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

Hollow porous nanoparticles with Pt skin on Ag-Pt alloy structure as highly active electrocatalyst for oxygen reduction reaction

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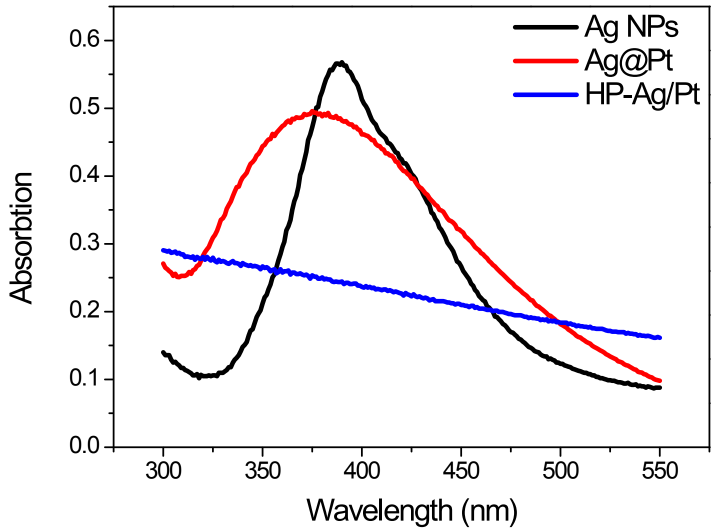

Figure S1 UV-Vis absorption spectrum of Ag nanoparticles (Ag NPs), Ag@Pt, and HP-Ag/Pt.

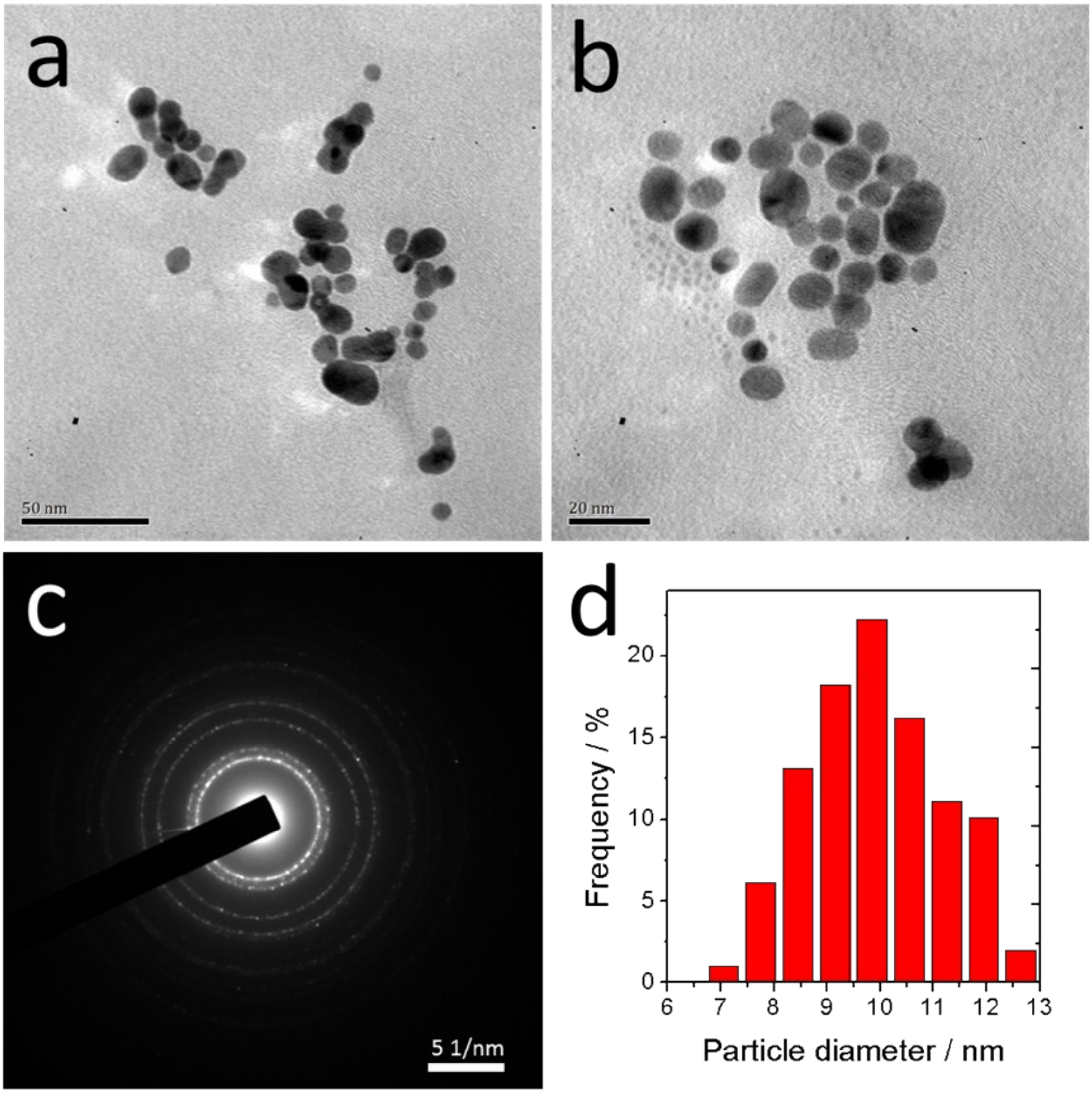

Figure S2 Typical TEM images (a, b), SAED pattern (c) and size distribution histogram (d) of Ag nanoparticles.

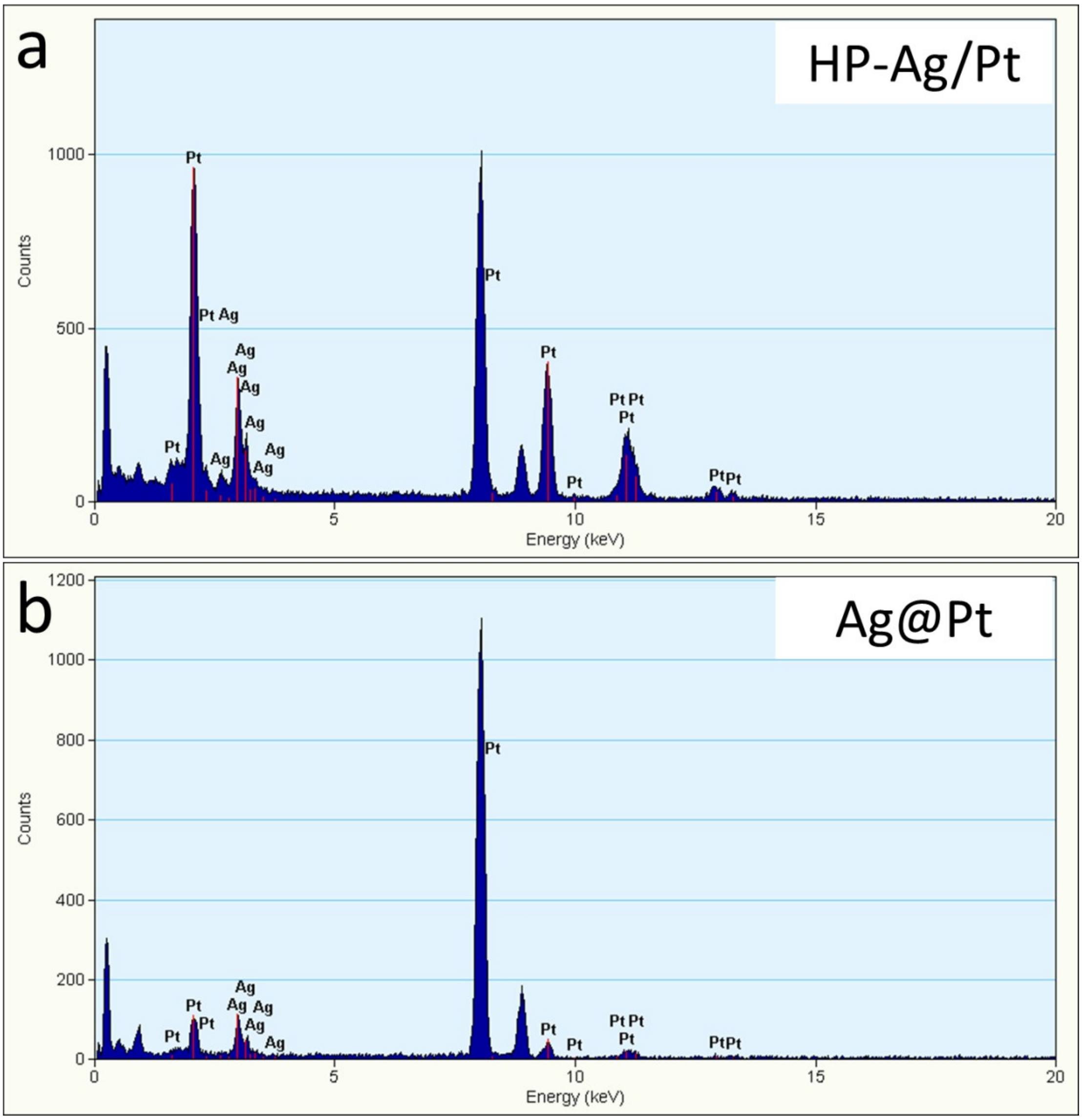

Figure S3 Typical EDS spetra of the HP-Ag/Pt and Ag@Pt nanoparticles.

Table S1 ICP Results of HP-Ag/Pt and Ag@Pt Nanoparticles (both loaded on Vulcan XC-72R).

Material	ρ_{Ag} (μg/mL)	ρ_{Pt} (μg/mL)	c_{Ag} (μmol/mL)	c_{pt} (μmol/mL)	Atom ratio (Ag to Pt)	Pt % in nanoparticles + carbon support
HP-Ag/Pt	10.7613	44.5684	0.0998	0.2285	30：70	39.8%
	10.9290	41.9928	0.1013	0.2153	32：68	40.1%
Ag@Pt	48.5758	77.2287	0.4503	0.3959	53：47	40.5%
	46.8397	72.1411	0.4342	0.3699	54：46	39.9%

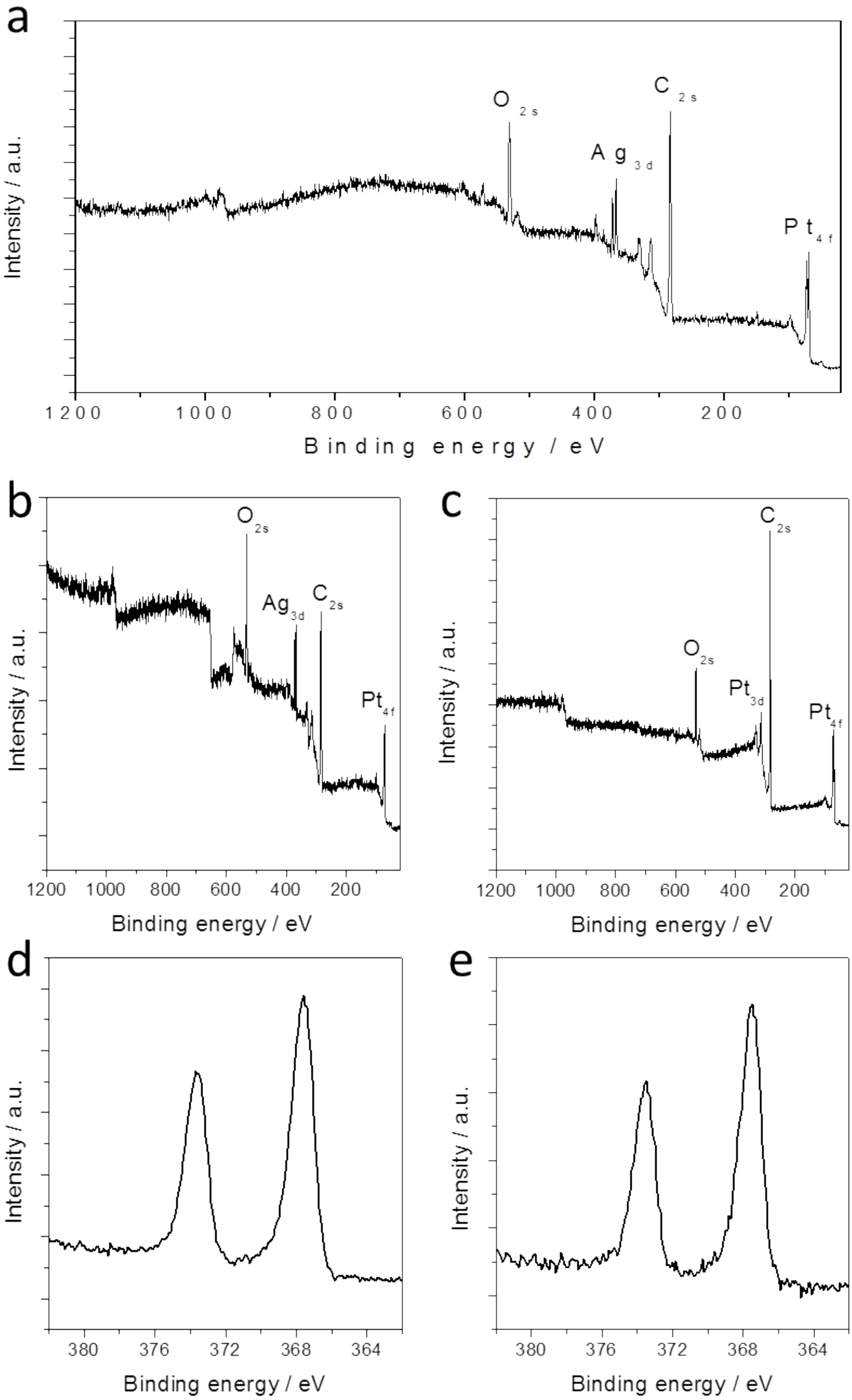

Figure S4 XPS survey spectrum of HP-Ag/Pt (a), Ag@Pt (b) and Pt/C (c), and high-resolution Ag 3d spectra for Ag@Pt (d) and HP-Ag/Pt (e).

Table S2 XPS Quantification Results of HP-Ag/Pt, Ag@Pt and Ag@Pt after accelerated durability test samples.

Material	Area (Pt_{4f})	Sensitive factor† of $Pt_{4f(Area)}$	Area (Ag_{3d})	Sensitive factor† of $Ag_{3d(area)}$	Atom ratio (Ag to Pt)
HP-Ag/Pt	26658	**4.4**	9411	**5.2**	23:77
Ag@Pt	9926		5521		31:69
Ag@Pt after ADT	19864		17707		43:57

†Data acquired from "Practical Surface Analysis", Vol. 1., 2nd Edition, by C. D. Wagner, eds. D. Briggs and M.P. Seah, Published by J. Wiley and Sons in 1990, ISBN 0-471-92081-9.

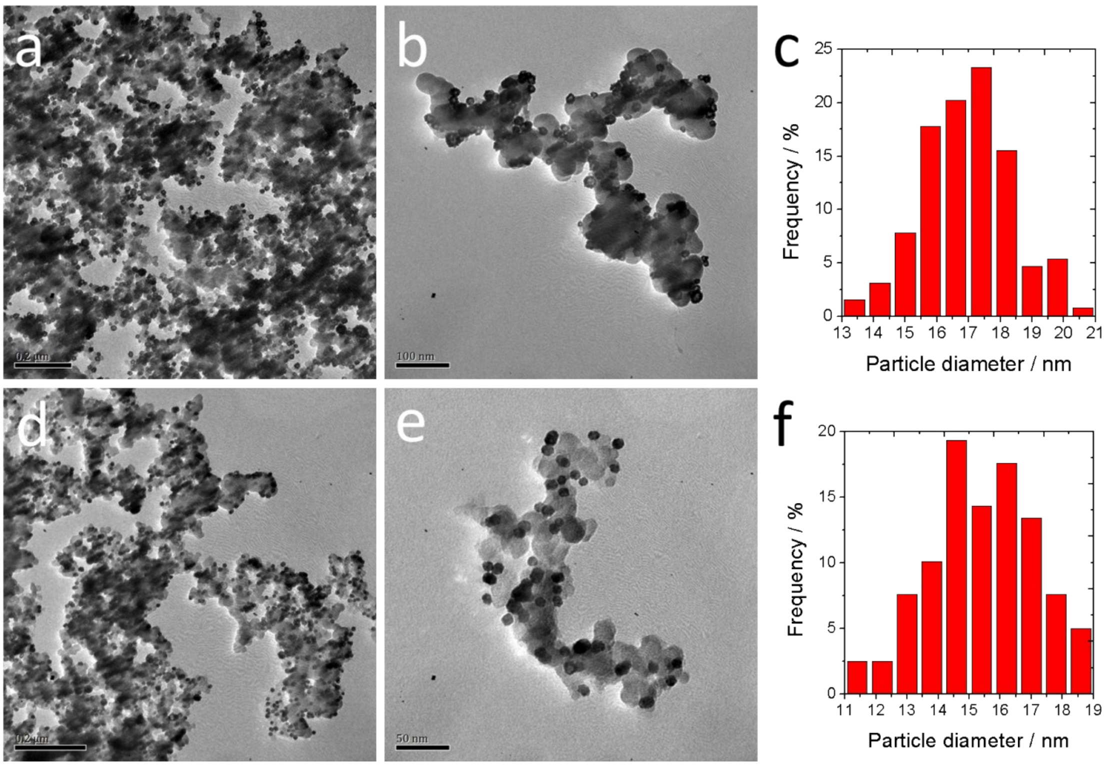

Figure S5 Typical TEM images and size distribution histogram of the HP-Ag/Pt on VC-72R (a, b, c) and Ag@Pt on VC-72R (d, e, f).

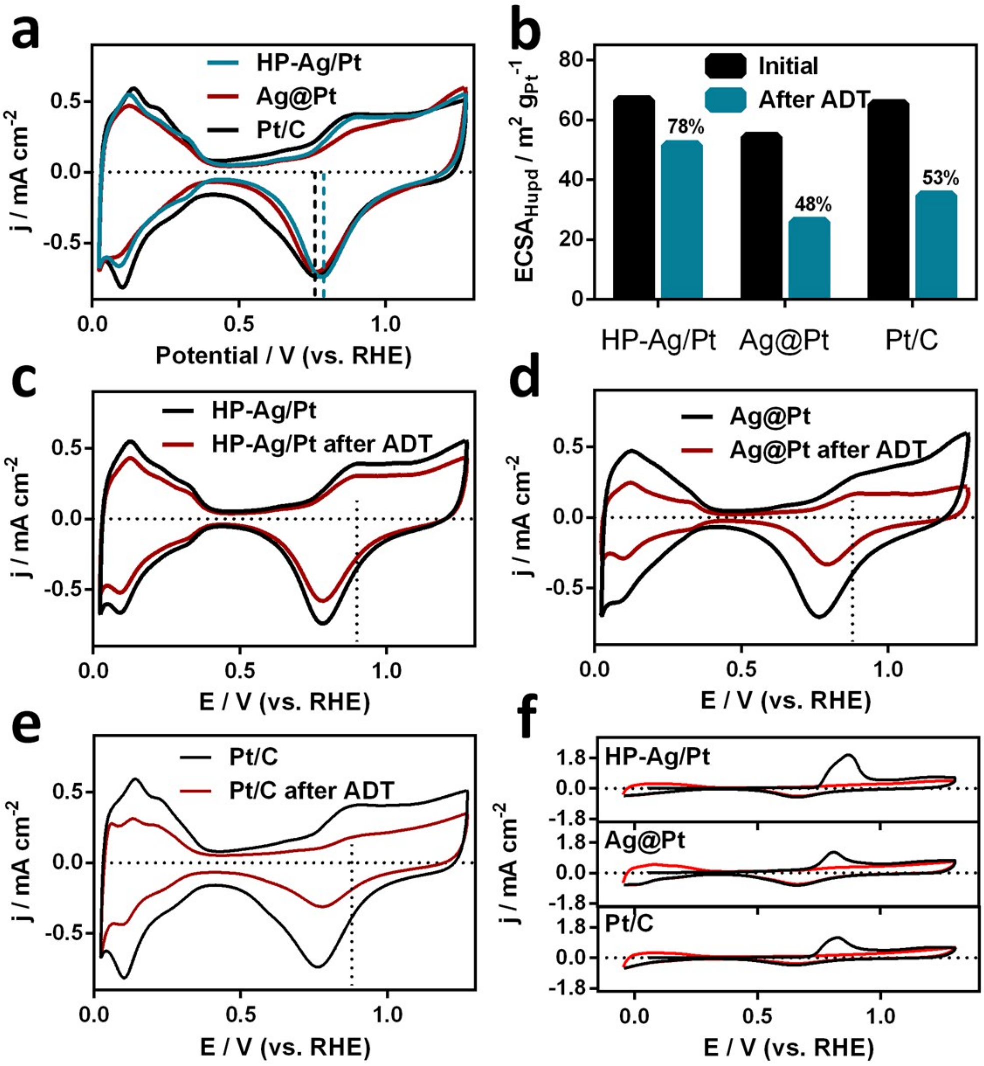

Figure S6 (a) Cyclic voltammograms of HP-Ag/Pt, Ag@Pt and Pt/C at a scan rate of 50 mV s^{-1} in N_2 saturated 0.1M $HClO_4$ at room temperature and a scan rate of 50 mV s^{-1}. (b) The electrochemical surface area (calculated from Hupd) of initial and after accelerated durability test (ADT), normalized by Pt mass. (c, d, e) CVs of catalysts in N_2-saturated 0.1 M $HClO_4$ solutions before and after accelerated durability test. (f) CO stripping voltammograms of the HP-Ag/Pt, Ag@Pt and Pt/C catalysts in 0.1M $HClO_4$ solution at a sweep rate of 50 mV s^{-1}.

Table S3 Surface Area and ORR Activities for HP-Ag/Pt/C, Ag@Pt/C and Pt/C (JM) Catalysts.

Catalyst	Pt loading (μg/cm^2)	*$ECSA_{Hupd}$ (m^2/g_{Pt})	Specific activity ($mA/cm^2_{ECSA_{Hupd}}$) at 0.90 V	$ECSA_{CO}$ (m^2/g_{Pt})	Specific activity ($mA/cm^2_{ECSA_{CO}}$) at 0.90 V	Mass activity (A/mg_{Pt})		
						at 0.80 V	at 0.85 V	at 0.90 V
HP-Ag/Pt/C	12.15	66.5	0.659	94.1	0.466	7.097	2.030	0.438
Ag@Pt/C	12.15	54.3	0.135	53.2	0.138	0.731	0.283	0.073
Pt/C (JM)	12.15	65.3	0.226	74.5	0.198	1.667	0.587	0.148

* calculated from the ratio of the charge in the hydrogen adsorption/desorption region after double layer correction to 210 μC cm^{-2} for the specific charge of monolayer adsorption of hydrogen. [1]

Table S4 Comparison of the mass and specific activities toward ORR of Pt-Ag systems from literature reprints and this work.

Catalyst	Electrolyte	Temperature (°C)	MA@0.85 V (A/mg_{Pt})	MA@0.90 V (A/mg_{Pt})	Ref.
Ag@Pt/C	0.1 M $HClO_4$	RT	0.593	-	[2]
AgPd@Pt	0.1 M $HClO_4$	30℃	-	0.148	[3]
Pt hollow	0.1 M $HClO_4$	RT	-	0.332	[4]
HP-Ag/Pt	0.1 M $HClO_4$	RT	2.030	0.438	This work

Table S5 Surface Area and ORR Activities for HP-Ag/Pt/C, Ag@Pt/C and Pt/C (JM) Catalysts after accelerated durability test.

Catalyst	Pt loading (μg/cm^2)	$ECSA_{Hupd}$ (m^2/g_{Pt})	Conser-vation rate (%)	Specific activity ($mA/cm^2_{ECSA_{Hupd}}$) at 0.90 V	$ECSA_{CO}$ (m^2/g_{Pt})	Conser-vation rate (%)	Specific activity ($mA/cm^2_{ECSA_{CO}}$) at 0.90 V	Mass activity (A/mg_{Pt}) at 0.90 V
HP-Ag/Pt/C	12.15	51.5	77.5	0.640	69.6	74.0	0.473	0.330
Ag@Pt/C	12.15	25.9	47.7	0.116	27.1	50.9	0.107	0.030
Pt/C (JM)	12.15	34.7	53.2	0.193	37.2	49.9	0.180	0.067

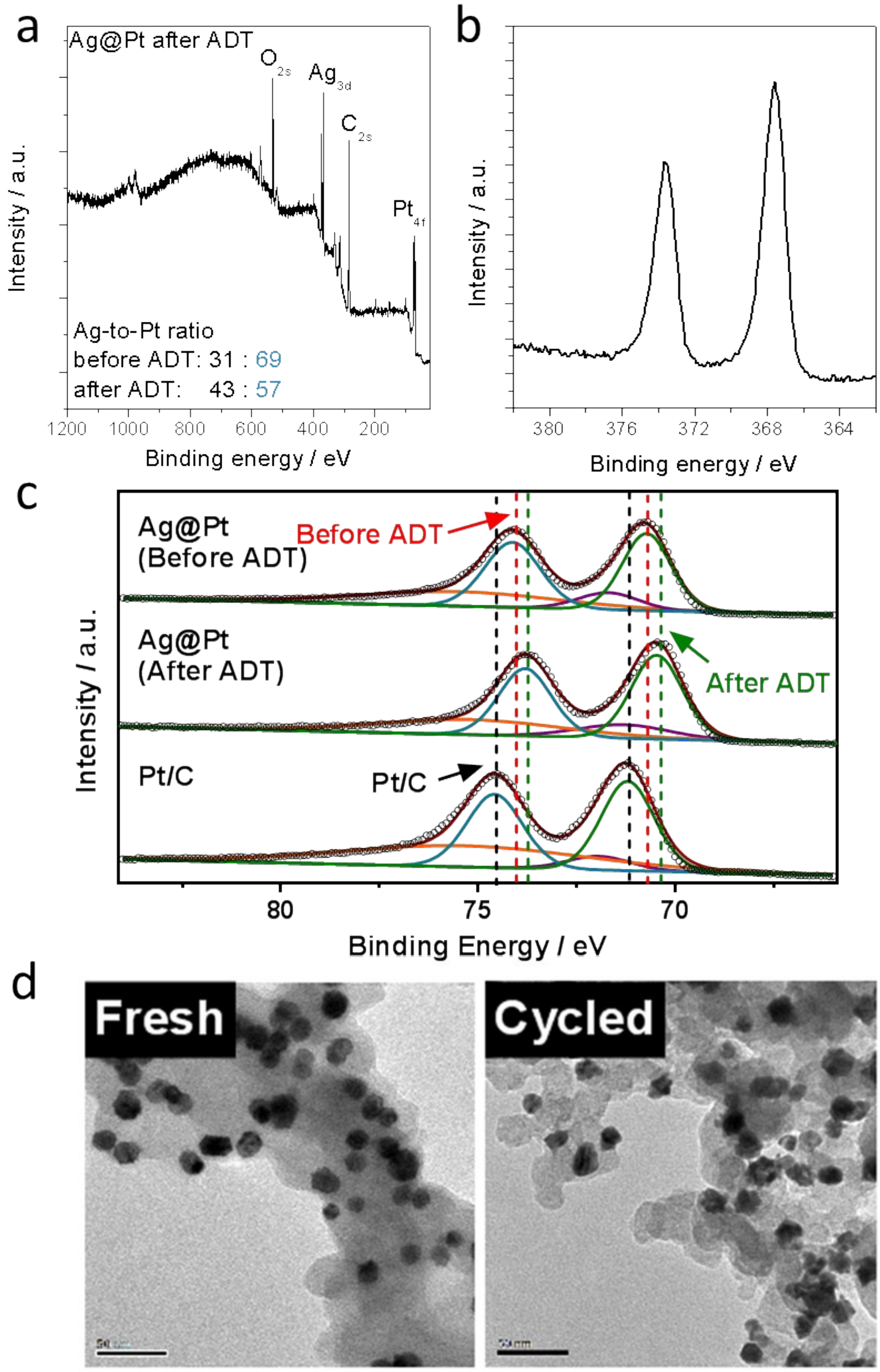

Figure S7 XPS survey spectrum (a) and high-resolution Ag 3d spectra for Ag@Pt after accelerated durability test. The high-resolution Pt 4f spectra of fresh and after ADT Ag@Pt and Pt/C sample (c) and the TEM images of fresh and cycled Ag@Pt samples (d).

Table S6 Binding Energies †, Chemical States, and Relative Intensities of Pt 4f XPS Peaks for Pt/C, Ag@Pt, HP-Ag/Pt and the Ag@Pt after accelerated durability test samples.

Material	Binding energy of Pt 4f 7/2 (eV)	Binding energy of Pt 4f 5/2(eV)	Assigned chemical state	Relative intensity (%)
Pt/C	71.20	74.57	Pt(0)	59.17
	71.93	75.37	Pt(II)	40.83
Ag@Pt	70.73	74.14	Pt(0)	65.25
	71.71	75.50	Pt(II)	34.75
HP-Ag/Pt	71.04	74.43	Pt(0)	61.25
	72.08	75.53	Pt(II)	38.75
Ag@Pt after ADT	70.63	73.98	Pt(0)	62.28
	71.54	75.43	Pt(II)	34.32

† In reference to the XC-72R carbon powder.

Reference

[1] Y. Garsany, O. A. Baturina, K. E. Swider-Lyons and S. S. Kocha, *Analytical Chemistry* 2010, **82**, 6321.

[2] J. Cao, M. Guo, J. Wu, J. Xu, W. Wang, Z. Chen, *Journal of Power Sources* 2015, **277**, 155.

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[4] Z. Peng, J. Wu, H. Yang, *Chemistry of Material* 2010, **23**, 1098.