Electronic Supplementary Information

Synergistic Effects of Platinum-Cerium Carbonate Hydroxides-Reduced Graphene Oxide on Enhanced Durability for Methanol Electro-Oxidation

Guanjun Chen,[a] Zhengfei Dai,[a,*] Lan Sun,[a] Long Zhang,[a] Shuai Liu,[b] Hongwei Bao,[a] Jinglei Bi,[a] Shengchun Yang,[a] and Fei Ma [a,*]

[a] State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, Shaanxi, People's Republic of China

[b] College of Sciences, Xi'an Shiyou University, Xi'an 710065, Shaanxi, People's Republic of China

Fig. S1 Guanjun Chen *et al.*

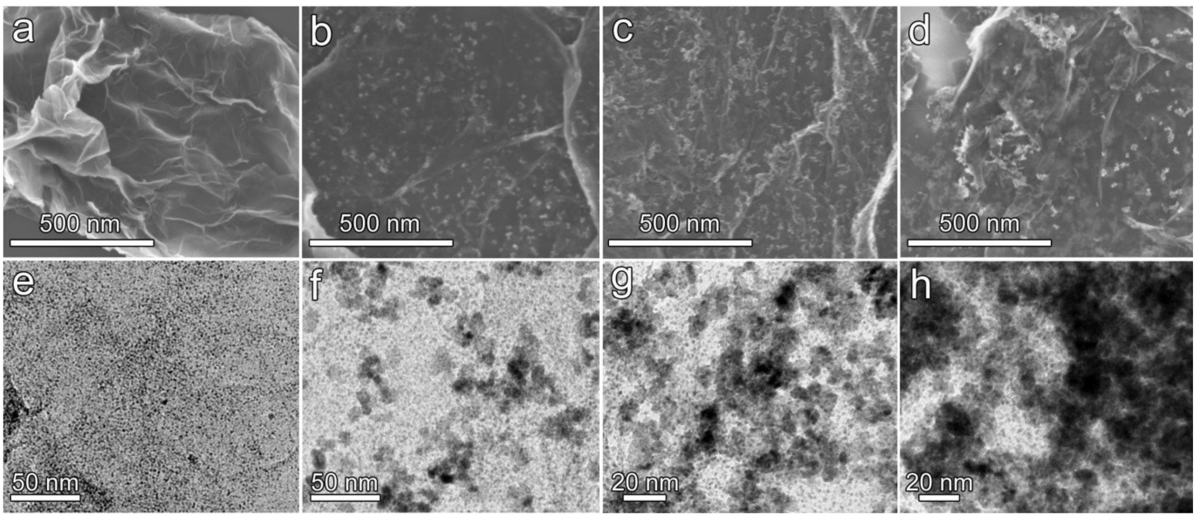

Fig. S1 (a-d) SEM images of rGO, $Ce(CO_3)OH$/rGO-1, $Ce(CO_3)OH$/rGO-2 and $Ce(CO_3)OH$/rGO-3; respectively. (e-h) TEM images of Pt/rGO, Pt-$Ce(CO_3)OH$/rGO-1, Pt-$Ce(CO_3)OH$/rGO-2 and Pt-$Ce(CO_3)OH$/rGO-3, respectively.

Fig S2. Guanjun Chen *et al.*

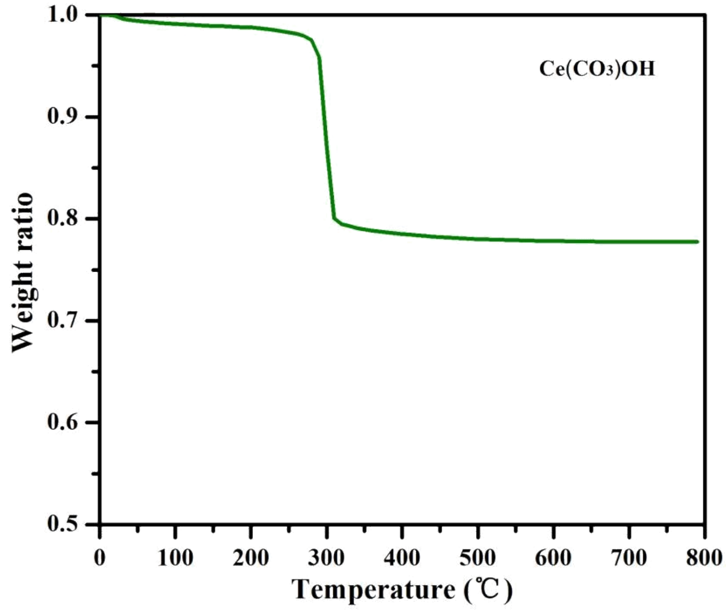

Fig. S2 TG results of $Ce(CO_3)OH$. During the TG process, $Ce(CO_3)OH$ is decomposed as follow: $Ce(CO_3)OH + O_2 \rightarrow CeO_2 + CO_2 + H_2O$. The residue is CeO_2, which accounts for 77.7% of the total weight.

Fig. S3 Guanjun Chen *et al.*

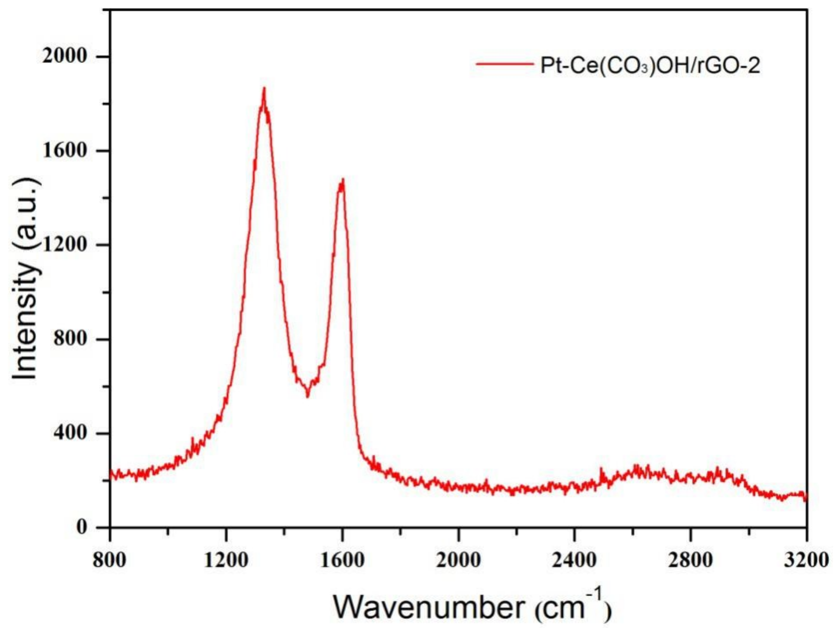

Fig. S3 Raman spectra of Pt-$Ce(CO_3)OH$/rGO-2, in which two peaks at 1580 cm^{-1} and 1350 cm^{-1} belongs to the G-band and D-band of graphene sheets. The intensity ratio of D to G bands (I_D/I_G) is 1.26, characteristic of rGO feature.

Fig. S4 Guanjun Chen *et al.*

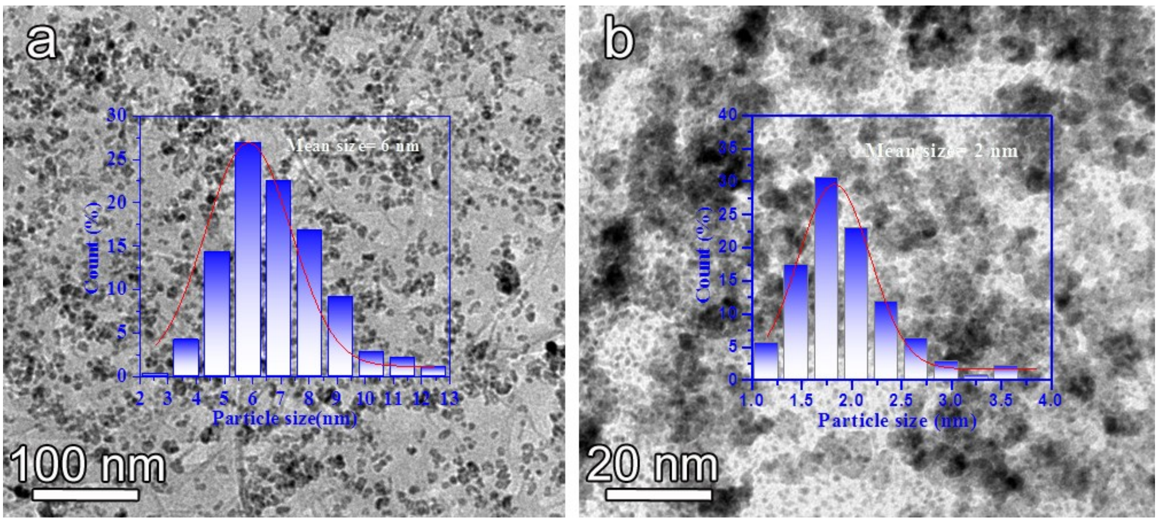

Fig. S4 TEM images and particle size distribution histograms of (a) $Ce(CO_3)OH/G$, (b) Pt-$Ce(CO_3)OH$/rGO.

Fig. S5 Guanjun Chen *et al.*

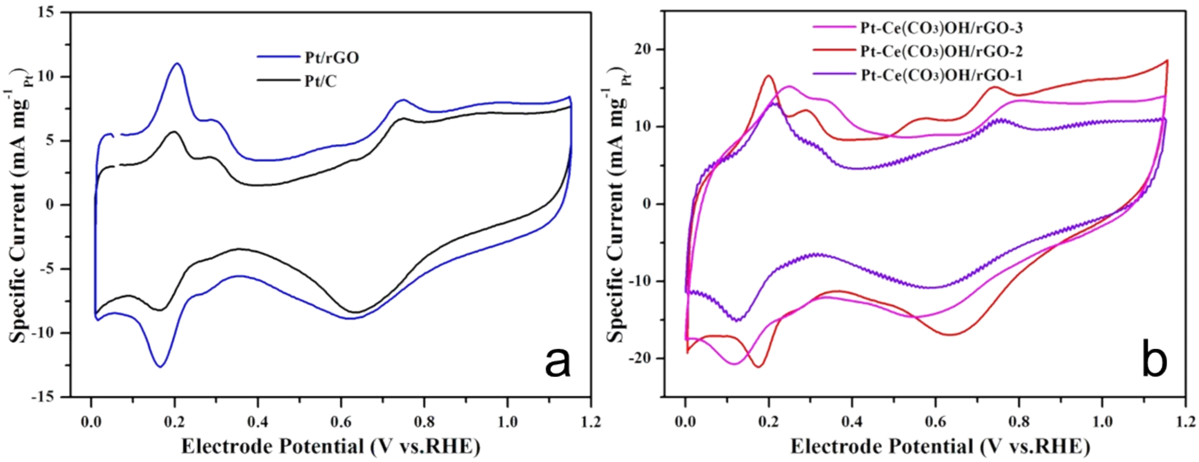

Fig. S5 Cyclic voltammetric curves of (a) Pt/rGO, Pt/C, (b) Pt-Ce(CO_3)OH/rGO-1, Pt-Ce(CO_3)OH/rGO-2, Pt-Ce(CO_3)OH/rGO-3 in 1 M KOH electrolyte for the MOR at a sweep rate of 50 mV s^{-1}.

Fig. S6 Guanjun Chen *et al.*

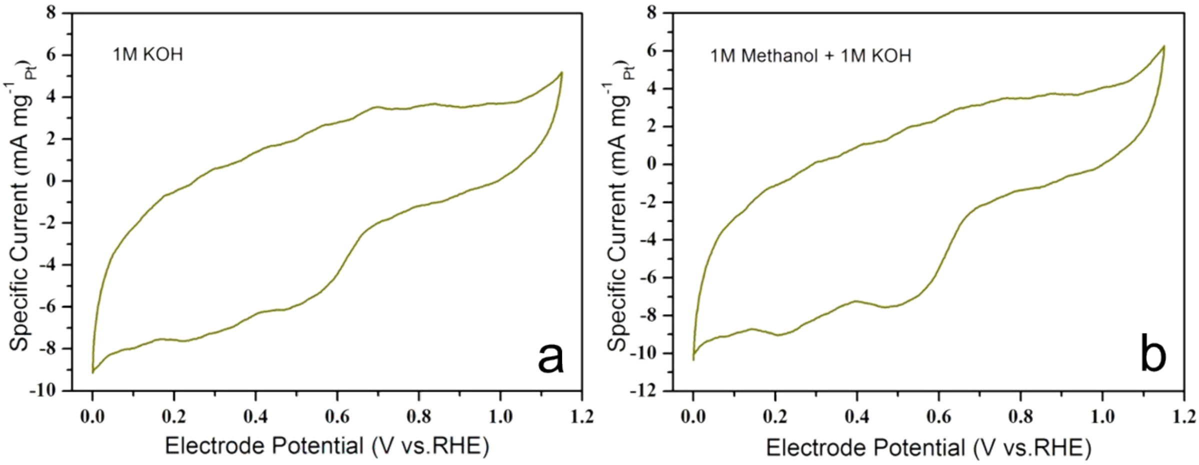

Fig. S6 Cyclic voltammetric curves of $Ce(CO_3)OH$/rGO for the MOR at a sweep rate of 50 mV s^{-1} in (a) 1 M KOH electrolyte, (b) 1 M Methanol and 1 M KOH electrolyte.

Fig. S7 Guanjun Chen *et al.*

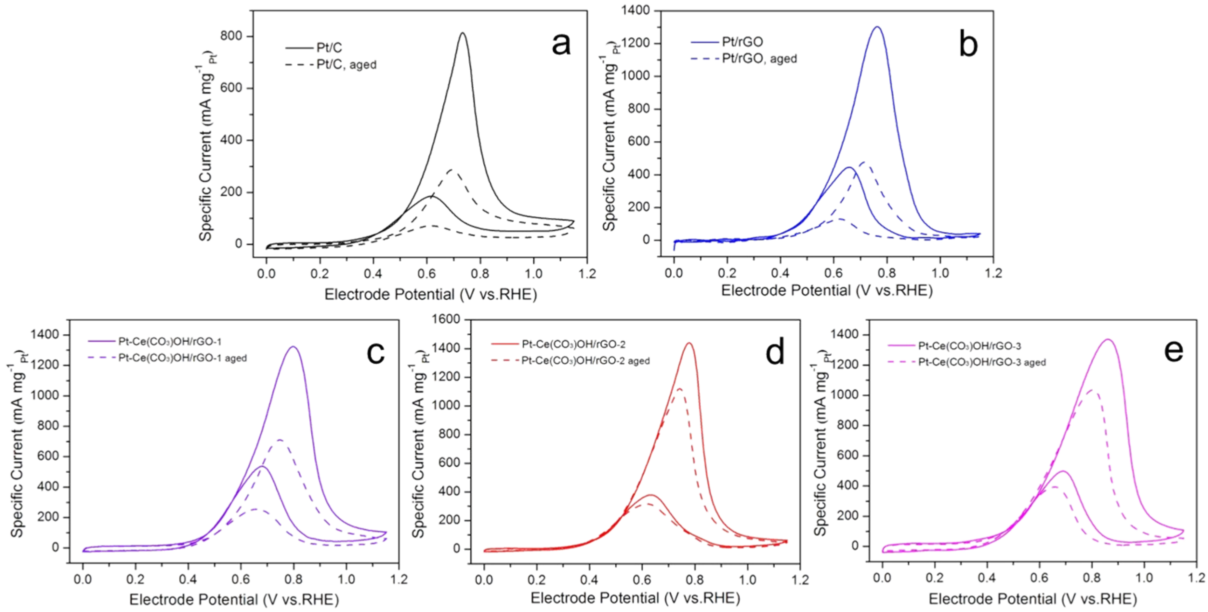

Fig. S7 Electrochemical degradation results of Pt/C, Pt/rGO, Pt-Ce(CO_3)OH/rGO-1, Pt-Ce(CO_3)OH/rGO-2 and Pt-Ce(CO_3)OH/rGO-3 catalysts before and after 5000 potential cycles.

Fig. S8 Guanjun Chen *et al.*

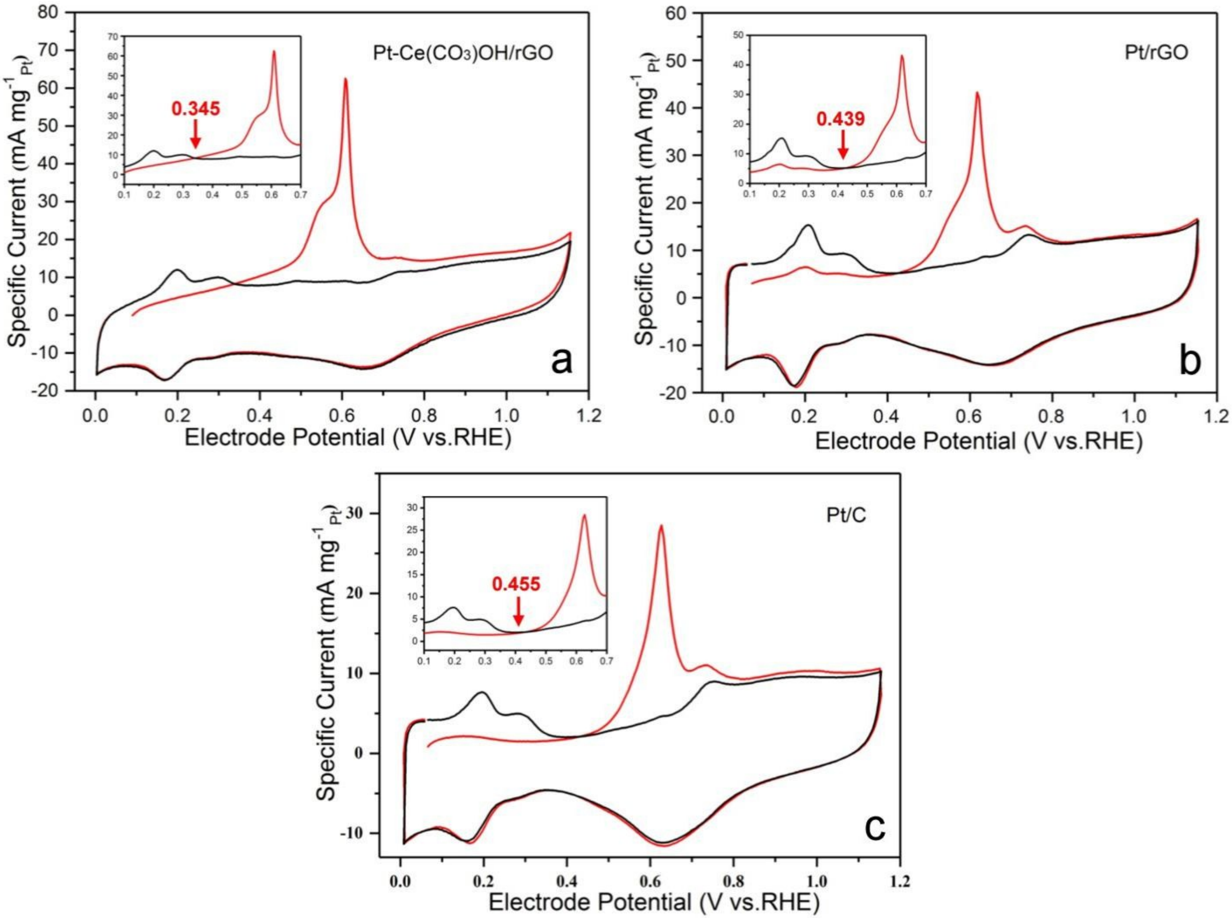

Fig. S8 CO stripping experiments of (a) Pt-Ce(CO_3)OH/rGO, (b) Pt/rGO, (c) Pt/C in 1 M KOH.

Fig. S9 Guanjun Chen *et al.*

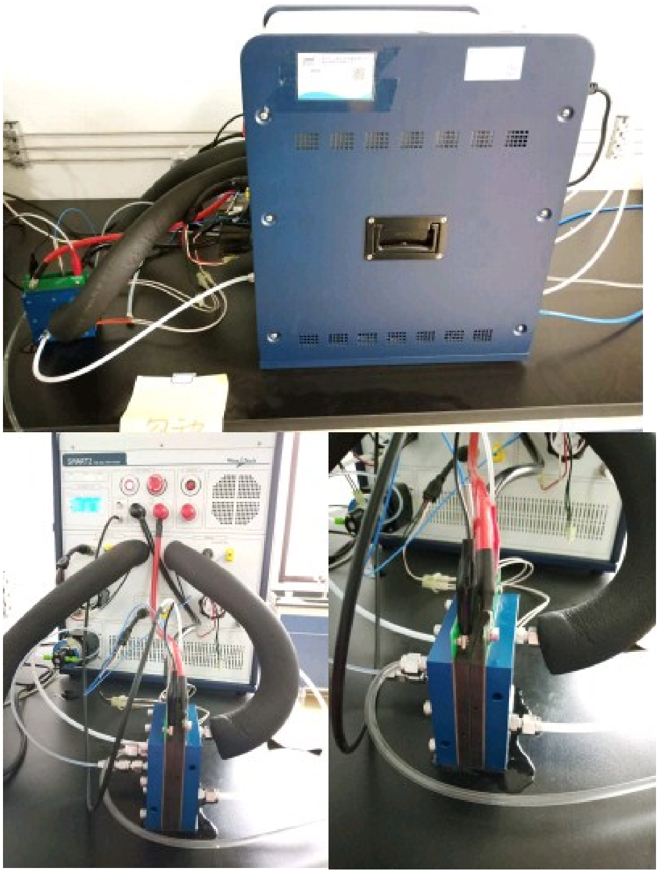

Fig. S9 .SMART2 PEM/DM test system.

Fig. S10 Guanjun Chen *et al.*

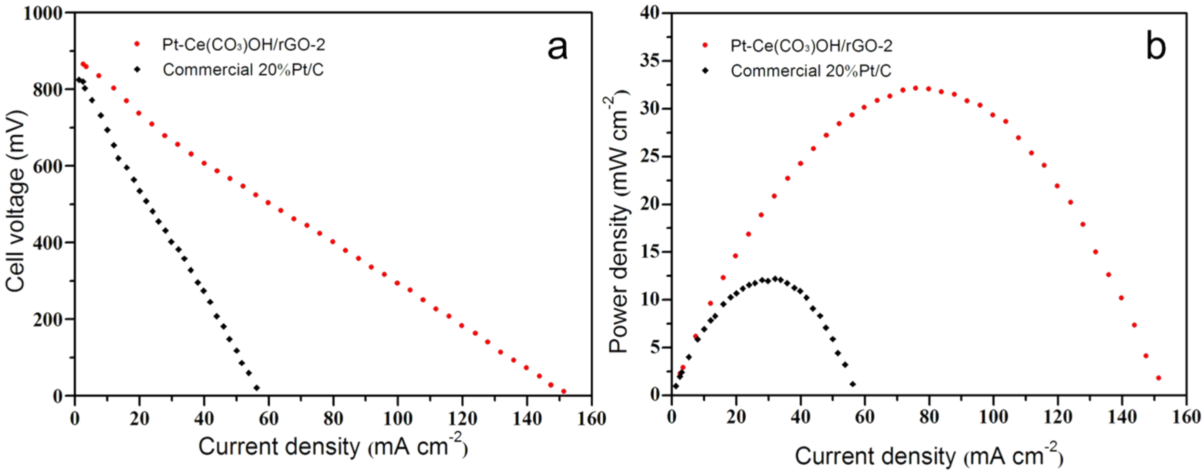

Fig. S10 (a) Polarization curves and (b) power density of Pt-Ce(CO_3)OH/rGO-2 and commercial 20% Pt/C in DMFCs.

Table S1 ICP-MS analysis of the mass fraction of Pt and Ce in the specimen, then combine the TGA data to obtain the mass fraction of $Ce(CO_3)OH$.

Specimen	Pt (wt%)	Ce (wt%)	$Ce(CO_3)OH$ (wt%)
Pt/C	26.91	--	--
Pt/rGO	27.14	--	--
Pt-$Ce(CO_3)OH$/rGO-1	26.53	13.18	17.2
Pt-$Ce(CO_3)OH$/rGO-2	26.87	28. 12	36.7
Pt-$Ce(CO_3)OH$/rGO-3	26.89	36.2	47.3

Table S2 XPS analysis of the surface compositions of Pt-Ce(CO_3)OH/rGO, Ce(CO_3)OH/rGO, Pt/rGO and Pt/C.

specimen	Weight (%)			
	C	O	Ce	Pt
Pt-Ce(CO_3)OH/rGO	37.37	8.83	8.62	45.18
Ce(CO_3)OH/rGO	51.32	19.99	28.69	--
20wt% Pt/rGO	53.58	11.78	--	32.45
20wt% Pt/C	72.04	5.81	--	22.16

Table S3 XPS results of Pt 4f.

Specimen	Origin	Binding Energy (ev)	Peak Area (%)		
			Pt (0)	Pt (II)	Pt (IV)
Pt/Ce(CO_3)OH/rGO	Pt $4f_{7/2}$	71.35	35.97	7.19	6.48
	Pt $4f_{5/2}$	74.6	35.97	9.71	4.68
	Pt $4f_{7/2}$ + Pt $4f_{5/2}$		71.94	16.90	11.16
Pt/rGO	Pt $4f_{7/2}$	71.6	30.58	10.7	9.79
	Pt $4f_{5/2}$	74.9	28.13	13.46	7.34
	Pt $4f_{7/2}$ + Pt $4f_{5/2}$		58.71	24.16	17.13
Pt/C	Pt $4f_{7/2}$	71.85	31.35	13.17	5.96
	Pt $4f_{5/2}$	75	23.19	17.24	9.09
	Pt $4f_{7/2}$ + Pt $4f_{5/2}$		54.54	30.41	15.05

Table S4 The electrochemical parameters of Pt-Ce(CO3)OH/rGO-1, Pt-Ce(CO3)OH/rGO-2, Pt-Ce(CO3)OH/rGO-3, Pt/rGO and Pt/C catalysts.

Specimen	ECSA ($m^2\ g^{-1}$)	One Set Potential (V)	Peak Potential (V)	Mass activity ($mA\ mg^{-1}$)
Pt/Ce(CO_3)OH/rGO-1	55.71	0.24	0.80	1277.5
Pt/Ce(CO_3)OH/rGO-2	60.36	0.21	0.78	1477.5
Pt/Ce(CO_3)OH/rGO-3	56.19	0.23	0.86	1284.5
Pt/rGO	49.28	0.24	0.76	1273.7
Pt/C	39.34	0.27	0.73	812.9

Table S5 Equivalent-circuit parameters on modeling the DMFC anode using constant phase elements.

Parameter	Pt/Ce(CO_3)OH/rGO-2	Pt/rGO	Pt/C
Rm (ohm cm^2)	1.35	1.34	1.35
Ri (ohm cm^2)	1.85	2.30	4.42
Ci (F cm^{-2})	0.04	0.03	0.03
Rct (ohm cm^2)	1.86	0.25	1.16
Cdl (F cm^{-2})	0.014	0.008	0.003
Rc (ohm cm^2)	0.40	0.42	0.16
Lco (H cm^{-2})	2.07×10^{-10}	0.05	0.19

Table S6 A summary of the activity and stability of MOR electrocatalysts in alkaline electrolyte available in literature.

Electrocatalyst	Electrolyte	Mass activity (mA mg^{-1})	Specific activity (mA cm^{-2})	Scan rate (mV s^{-1})	Durability	Reference
Pt-Ce(CO_3)OH /rGO	1.0 M KOH + 1.0 M methanol	1477.5	2.45	50	66 % activity retention after 3600s; 52 % activity retention after 14400s	This work
Pd-Ni-Pt Core-Sandwich-Shell	0.1 M KOH + 0.05M methanol	--	1.6	100	38 % activity retention after 1000s	*ACS Nano* **2014,** 7, 7239.
Pt-Ni$(OH)_2$/rGO	1.0 M KOH + 1.0 M methanol	1276	--	20	30 % activity retention after 50000s	*Nat. Commun.* **2015,** 6, 10035
Pd1Cu5	1.0 M KOH + 1.0 M methanol	1090	--	50	20 % activity retention after 2000s	*J. Mater. Chem. A,*2018, 6, 3906
$Cu_4Pt_2Pd_2$	1.0 M KOH + 1.0 M methanol	--	8.45	50	5 % activity retention after 10000s	*ACS Appl. Mater. Interfaces.* **2017,** 9, 25995
Pt/karst-Ni	1.0 M KOH + 1.0 M methanol	--	13.5	20	25 % activity retention after 3600s	*Appl. Catal. B-Environ.***2011,** 104, 382
Pt-Au CSANCs	0.5 M KOH + 0.5 M methanol	946	--	50	30 % activity retention after 4000s	*J. Power Sources.* **2016**, 302, 140
Pt-Pd/PPVK	1 M KOH + 1.0 M methanol	680	--	50	28 % activity retention after 3600s	*Fuel* **2012,** 102, 560
Fe_3O_4@CeO_2/Pt	0.5 M KOH + 1.0 M methanol	273	--	50	25 % activity retention after 3600s	*J. Mater. Chem. A* **2015,** 3, 139
Au_1Pt_3 bimetallic	0.5 M KOH + 0.5 M methanol	--	9	50	18 % activity retention after 1000s	*ACS Sustainable Chem. Eng.* **2014,** 2, 533
$CoPt_3$ mesoporous films	1.0 M NaOH + 1.0 M methanol	--	4.8	20	20 % activity retention after 7200s	*J. Mater. Chem. A* **2016,** 4, 7805