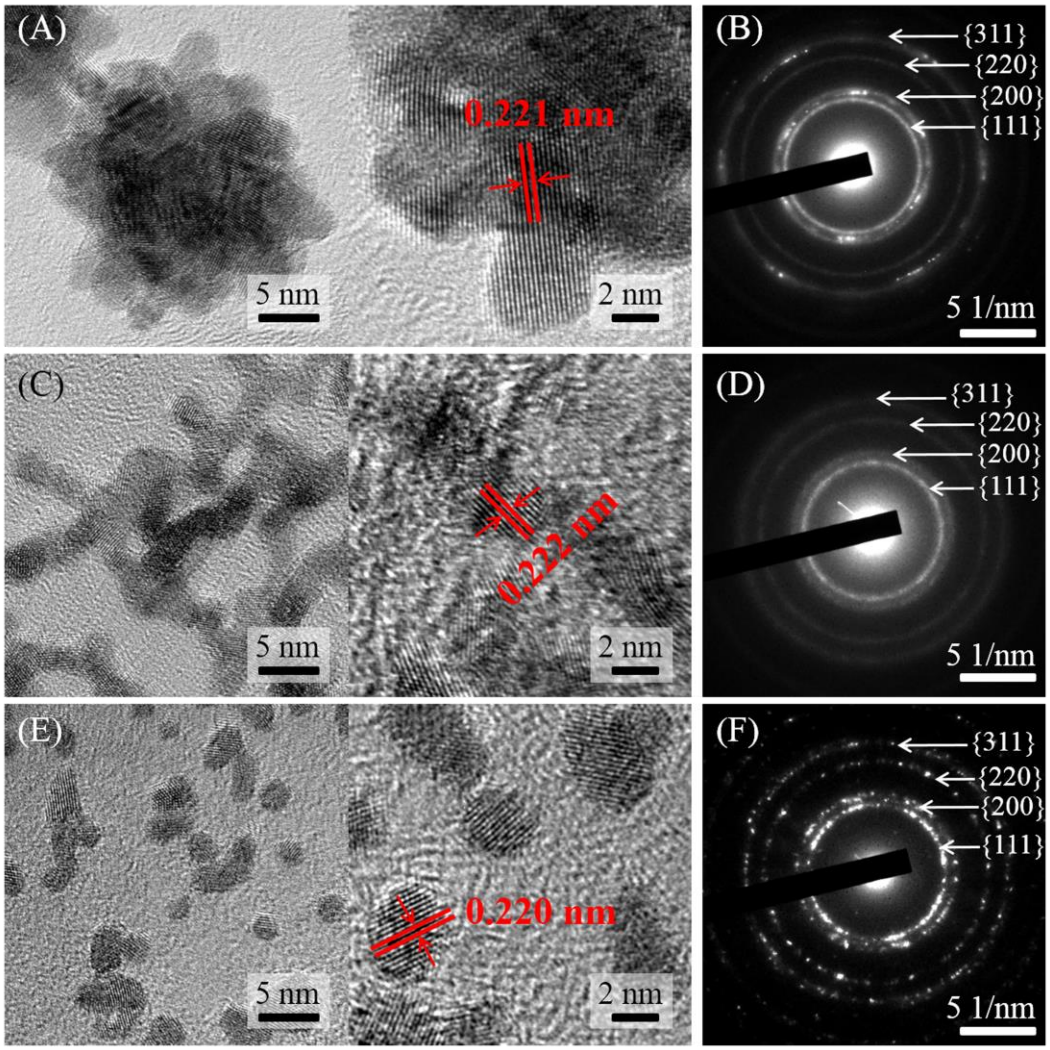

Figure S2 High resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) images of (A, B) D-Pt_3Cu_1/GNPs, (C, D) W-Pt_3Cu_1/GNPs and (E, F) Pt_3Cu_1/GNPs.

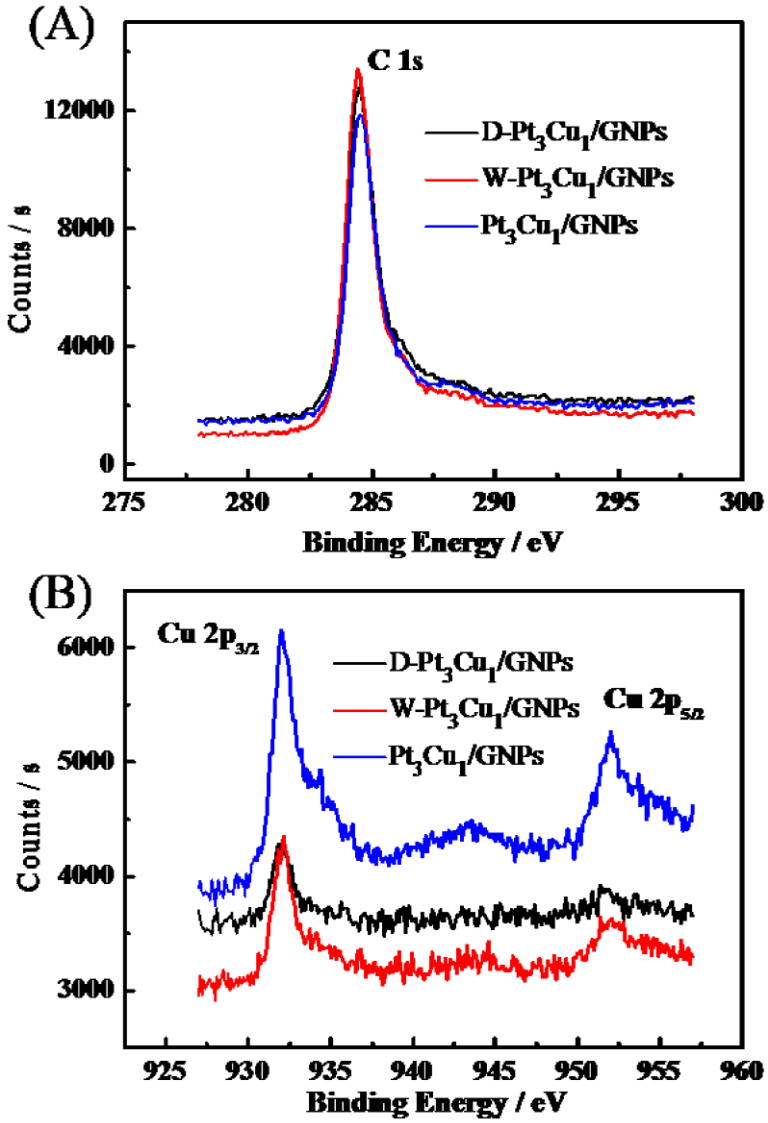

Figure S3 XPS spectra of C 1s and Cu 2p regions for D-Pt_3Cu_1/GNPs, W-Pt_3Cu_1/GNPs, Pt_3Cu_1/GNPs and Pt/GNPs.

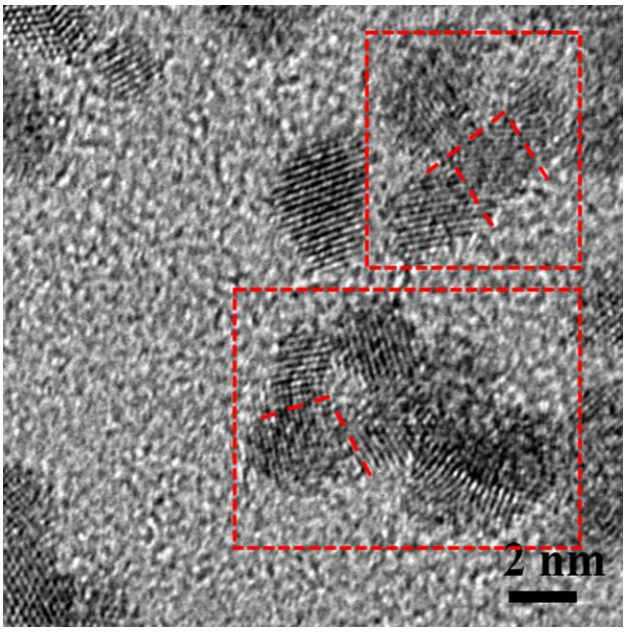

Figure S4 HRTEM images of Pt_3Cu_1 NDs obtained at the reaction time t = 1 min.

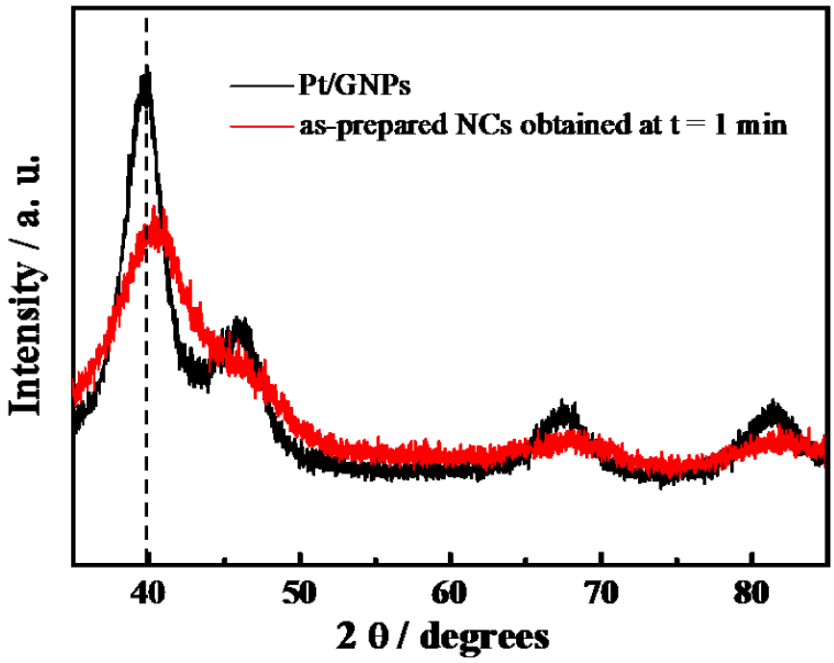

Figure S5 XRD pattern of NCs obtained at dropping time t = 1 min while the pH of reaction solution was 3.

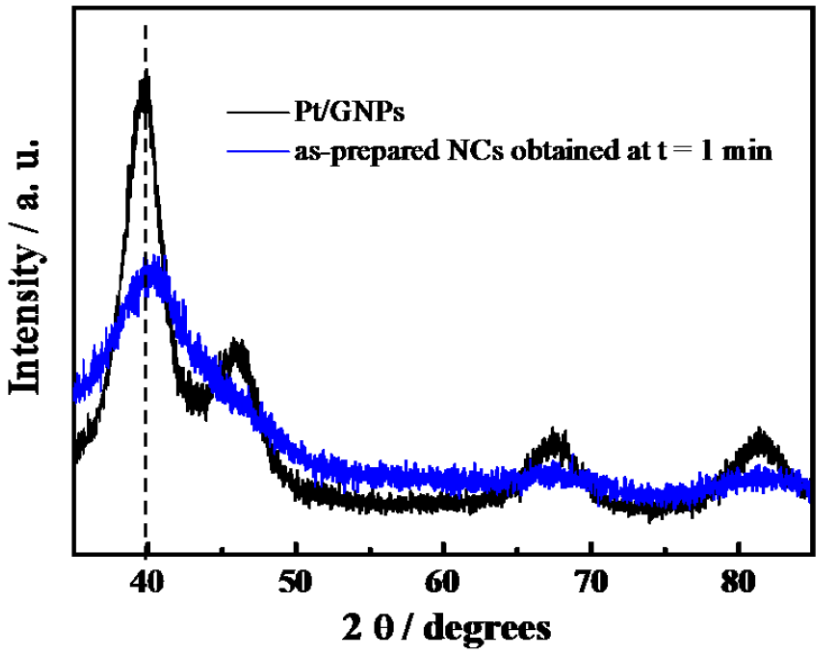

Figure S6 XRD pattern of NCs obtained at dropping time t = 1 min while the pH of reaction solution was 4.5.

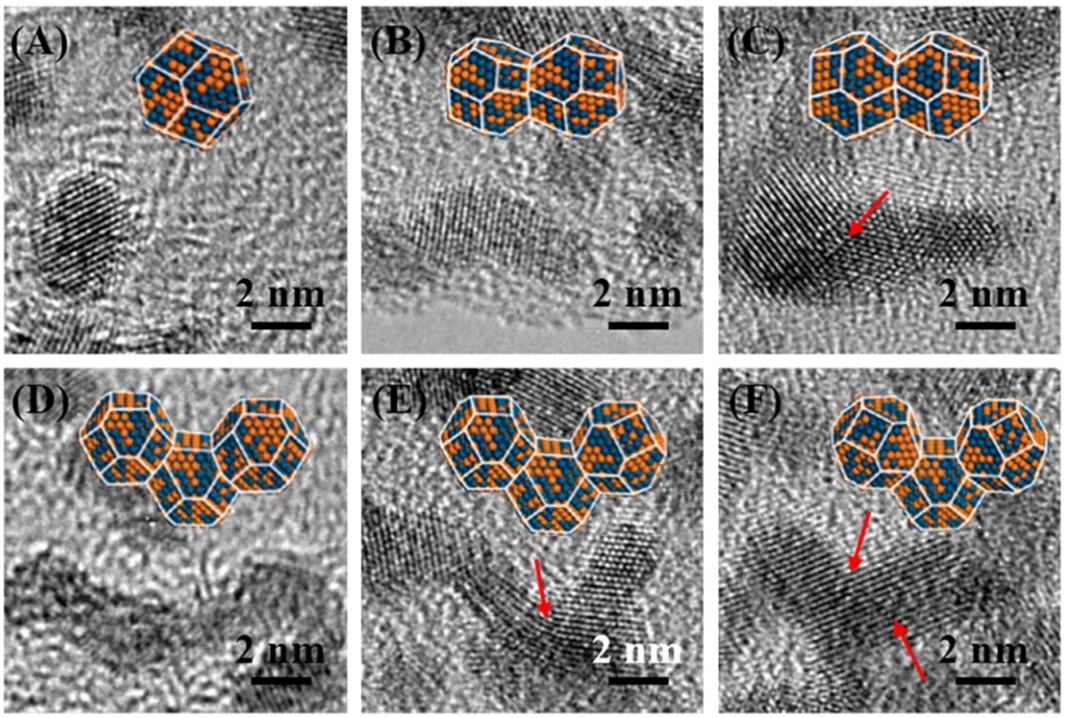

Figure S7 HRTEM images and the corresponding schematic illustrations showing the early growing stages: (A) a primary particle; two particles connected through (B) MA and (C) TA growths; (D-F) three particles connected through either MA or TA growth, respectively. The twin planes were indicated by red arrows.

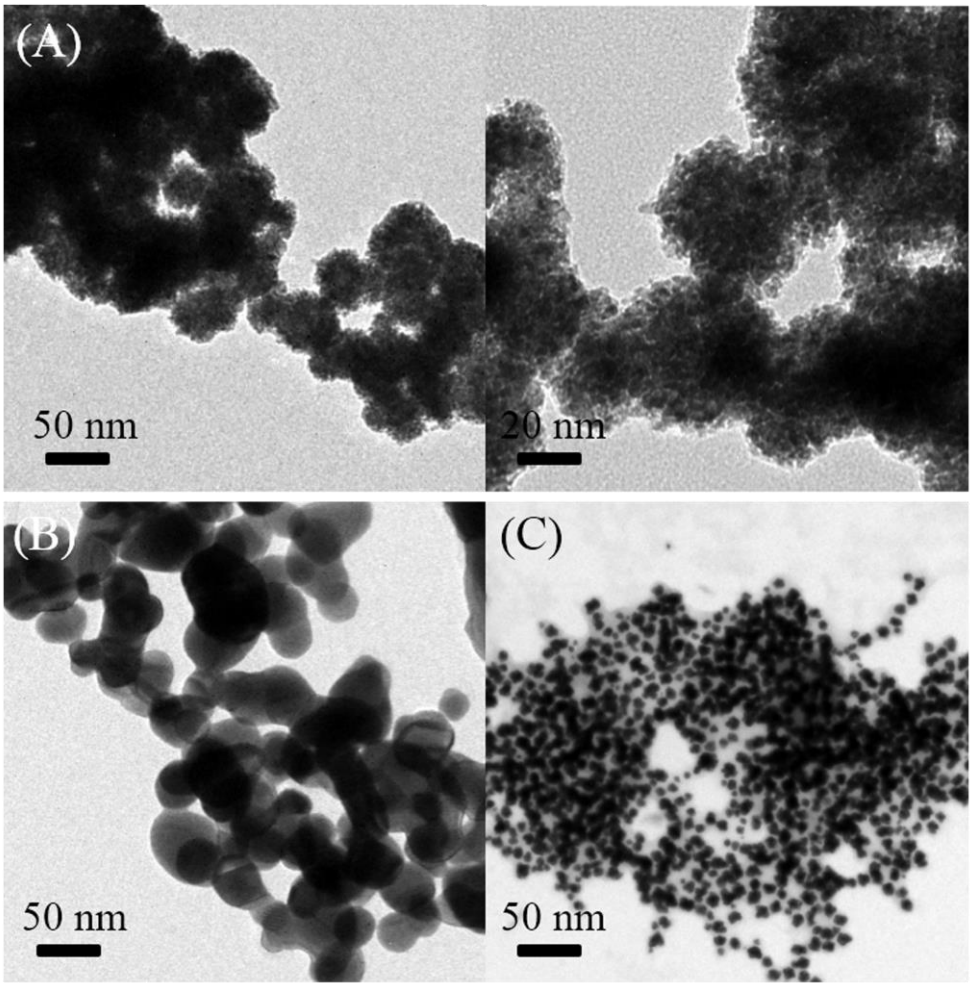

Figure S8 Representative TEM images of the unsupported NCs synthesized in the absence of GNPs while the pH values of reaction solution were (A) 3, (B) 4.5 and (C) 6.

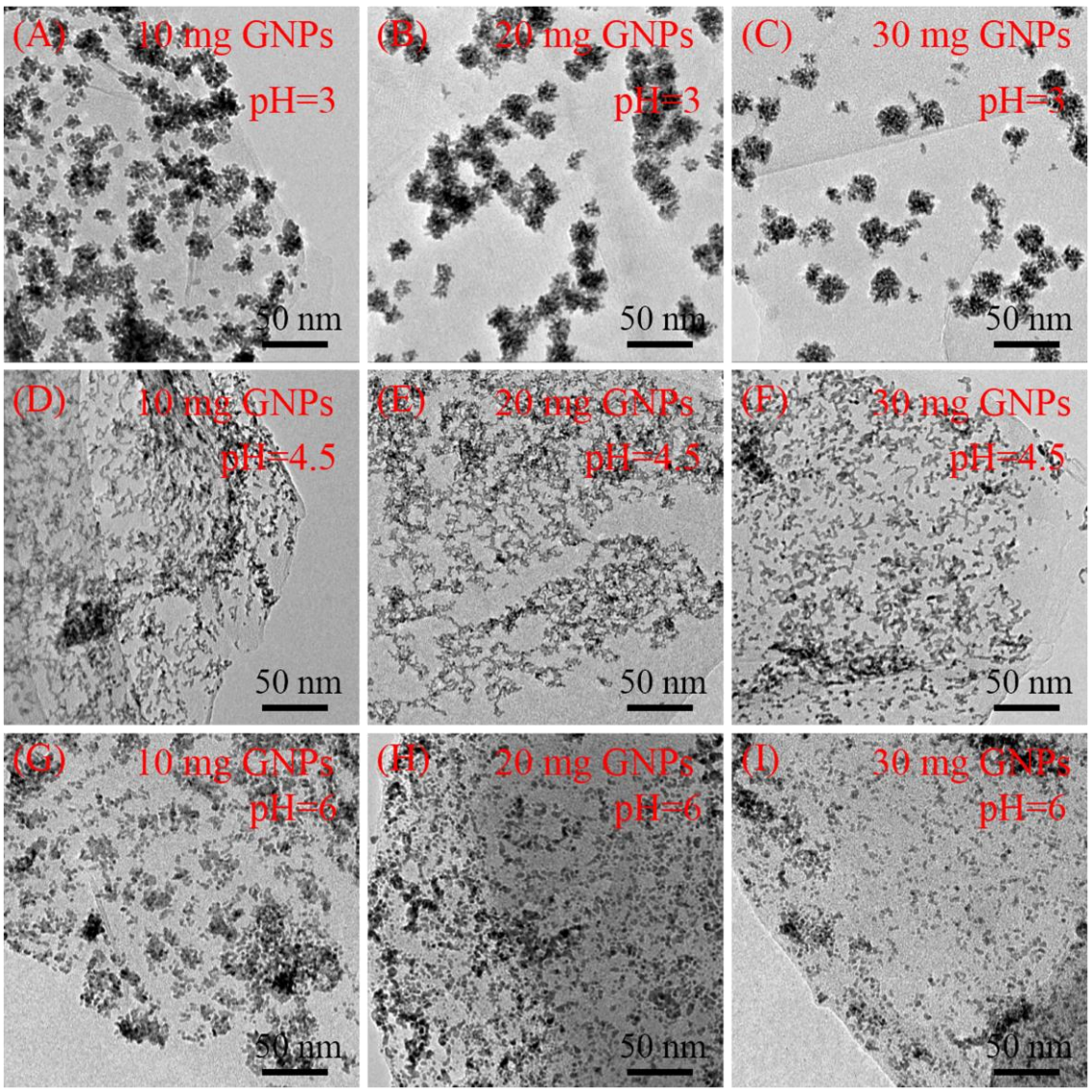

Figure S9 Representative TEM images of the Pt-Cu NCs obtained using the standard procedure but the pH values of the reaction solution were varying with the introduction of different amounts of GNPs: (A) 10 mg, (B) 20 mg and (C) 30 mg while the pH of reaction solution was 3; (D) 10 mg, (E) 20 mg and (F) 30 mg while the pH of reaction solution was 4.5; (G) 10 mg, (H) 20 mg and (I) 30 mg while the pH of reaction solution was 6.

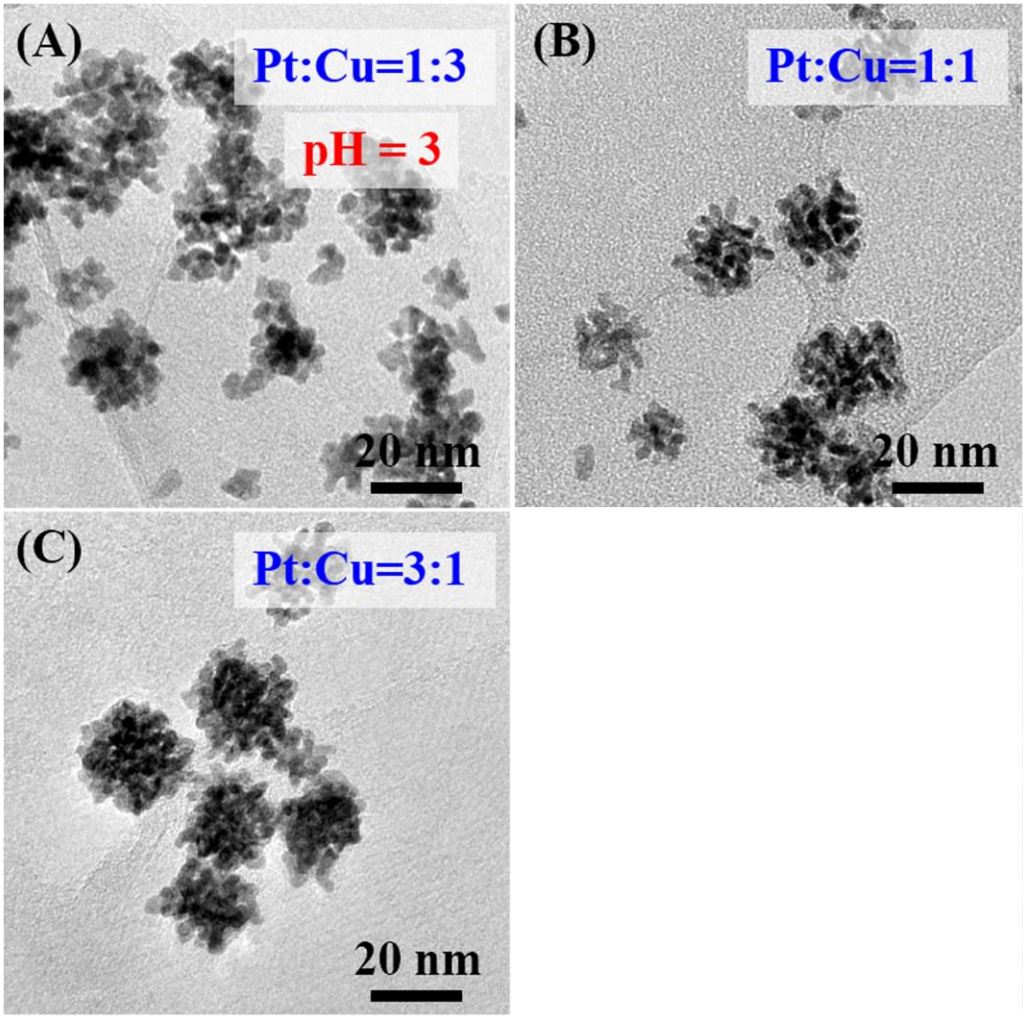

Figure S10 TEM images of Pt-Cu NCs with different morphologies supported on GNPs that were prepared using the standard procedure, but the $PtCl_6^{2-}/Cu^{2+}$ molar ratios were different: (A) 1:3, (B) 1:1, (C) 3:1.

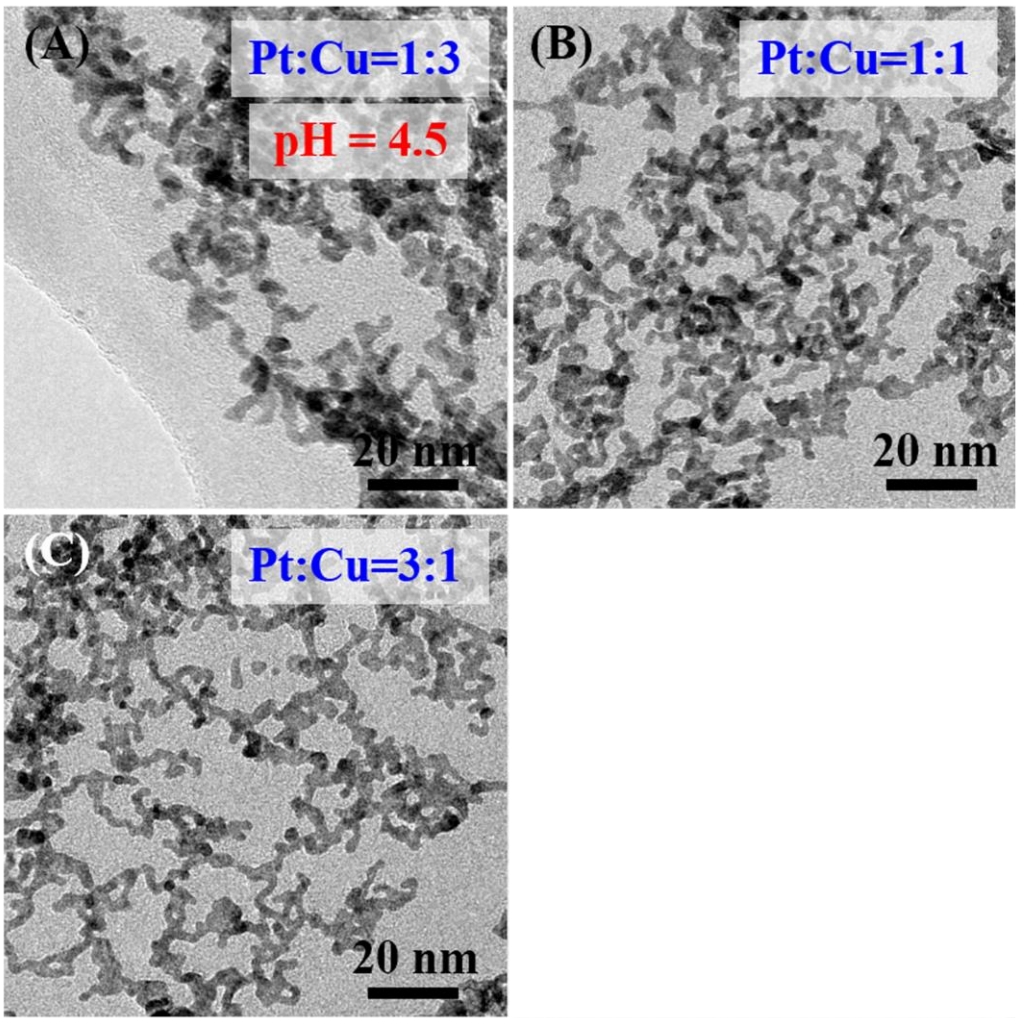

Figure S11 TEM images of Pt-Cu NCs with different morphologies supported on GNPs that were prepared using the standard procedure but the pH values of the reaction solution were adjusted to 4.5, with the different $PtCl_6^{2-}/Cu^{2+}$ molar ratios: (A) 1:3, (B) 1:1, (C) 3:1.

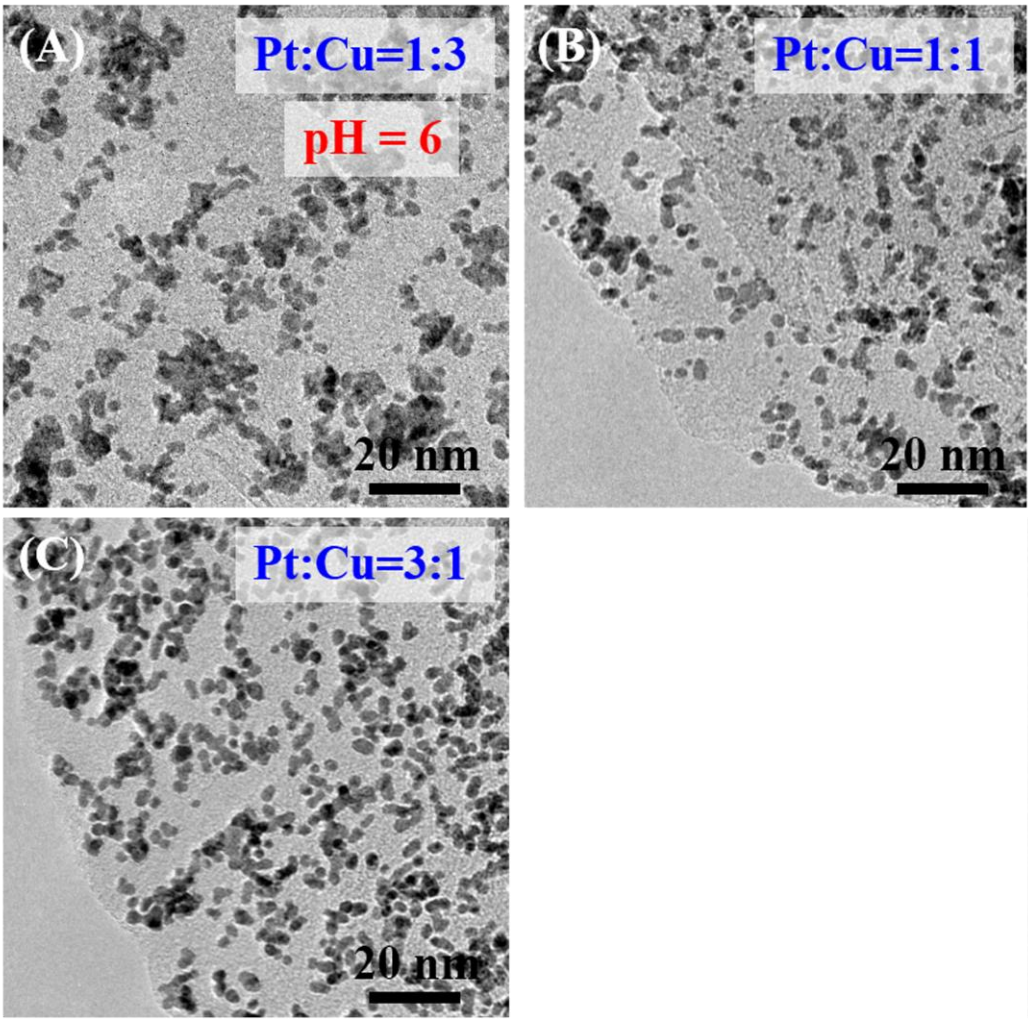

Figure S12 TEM images of Pt-based NCs with different morphologies supported on GNPs that were prepared using the standard procedure but the pH values of the reaction solution were adjusted to 6, with the different $PtCl_6^{2-}/Cu^{2+}$ molar ratios: (A) 1:3, (B) 1:1, (C) 3:1.

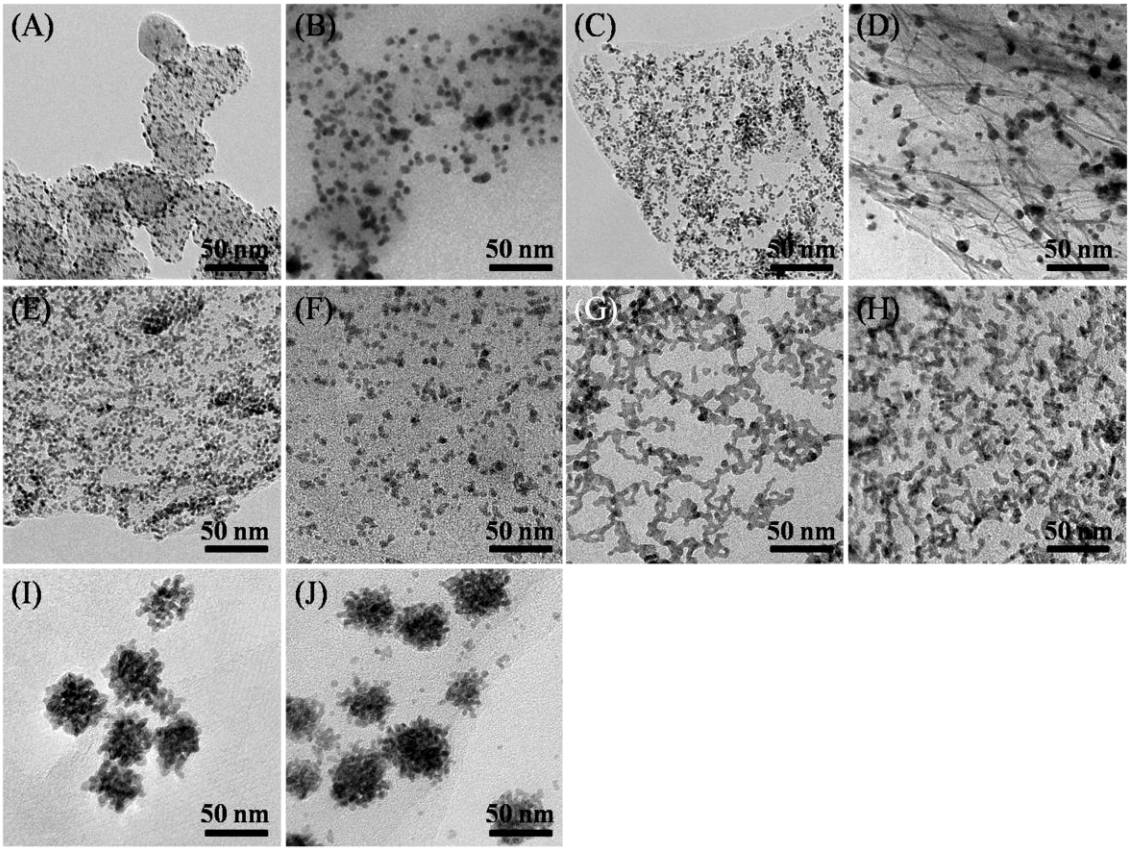

Figure S13 TEM images of (A, B) Pt/C-JM, (C, D) Pt/GNPs, (E, F) Pt_3Cu_1/GNPs, (G, H) W-Pt_3Cu_1/GNPs and (I, J) D-Pt_3Cu_1/GNPs before (A, C, E, G and I) and after (B, D, F, H and J) 500 cycles CVs in a 0.5 M KOH solution containing 0.5 M ethanol at 50 mV s^{-1}.

Table S1 Measured and calculated lattice spacings from both HRTEM images as well as SAED, corresponding to the (111) plane of the Pt fcc lattice.

Sample	Measured by HRTEM	Measured by SAED	Calculated
Pt	-	-	0.2265 nm[1]
D-Pt_3Cu_1/GNPs	0.221 nm	0.222 nm	0.2219 nm
W-Pt_3Cu_1/GNPs	0.222 nm	0.221 nm	0.2219 nm
Pt_3Cu_1/GNPs	0.220 nm	0.223 nm	0.2219 nm
Cu	-	-	0.208 nm[2]

Table S2 Summary of the loading and composition data for the catalysts on the basis of ICP-MS and XPS analysis.

Catalysts	$PtCl_6^{2-}/Cu^{2+}$ (mol/mol)	Metal Loading by ICP-MS (wt. %)			Pt/Cu by ICP-MS (mol/mol)	Pt/Cu by XPS (mol/mol)
		Pt	Cu	Total Metal		
D-Pt_3Cu_1/GNPs	3 : 1	17.43	1.85	19.28	3.06:1	2.96:1
W-Pt_3Cu_1/GNPs	3 : 1	17.29	1.84	19.13	3.09:1	2.99:1
Pt_3Cu_1/GNPs	3 : 1	17.17	1.85	19.02	3.04:1	3.05:1

Table S3 Electrochemical surface areas (ECSAs) of all catalysts estimated from the columbic charges corresponding to the oxide reduction peak and mass activities for ethanol oxidation in this work.

Catalyst	**ECSA / m^2 g_{Pt}^{-1}**	**Mass activity / A mg_{Pt}^{-1}**	**Specific activity / mA cm^{-2}**
D-Pt_3Cu_1/GNPs	93.93	6.01	85.84
W-Pt_3Cu_1/GNPs	84.79	4.52	64.08
Pt_3Cu_1/GNPs	77.86	3.16	44.52
Pt/GNPs	64.23	1.331	21.82
Pt/C-JM	52.36	0.796	13.06

1. Y. Shiraishi, Y. Takeda, Y. Sugano, S. Ichikawa, S. Tanaka and T. Hirai, *Chemical Communications*, 2011, **47**, 7863-7865.
2. F. Wiame, V. Maurice and P. Marcus, *Surface science*, 2007, **601**, 1193-1204.