Electronic supplementary information

Graphitic-C_3N_4 quantum dots modified carbon nanotubes as novel support material for low Pt loading fuel cell catalyst

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Table S1

Sample	Solution	ESA (m^2 $g^{-1)}$	Mass activity (mA mg^{-1})
PtRu/N-CNT[5]	H_2SO_4 (0.5 M)+CH_3OH (1.0 M)	30.0	120.0
PtRu/O-CNT[5]	H_2SO_4 (0.5 M)+CH_3OH (1.0 M)	28.8	69.0
PtRu/CNT-PCA[6]	H_2SO_4 (0.5 M)+CH_3OH (1.0 M)	60.0	390.2
PtRuNP/CNT[6]	H_2SO_4 (0.5 M)+CH_3OH (1.0 M)	49.4	232.4
PtRu/PPA-CNTs[7]	H_2SO_4 (0.5 M)+CH_3OH (1.0 M)	61.1	372.9
PtRu/PD-CNT[8]	H_2SO_4 (0.5 M)+CH_3OH (1.0 M)	156.2	373.0
PtRu/CNTs-PIL[9]	H_2SO_4 (0.5 M)+CH_3OH (1.0 M)	91.2	242.3

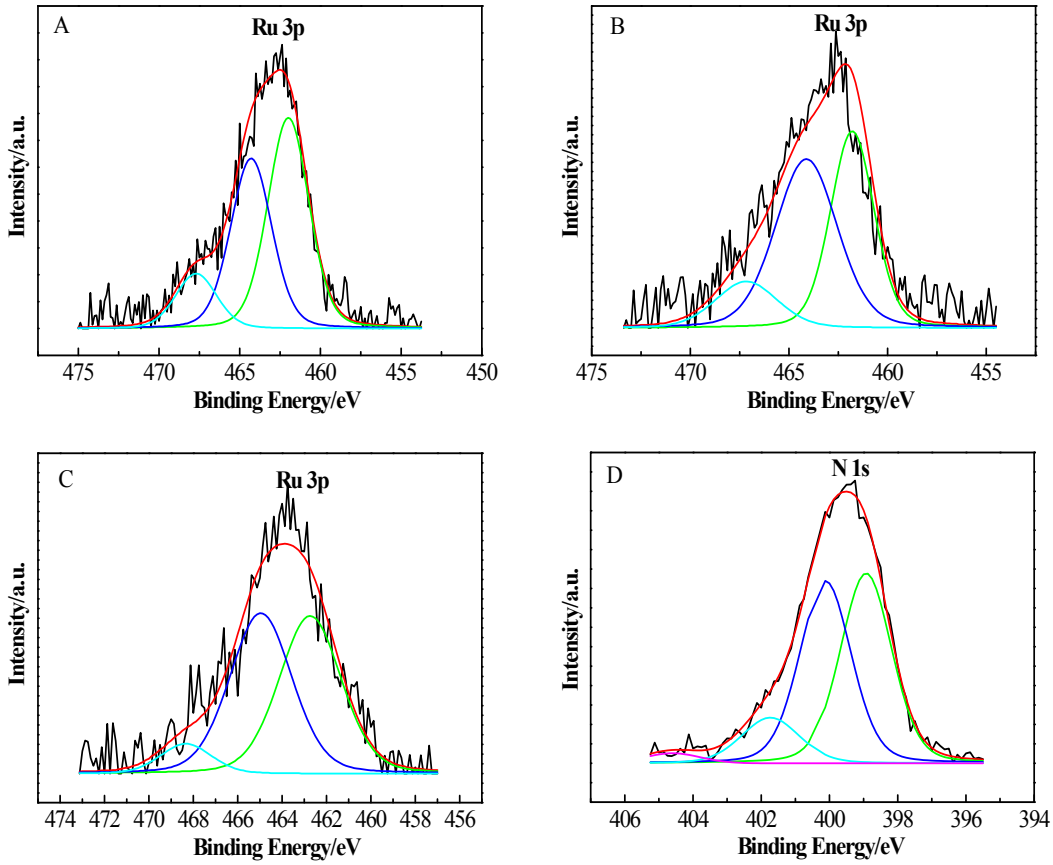

Fig. S1 XPS Ru3p core level spectra of PtRu/CNT (A), PtRu/T-CNT (B) and PtRu/CNT-QDs (C); XPS N1s core level spectra of PtRu/CNT-QDs (C).

Table S2 Results of the fits of the Pt 4f spectra.

Catalysts	Species	Orbital spin	Binding energy/eV	Assignment	Relative content/%
PtRu/CNT	Pt 4f	4f7/2	71.75	Pt	19.3
		4f5/2	75.05	Pt	14.5
		4f7/2	72.53	PtO	27.6
		4f5/2	75.83	PtO	20.7
		4f7/2	74.59	PtO_2	10.2
		4f5/2	77.89	PtO_2	7.7
PtRu/T-CNT	Pt 4f	4f7/2	71.76	Pt	25.1
		4f5/2	75.06	Pt	18.8
		4f7/2	72.59	PtO	20.3
		4f5/2	75.89	PtO	15.3
		4f7/2	74.55	PtO_2	11.7
		4f5/2	77.85	PtO_2	8.8
PtRu/CNT-QDs	Pt 4f	4f7/2	72.01	Pt	29.1
		4f5/2	75.31	Pt	21.8
		4f7/2	73.03	PtO	19.8
		4f5/2	76.33	PtO	14.8
		4f7/2	75.32	PtO_2	8.3
		4f5/2	78.62	PtO_2	6.2

Table S3 Results of the fits of the Ru 3p spectra.

Catalysts	Species	Orbital spin	Binding energy/eV	Assignment	Relative content/%
PtRu/CNT	Ru 3p	3p1/2	461.98	Ru	48.5
		3p1/2	464.28	RuO_2	39.0
		3p1/2	467.70	RuO_xH_y	12.5
PtRu/OCNT	Ru 3p	3p1/2	461.79	Ru	39.1
		3p1/2	464.12	RuO_2	47.8
		3p1/2	467.16	RuO_xH_y	13.1
PtRu/CNT-QDs	Ru 3p	3p1/2	462.73	Ru	46.0
		3p1/2	464.96	RuO_2	46.8
		3p1/2	468.34	RuO_xH_y	7.2

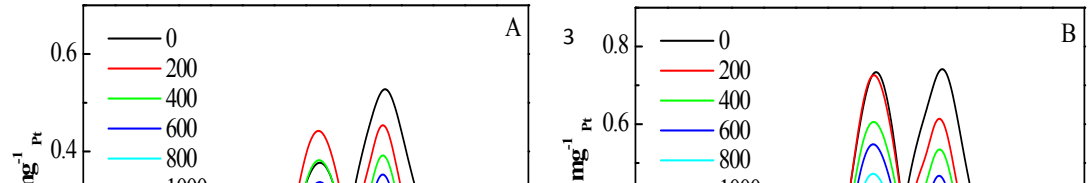

Fig. S2 Cyclic voltammograms in an Ar-saturated solution of 0.5 mol L^{-1} CH_3OH and 0.5 mol L^{-1} H_2SO_4 at 25°C for different catalysts during the accelerated potential cycling test. Scanning rate: 50 mV/s; Test temperature: 25°C； PtRu/CNT (A), PtRu/T-CNT (B) and PtRu/CNT-QDs (C).

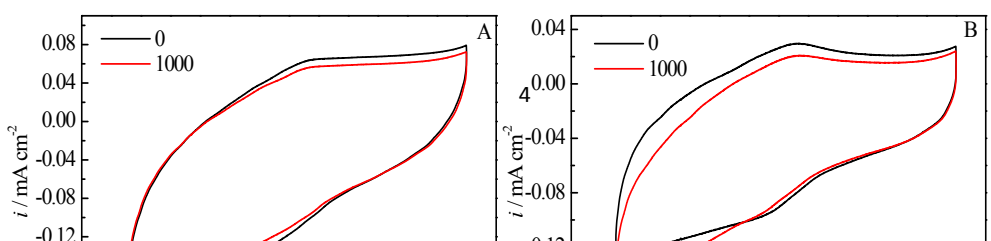

Fig. S3 Continued voltammogram cycles (1000 cycles) in an Ar-saturated solution of 0.5 mol L^{-1} H_2SO_4 at 25 °C on the CNT (a), T-CNT (b) and CNT-QDs (C). Scanning rate: 50 mV s^{-1}.

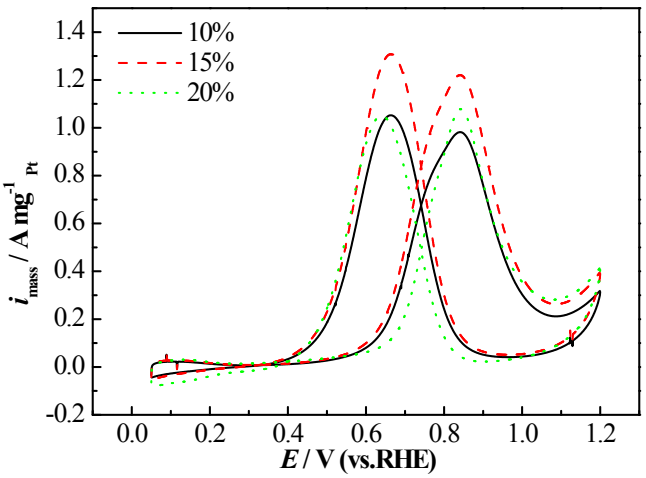

Fig. S4 Voltammogram cycles of catalysts with different g-C_3N_4 QDs content.

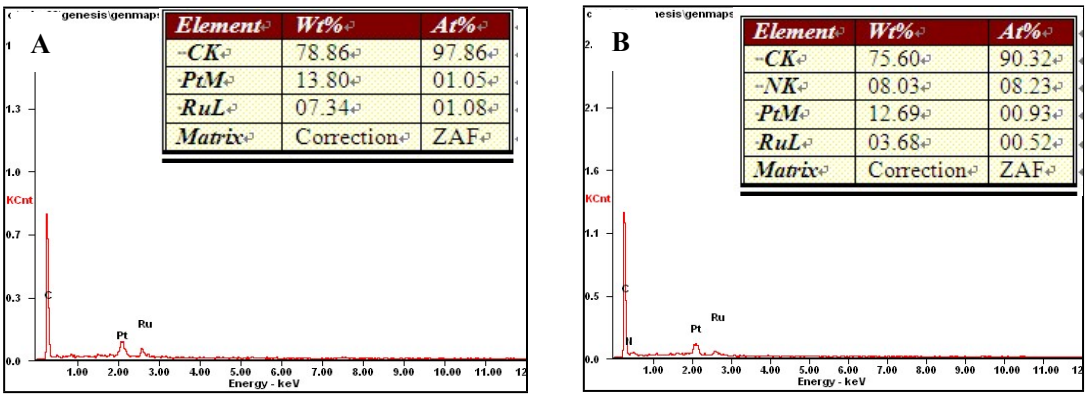

Fig. S5 EDAX patterns of PtRu/CNT(A) and PtRu/CNT-QDs(B).

Reference:

[1] C.-Z. Li, Z.-B. Wang, X.-L. Sui, L.-M. Zhang, D.-M. Gu, S. Gu, J. Mater. Chem., A 2014, 2, 20139.

[2] Z.-B. Wang, C.-Z. Li, D.-M. Gu, G.-P. Yin, J. Power Sources 2013, 238, 283.

[3] Z.-Z. Jiang, Z.-B. Wang, Y.-Y. Chu, D.-M. Gu, G.-P. Yin, Energy Environ. Sci. 2011, 4, 2558; Y. Y. Chu, Z. B. Wang, Z. Z. Jiang, D. M. Gu, G. P. Yin, Adv. Mater. 2011, 23, 3100.

[4] Z.-Z. Jiang, Z.-B. Wang, Y.-Y. Chu, D.-M. Gu, G.-P. Yin, Energy Environ. Sci. 2011, 4, 728.

[5] R. Chetty, S. Kundu, W. Xia, M. Bron, W. Schuhmann, V. Chirila, W. Brandl, T. Reinecke, M. Muhler, Electrochim. Acta 2009, 54, 4208.

[6] Y. Kuang, Y. Cui, Y. Zhang, Y. Yu, X. Zhang, J. Chen, Chemistry 2012, 18, 1522.

[7] L. Meng, D. Cao, W. Liu, Y. Zhang, M. Zhao, Ionics 2014, 20, 1127.

[8] X. Yang, X. Liu, X. Meng, X. Wang, G. Li, C. Shu, L. Jiang, C. Wang, J. Power

Sources 2013, 240, 536.

[9] B. Wu, D. Hu, Y. Kuang, B. Liu, X. Zhang, J. Chen, Angew Chem Int Ed Engl 2009, 48, 4751.