Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Facile synthesis of graphene nanoplates-supported porous Pt-Cu alloys with high electrocatalytic property for methanol oxidation

Genlei Zhang[a], Zhenzhen Yang[b], Wen Zhang[a], Yuxin Wang[a, *]

[a] School of Chemical Engineering and Technology, State Key Laboratory of Chemical Engineering, Co-Innovation Center of Chemical Science & Engineering, Tianjin Key Laboratory of Membrane Science and Desalination Technology, Tianjin University, Weijin Road, Tianjin 300072, PR China

[b] School of Chemical Engineering and Technology, State Key Laboratory of Chemical Engineering, Co-Innovation Center of Chemical Science & Engineering, Tianjin University, Weijin Road, Tianjin 300072, PR China

* Corresponding author. Tel./fax: +86 22 27890515.

E-mail address: yxwang@tju.edu.cn (Y. Wang)

1 Experimental Section

1.1 The p-Pt/AP-GNPs catalyst preparation

Synthesis of Cu_2O/AP-GNPs

Cu_2O nanocubes were prepared through a modified reductive solution chemistry route according to the previous literature.[1] In a typical procedure, 20 mg of AP-GNPs and 0.50 g of poly(ethylene glycol) (PEG, MW: 10000) were first dissolved in 10 ml of $CuCl_2$ aqueous solution (0.1 mM) under mechanical stirring at room temperature. Then N_2 was purged into the reaction solution, and purging was maintained during the whole reaction process. After magnetic stirring for 1h at room temperature, 50 ml of NaOH solution (6.0 M) was added dropwise. After 10 min, 2 ml of AA solution (0.1 M) was added dropwise to the solution. The product was collected by filtration after a reaction time of 30 min by repeatedly rinsing with DI water and ethanol in order to minimize the surface adsorbed PEG molecules, then dried at 60 ºC in an oven for 12 h.

Synthesis of p-Pt/AP-GNPs

20 mg of as-prepared Cu_2O/AP-GNPs were ultrasonically re-dispersed in 5 ml of DI water. Then 2.56 ml Na_2PtCl_4 (10 mM) were added to the Cu_2O/AP-GNPs suspension under magnetic stirring. The pH value of the suspension was adjusted to 3 by 0.5 M HCl aqueous solution. The reaction was maintained for 1 h and the product was collected by filtration after a reaction time of 30 min by repeatedly rinsing with DI water, then dried at 60 ºC in an oven for 12 h and denoted as p-Pt/AP-GNPs.

1.2 Synthesis of Pt_1Cu_1/AP-GNPs[2]

In a typical synthesis, 20 mg AP-GNPs were ultrasonically re-dispersed in 60 mL EG/H_2O mixed aqueous solution (V/V, 2/1) and placed in a 250 mL beaker under mechanical stirring for 1 h at room temperature. Then, 2.56 mL Na_2PtCl_6 (10 mM) and 2.56 mL $Cu(CH_3COO)_2$ (10 mM) were added into the above mixture solution and the mechanical stirring was continued for 1 h at room temperature. The pH value of the obtained solution was adjusted to 11 by 1.0 M NaOH aqueous solution and N_2 was feed into the ink for 30 min to remove O_2. The suspension was heated up to boiling point by microwave and refluxed for 7 min so that the $PtCl_6^{2-}$ and Cu^{2+} ions were reduced completely. The suspension was allowed to cool down to room temperature with continuous stirring, and then the suspension was filtered with DI water and ethanol. Then the filter cake was dried at 60 ºC in an oven for 12 h and the as-prepared catalyst was denoted as Pt_1Cu_1/AP-GNPs.

2 Figures and Supporting Tables.

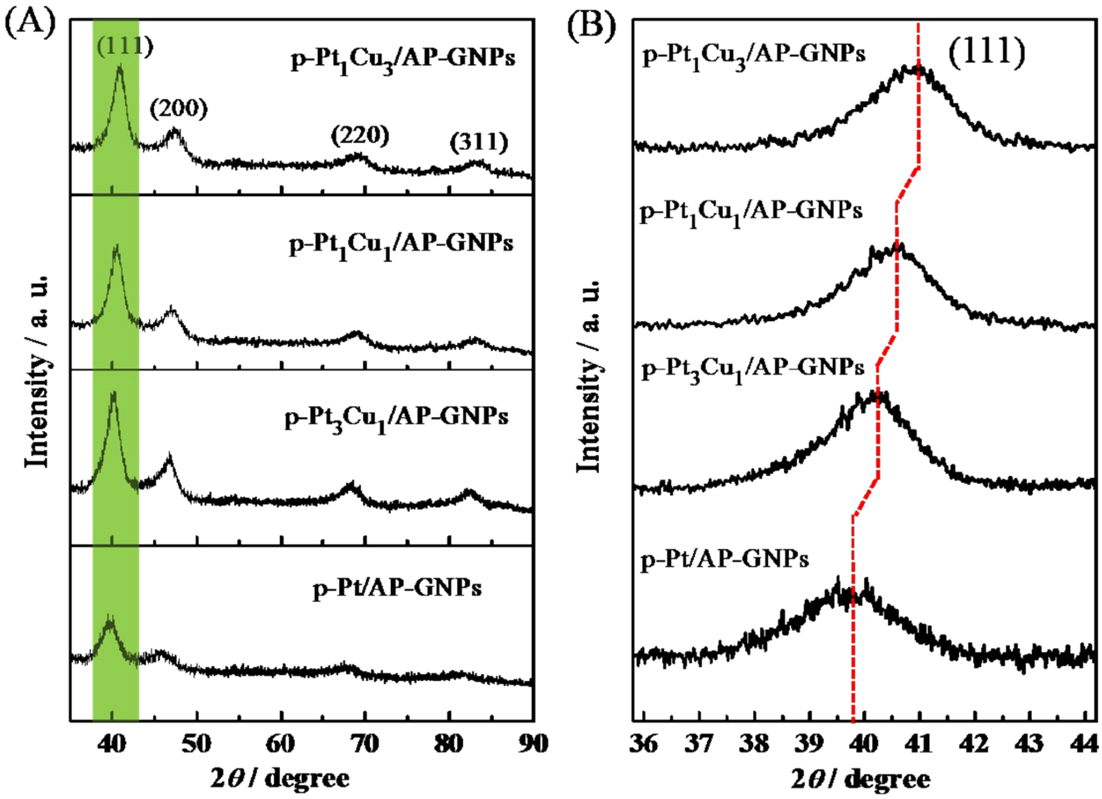

Figure S1 (A) XRD patterns of p-Pt/AP-GNPs, p-Pt_3Cu_1/AP-GNPs, p-Pt_1Cu_1/AP-GNPs and p-Pt_1Cu_3/AP-GNPs catalysts, respectively. (B) Enlarged image of the XRD patterns in the range of $2\theta = 36^\circ \sim 45^\circ$.

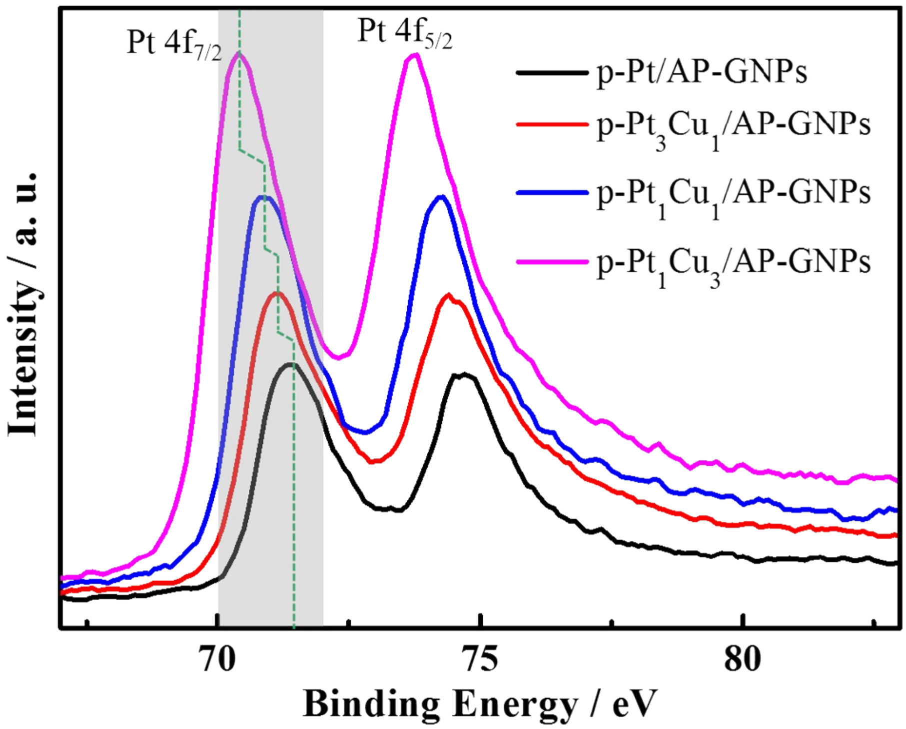

Figure S2 XPS spectra of Pt 4f region for p-Pt/AP-GNPs, p-Pt_3Cu_1/AP-GNPs, p-Pt_1Cu_1/AP-GNPs and p-Pt_1Cu_3/AP-GNPs catalysts, respectively.

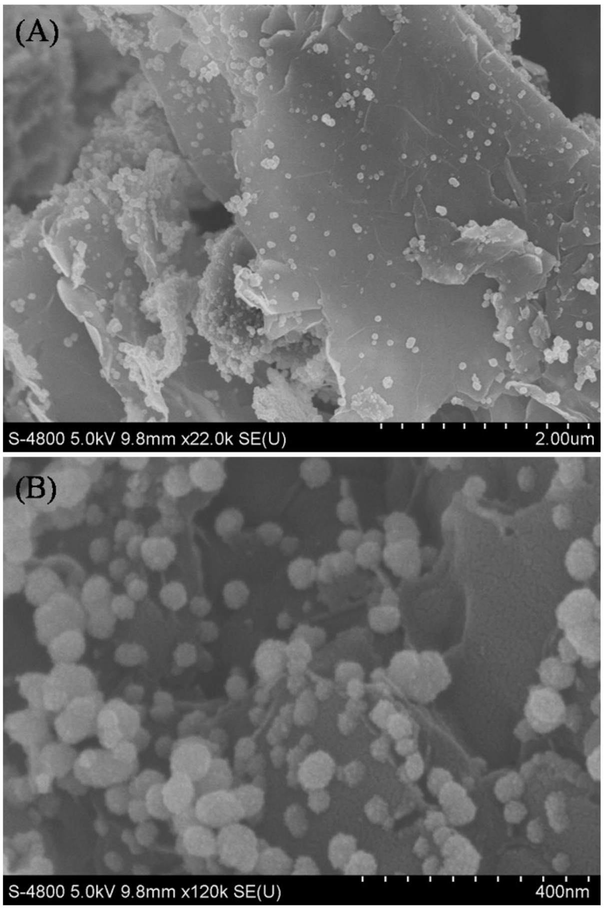

Figure S3 SEM images of the p-Pt$_1$Cu$_1$/AP-GNPs catalyst.

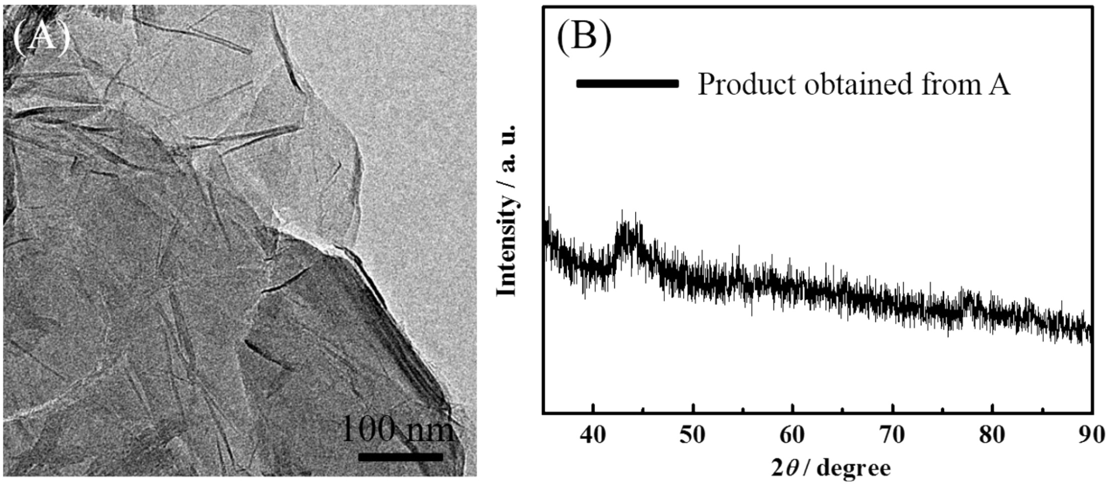

Figure S4 (A) The TEM image and (B) XRD pattern of the product obtained while using the same procedure keeping all synthetic conditions identical but in the absence of Na_2PtCl_6.

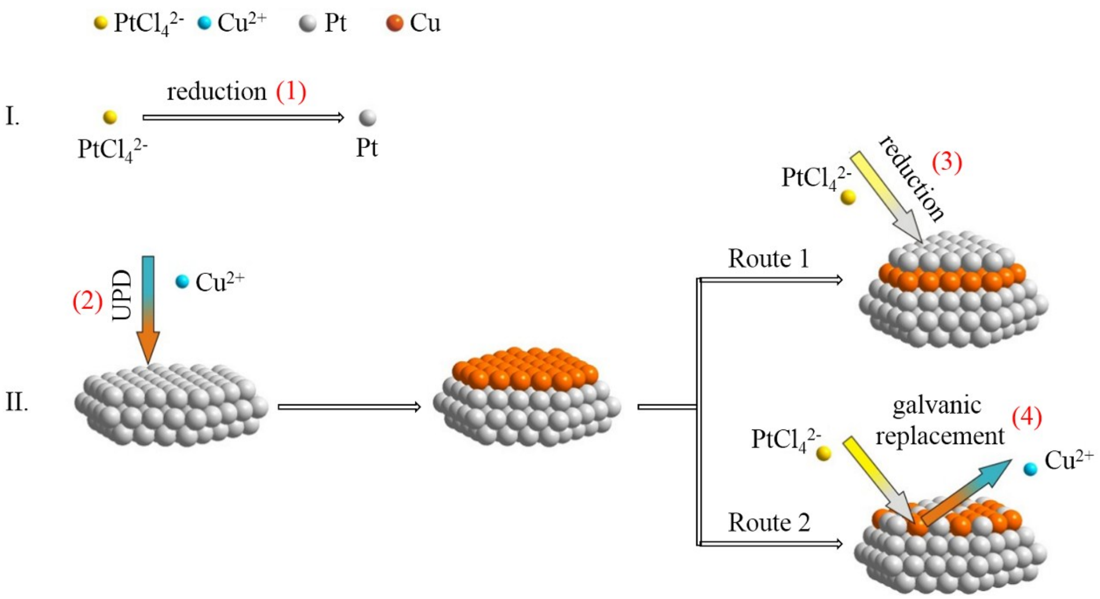

Figure S5 A schematic illustration showing the Cu under potential deposition (UPD) process during the formation of Pt-Cu NCs.

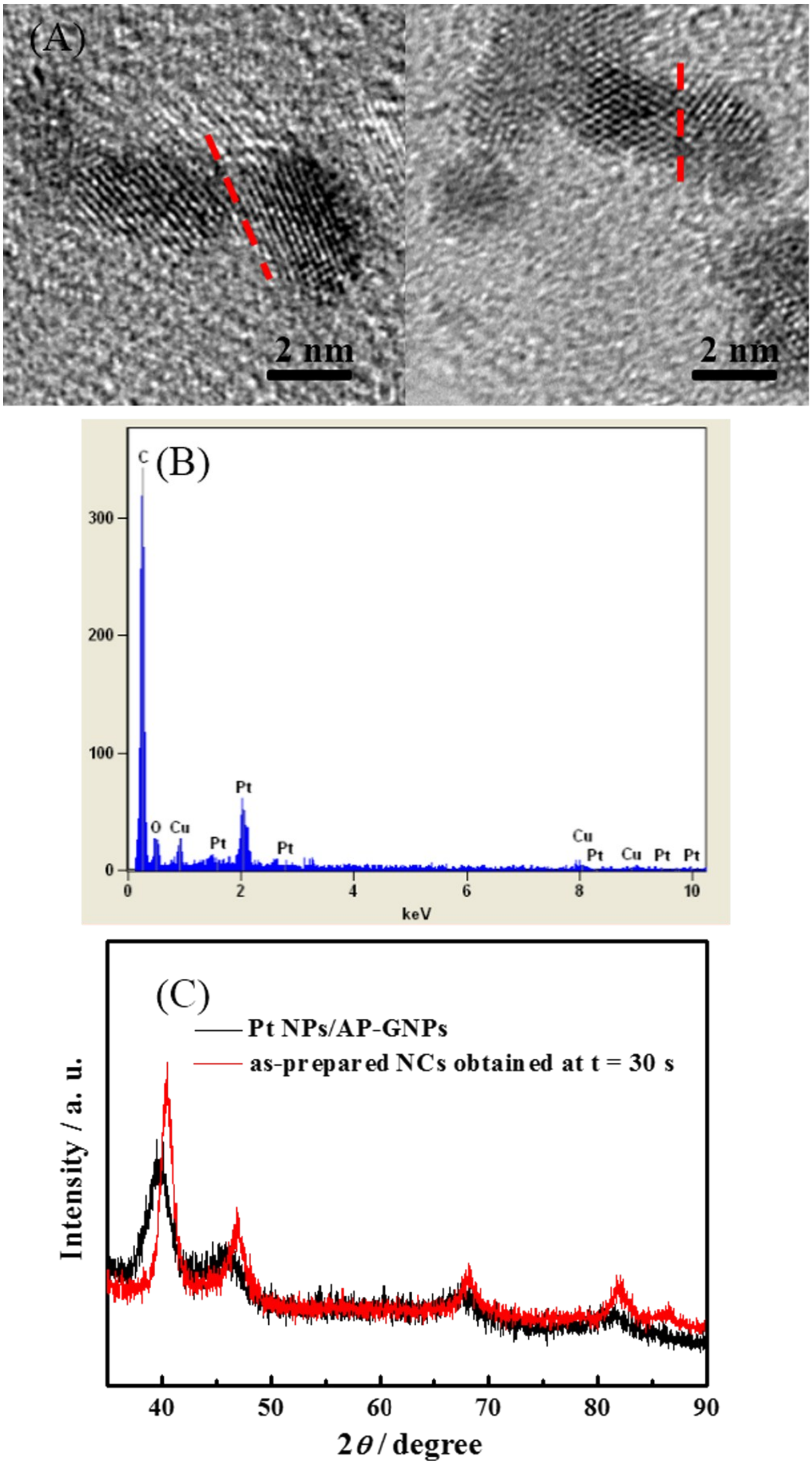

Figure S6 (A) HRTEM images, (B) the EDS and (C) the XRD pattern of NCs obtained at dropping time t = 30 s.

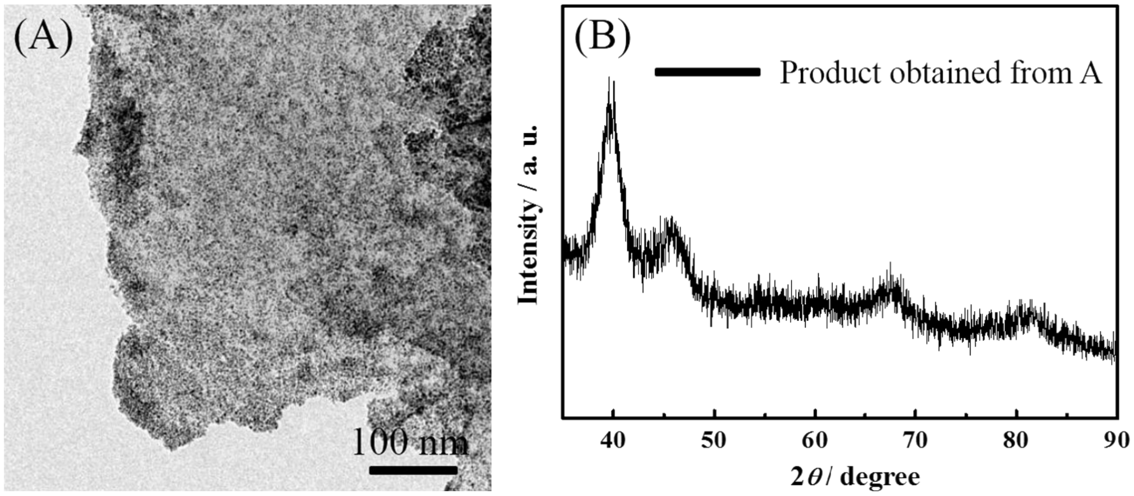

Figure S7 (A) The TEM image and (B) XRD pattern of the product obtained while using the same procedure keeping all synthetic conditions identical but in the absence of $CuCl_2$.

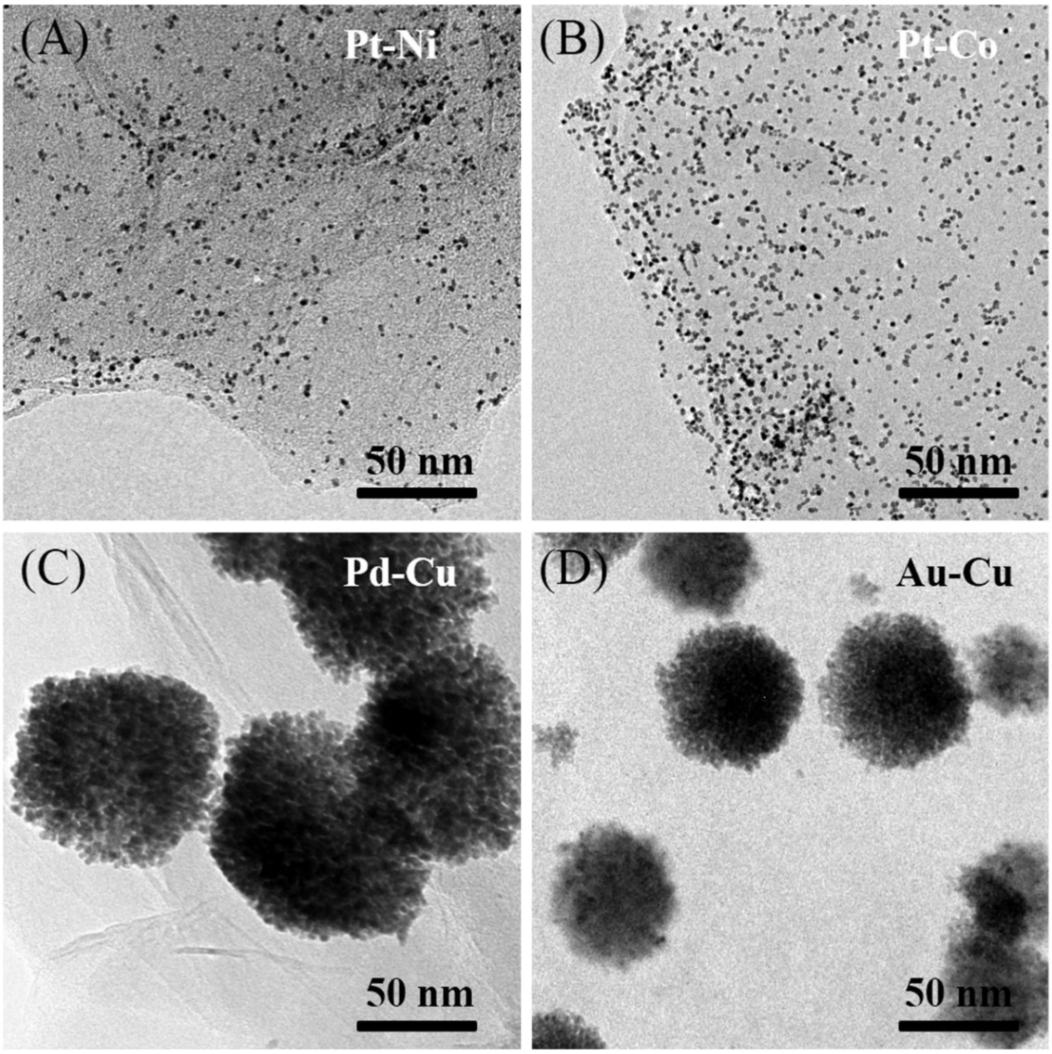

Figure S8 TEM images of products which were obtained when Cu^{2+} ions were substituted by an equal molar amount of (A) Ni^{2+} or (B) Co^{2+} ions, and when the $PtCl_6^{2-}$ ions were switched to (C) $PdCl_4^{2-}$ or (D) $AuCl_4^{-}$ ions.

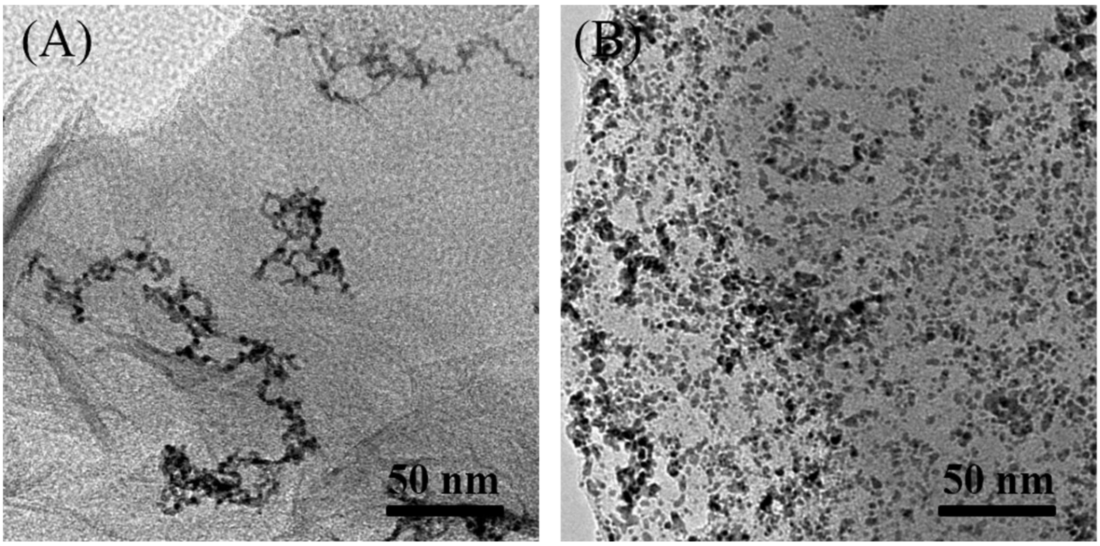

Figure S9 TEM images of the product prepared by using (A) 0.1 M sodium borohydride and (B) 0.1 M oxalic acid as reducing agent replacing AA.

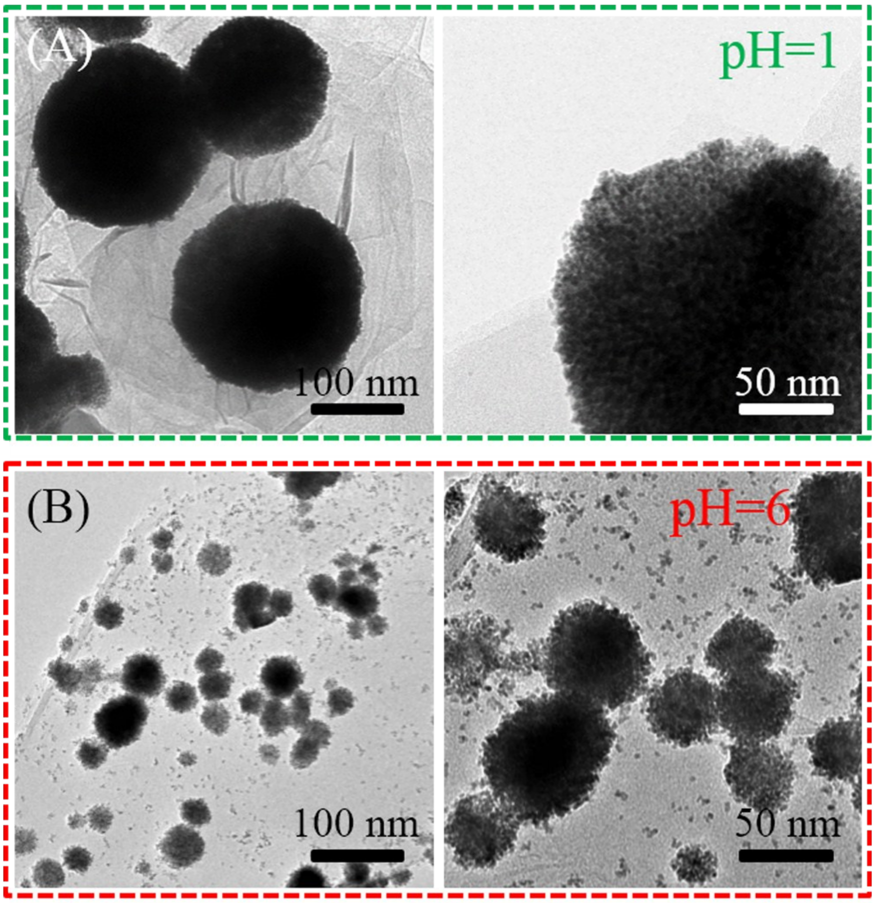

Figure S10 TEM images of Pt-Cu NCs with the Pt/Cu molar ratio of 1/1 supported on AP-GNPs formed at varying pH (A) 1 and (B) 6, respectively.

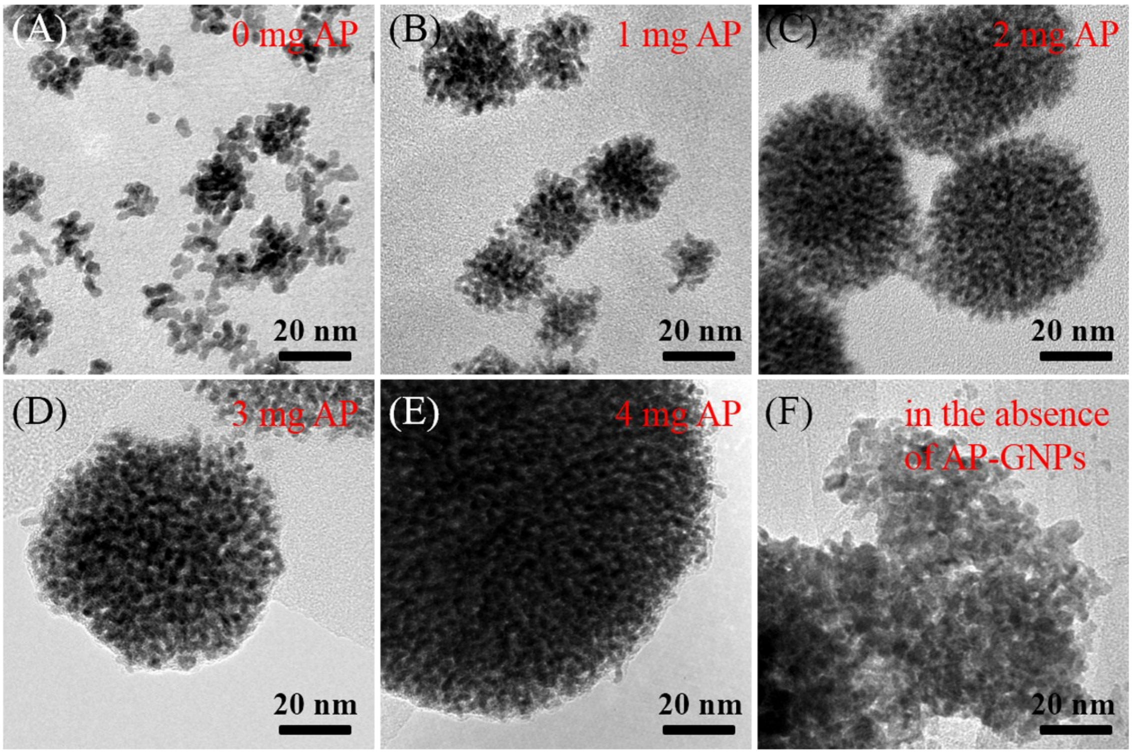

Figure S11 TEM image of Pt-Cu NCs with the Pt/Cu molar ratio of 1/1 which were synthesized in the presence of AP-GNPs which were functionalized by varying amount of AP: (A) 0, (B) 1, (C) 2, (D) 3, (E) 4 mg, respectively; and (F) in the absence of AP-GNPs.

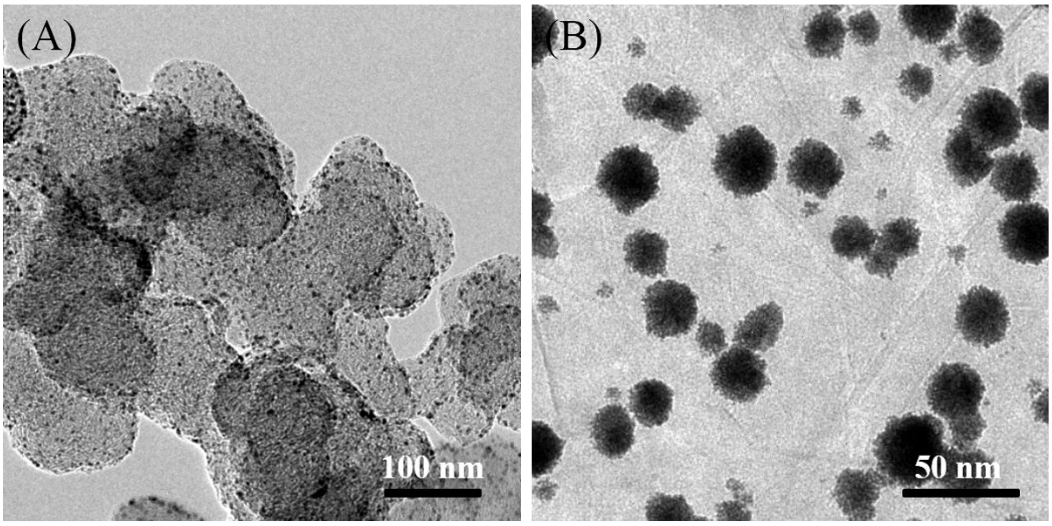

Figure S12 TEM images of (A) the commercial Pt/C-JM and (B) p-Pt/AP-GNPs.

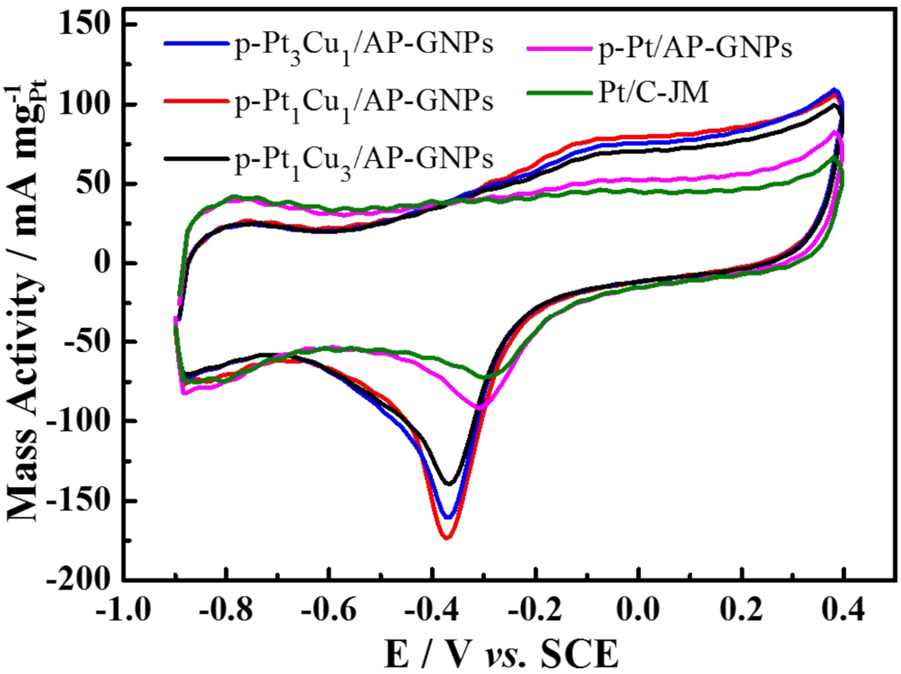

Figure S13 CVs of p-Pt_1Cu_3/AP-GNPs, p-Pt_1Cu_1/AP-GNPs, p-Pt_3Cu_1/AP-GNPs, p-Pt/AP-GNPs and Pt/C-JM in N_2-saturated 0.1 M NaOH solution at a scan rate of 50 mV s^{-1}.

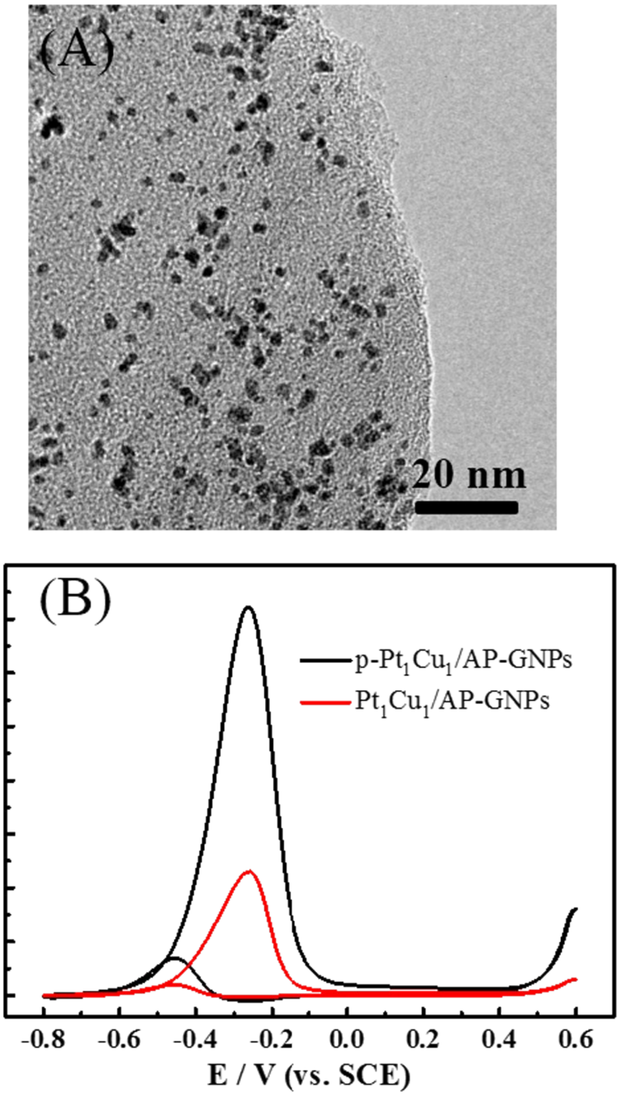

Figure S14 (A) TEM image of isolated Pt-Cu nanoparticles with the Pt/Cu molar ratio of 1/1 supported on AP-GNPs; (B) CVs of p-Pt$_1$Cu$_1$/AP-GNPs and Pt$_1$Cu$_1$/AP-GNPs in a N$_2$-saturated 0.1 M NaOH solution containing 0.5 M methanol at a scan rate of 50 mV s^{-1}.

Table S1 Summary of the loading and composition data for the catalysts on the basis of ICP-MS analysis

Catalysts	**$PtCl_6^{2-}/Cu^{2+}$ (mol/mol)**	**Metal Loading (wt. %)**			**Pt/Cu in products (mol/mol)**	**Cu/Pt+Cu in products (mol/mol, %)**
		Pt	**Cu**	**Total**		
p-Pt_1Cu_3/GNPs	1 : 3	10.24	8.28	18.52	1 : 2.48	71.26
p-Pt_1Cu_1/GNPs	1 : 1	14.44	4.09	18.53	1.15 : 1	46.51
p-Pt_3Cu_1/GNPs	3 : 1	16.78	1.79	18.57	3.06 : 1	24.63

Table S2 Electrochemical surface area (ECSA) estimated from hydrogen absorption comparison in 0.5 M H_2SO_4 solution, the mass activity expressed as the forward scan peak current of methanol oxidation and i_f/i_b ratios in 0.1 M NaOH containing 0.5 M methanol for p-Pt_1Cu_3/AP-GNPs, p-Pt_1Cu_1/AP-GNPs, p-Pt_3Cu_1/AP-GNPs, p-Pt/AP-GNPs and Pt/C-JM used in this work.

Catalyst	**ECSA / m^2 g^{-1}**	**Mass activity / A mg_{Pt}^{-1}**	i_f/i_b
p-Pt_1Cu_3/AP-GNPs	76.58	2.13	9.31
p-Pt_1Cu_1/AP-GNPs	91.89	3.61	10.44
p-Pt_3Cu_1/AP-GNPs	80.60	2.75	9.50
p-Pt/AP-GNPs	69.11	0.619	5.49
Pt/C-JM	62.89	0.497	2.57

Table S3 The positive scan peak current density normalized as mass activity for the p-Pt_1Cu_1/AP-GNPs catalyst and other recently reported catalysts.

Catalyst	**Mass Activity / mA mg_{Pt}^{-1}**	**Scanning rate / mV s^{-1}**	**Condition**	**Ref.**
p-Pt_1Cu_1/AP-GNPs	3611	50	0.1 M KOH + 0.5 M CH_3OH	This work
PtCu NWs	1740	50	1 M KOH + 1 M CH_3OH	[3]
PtPd/CNTs	1000	50	0.5 M KOH + 0.5 M CH_3OH	[4]
Pt/$In_{0.1}SnO_2$	2320	20	0.5 M KOH + 2 M CH_3OH	[5]
Pt/SG (PVA)	2371.31	50	1.0 M KOH + 0.5 M CH_3OH	[6]
Pd-Pt ANFs/RGO	about 1487.18	50	1.0 M KOH + 0.5 M CH_3OH	[7]
$Pd_{50}Pt_{50}$ BANS	about 2250	50	1 M KOH + 1 M CH_3OH	[8]
PtPd NSs/RGOs	803.86	50	1 M NaOH + 1 M CH_3OH	[9]
PtAuRu/RGO	1605.5	50	1 M NaOH + 1 M CH_3OH	[10]
N-Pt/RGO	1072.96	50	1 M NaOH + 1 M CH_3OH	[11]
Pt-Au CSANCs	946	50	0.5 M KOH + 0.5 M CH_3OH	[12]
Pt/G3DN	910.11	50	1 M NaOH + 1 M CH_3OH	[13]
Pt/PAIn/GE	329.3	50	1 M NaOH + 1 M CH_3OH	[14]
Pt/P_1-MCNTs	835	10	0.1 M NaOH + 1 M CH_3OH	[15]

Reference

1. Q. Li, P. Xu, B. Zhang, G. Wu, H. Zhao, E. Fu and H.-L. Wang, *Nanoscale*, 2013, **5**, 7397-7402.
2. M. Huang, Y. Jiang, C. Jin, J. Ren, Z. Zhou and L. Guan, *Electrochim. Acta*, 2014, **125**, 29-37.
3. W. Hong, J. Wang and E. Wang, *Nano Res.*, 2015, 1-9.
4. G. Yang, Y. Zhou, H.-B. Pan, C. Zhu, S. Fu, C. M. Wai, D. Du, J.-J. Zhu and Y. Lin, *Ultrason. Sonochem.*, 2016, **28**, 192-198.
5. Y.-Y. Feng, W.-Q. Kong, Q.-Y. Yin, L.-X. Du, Y.-T. Zheng and D.-S. Kong, *J. Power Sources*, 2014, **252**, 156-163.
6. J.-M. Yang, S.-A. Wang, C.-L. Sun and M.-D. Ger, *J. Power Sources*, 2014, **254**, 298-305.
7. K. Wu, Q. Zhang, D. Sun, X. Zhu, Y. Chen, T. Lu and Y. Tang, *Int. J. Hydrogen Energy*, 2015, **40**, 6530-6537.
8. C. Zhu, S. Guo and S. Dong, *Chemi. Eur. J.*, 2013, **19**, 1104-1111.

9. S.-S. Li, J.-J. Lv, Y.-Y. Hu, J.-N. Zheng, J.-R. Chen, A.-J. Wang and J.-J. Feng, *J. Power Sources*, 2014, **247**, 213-218.
10. F. Ren, C. Wang, C. Zhai, F. Jiang, R. Yue, Y. Du, P. Yang and J. Xu, *J. Mater. Chem. A*, 2013, **1**, 7255-7261.
11. Z. Yao, R. Yue, C. Zhai, F. Jiang, H. Wang, Y. Du, C. Wang and P. Yang, *Int. J. Hydrogen Energy*, 2013, **38**, 6368-6376.
12. L.-X. Chen, L. Liu, J.-J. Feng, Z.-G. Wang and A.-J. Wang, *J. Power Sources*, 2016, **302**, 140-145.
13. M. Wang, X. Song, Q. Yang, H. Hua, S. Dai, C. Hu and D. Wei, *J. Power Sources*, 2015, **273**, 624-630.
14. R. Yue, Q. Zhang, C. Wang, Y. Du, P. Yang and J. Xu, *Electrochim. Acta*, 2013, **107**, 292-300.
15. Z. Liu, Q. Shi, F. Peng, H. Wang, H. Yu, J. Li and X. Wei, *Catal. Commun.*, 2012, **22**, 34-38.