Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

for

Carbon nitride simultaneously boosted PtRu electrocatalyst's stability and electrocatalytic activity toward concentrated methanol

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Electrochemical measurement

The electrochemical measurements were performed using glassy carbon electrode (GCE) attached to CHI640e potentiostat with a conventional three-electrode configuration at 25 ºC. GCE (D=5 mm) was used as the working electrode. Graphite carbon and $Hg/HgCl_2$ were used as the counter and reference electrodes, respectively. Catalyst ink was prepared as follow: the electrocatalyst (1.0 mg) was ultrasonically dispersed in isopropanol/water solution (4.0 mL) to form a homogeneous solution. The electrocatalyst ink was dropped onto the GCE to form a uniform electrocatalyst layer (Pt loading was controlled at 20 μg cm^{-2}). Finally, the casted GCE was dried before testing. The cyclic voltammetry (CV) tests of the electrocatalysts at the scan rate of 50 mV s^{-1} were carried out in N_2-saturated 0.5 M H_2SO_4 solution in order to evaluate the electrochemical surface area (ECSA). The PtRu durability was evaluated based on the protocol from Fuel Cell Commercialization Conference of Japan (FCCJ) (see Supporting Information, **Figure S1**). CO stripping voltammetry was performed by feeding the GCE with CO for 20 min with flow rate of 100 mL min^{-1} and bubbled with N_2 for another 20 min. CO stripping was tested with scan rate of 50 mV s^{-1}. Methanol oxidation reaction (MOR) was estimated before and after the durability tests in N_2-saturated 0.5 M H_2SO_4 with various methanol concentrations at the scan rate of 50 mV s^{-1} at room temperature. The cell performance of the prepared MEAs was estimated from 80 ºC using Scribner Model 850e fuel cell testing system. The I-V and power density curves were recorded at atmospheric pressure by flowing 1M methanol (flow rate=3 mL min^{-1}) and 100% humidified air (flow rate= 100 mL min^{-1}) to the anode and cathode, respectively. Durability was estimated at 0.1 A cm^{-2} for 2 h.

Table S1 Ru valences of commerical PtRu/CB and PtRu/CB@C_3N_4 calculated from Ru 3p peaks.

Electrocatalyst	**Ru(0) (%)**	**Ru(IV) (%)**	**Ru(II) (%)**
PtRu/CB	75	13.5	11.5
PtRu/CB@C_3N_4	48.3	37.5	14.2

Table S2 Power densities of PtRu/CB and PtRu/CB@C_3N_4 measured with various methanol concentrations.

	1M (mW cm^{-2})	2M (mW cm^{-2})	4M (mW cm^{-2})	8M (mW cm^{-2})
PtRu/CB	48	48	37	20
PtRu/CB@C_3N_4	64	66	63	52

Table S3 Comparison of power densities measured with 1M methanol of recently published electrocatalysts.

	Tem. (°C)	PtRu (mg cm^{-2})	PD (mW cm^{-2})	Ref.
PtRu/CB@C_3N_4	80	2.0	64	This work
N-GA/PtRu	90	2.5	93	[1]
PtRu/TiN	80	2.0	32.6	[2]
PtRu/C/Nafion	25	1.0	35.4	[3]
PtRu/CECNF	80	1.9	71	[4]
Pt/$Ce_{0.6}Mo_{0.4}O_{2-\delta}$-C	60	2.0	69.4	[5]
PtSnO_2/C	100	1.0	47	[6]

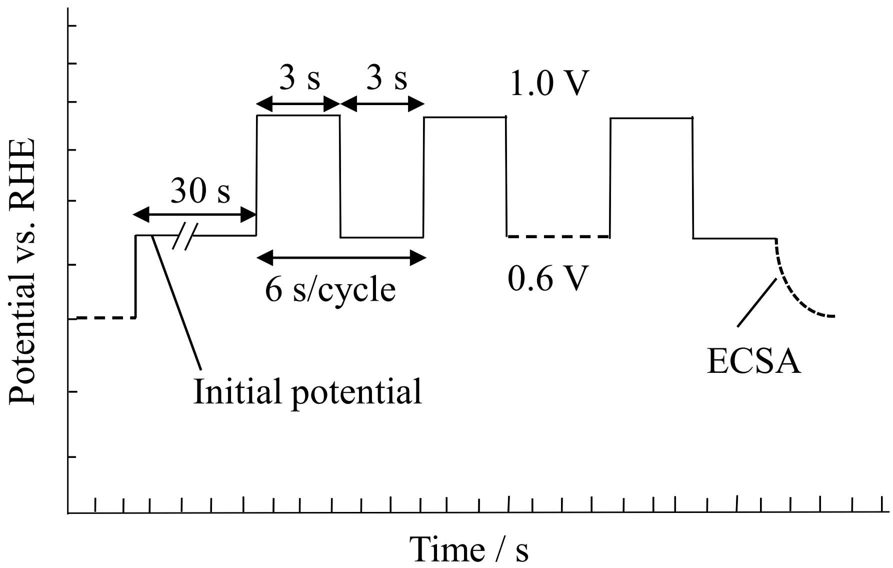

Figure S1 New test protocol of the Pt stability test in half-cell proposed by the Fuel Cell Commercialization Conference of Japan (FCCJ).

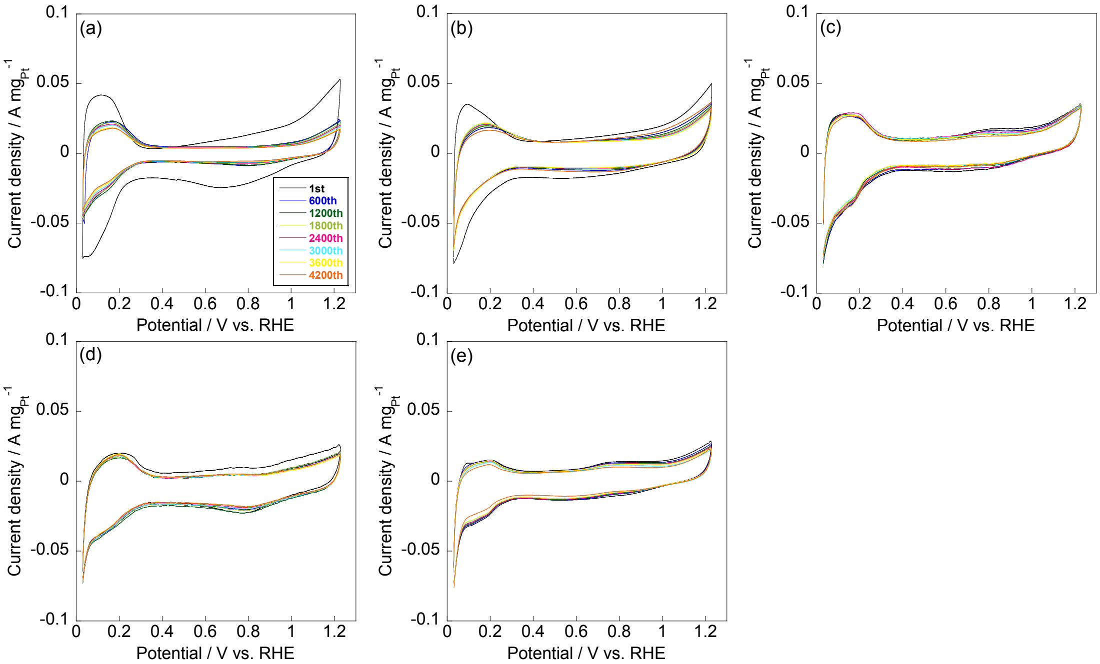

Figure S2 Recorded durability results of commercially available PtRu/CB, PtRu/CB@C_3N_4 (2:1), PtRu/CB@C_3N_4 (1:1), PtRu/CB@C_3N_4 (1:2) and PtRu/CB@C_3N_4 (1:3).

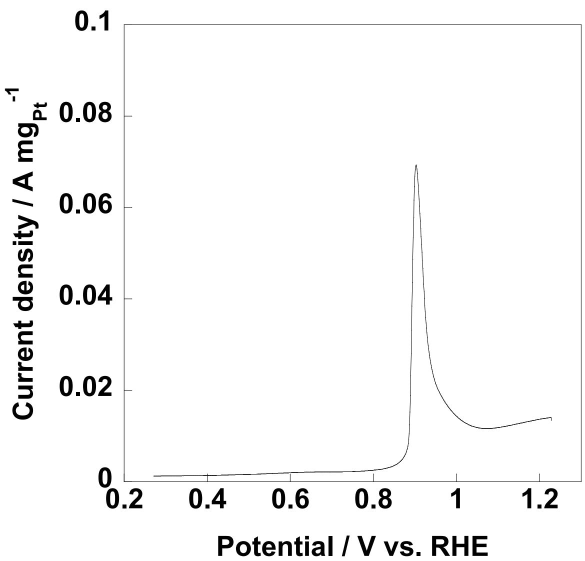

Figure S3 CO stripping curve of commercial Pt/CB measured in N_2-saturated 0.5 M H_2SO_4 electrolyte.

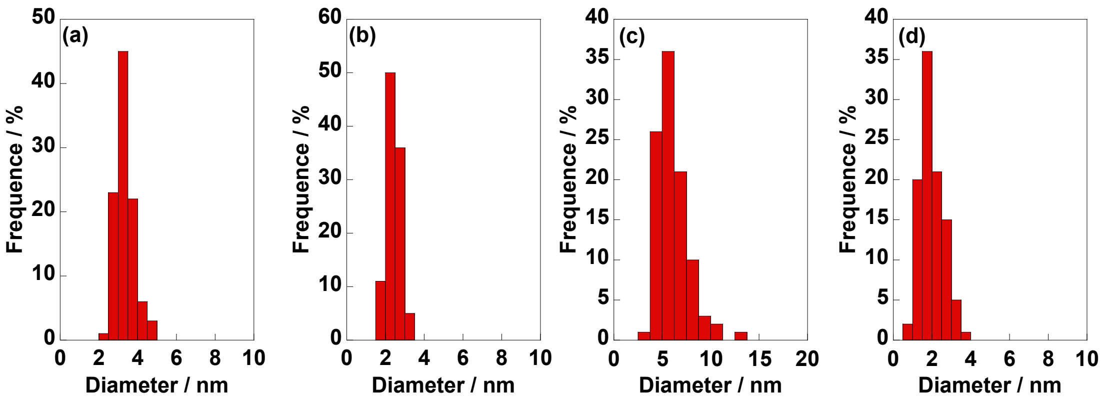

Figure S4 Histograms of PtRu size distribution of commercial PtRu/CB (a, c) and PtRu/CB@C_3N_4 (b, d) before and after durability test.

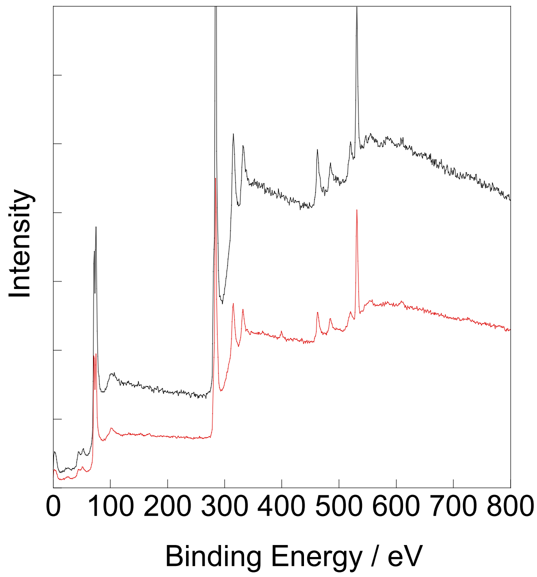

Figure S5 XPS spectra of commercially available PtRu/CB (black line), PtRu/CB@C_3N_4 (red line), respectively.

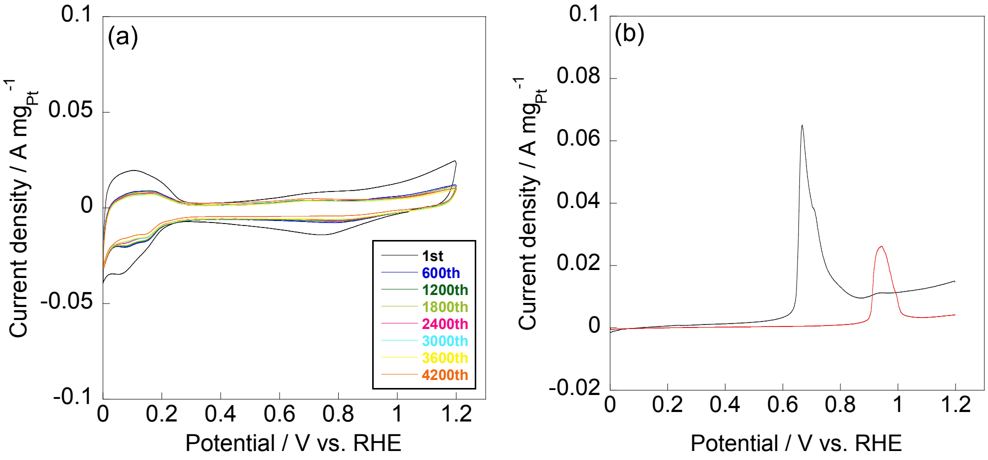

Figure S6 CV curves of PtRu/CB-H recorded after various potential cycles. (b) CO stripping voltammetry curves of PtRu/CB-H before (black line) and after (red line) stability evaluation.

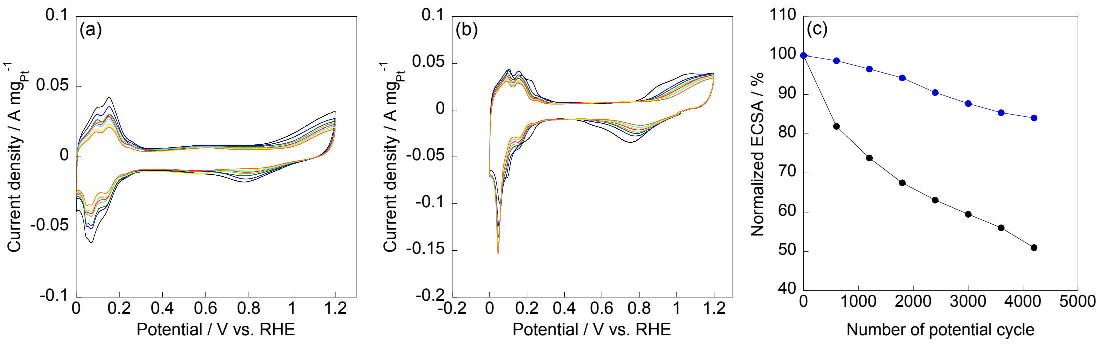

Figure S7 CV curves of commercial Pt/CB (a) and Pt/CB@C_3N_4 (b) recorded after various potential cycles. (c) Normalized ECSA values of commercial Pt/CB (black line) and Pt/CB@C_3N_4 (blue line) as a function of potential cycles.

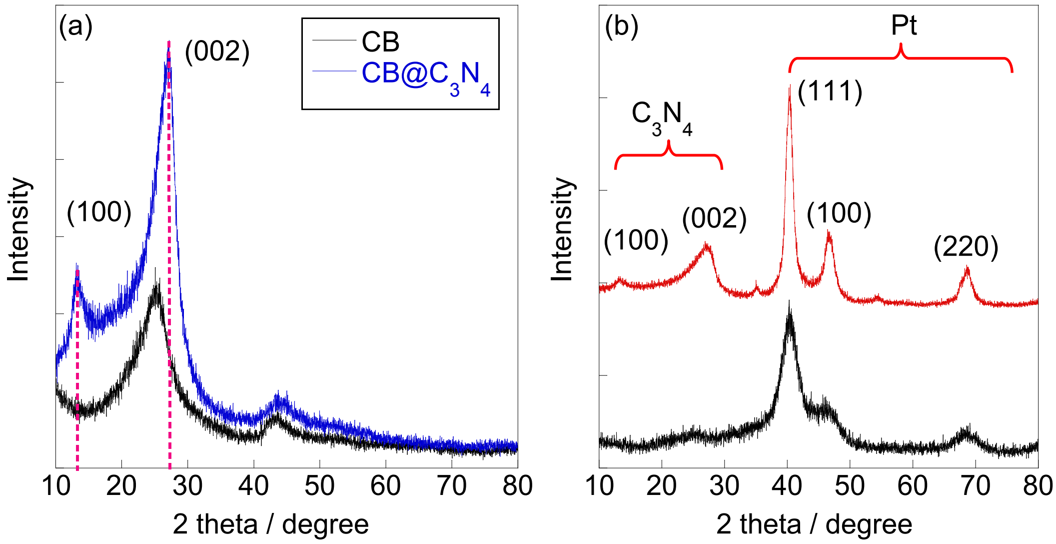

Figure S8 XRD patterns of CB, $CB@C_3N_4$ (a), PtRu/CB and $PtRu/CB@C_3N_4$ (b).

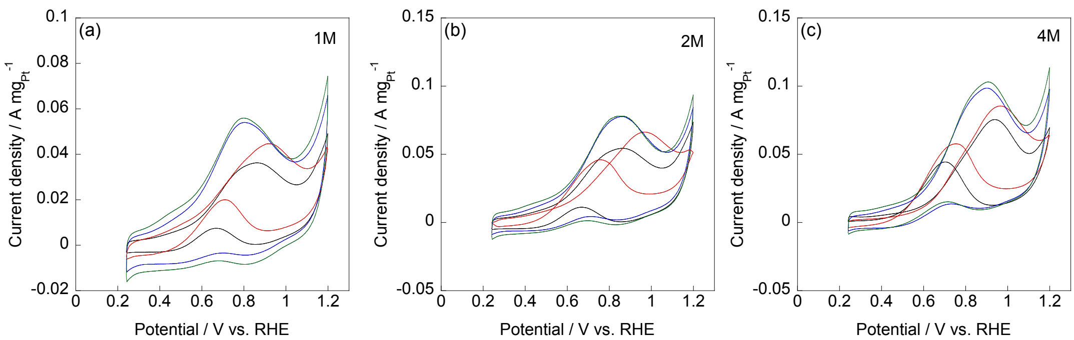

Figure S9 Methanol oxidation reaction curves of commercial PtRu/CB (black line), $PtRu/CB@C_3N_4$ (2:1, red line), $PtRu/CB@C_3N_4$ (1:2, blue line) and $PtRu/CB@C_3N_4$ (1:3, green line) measured with 1M, 2M and 4M methanol in 0.5M H_2SO_4 electrolyte.

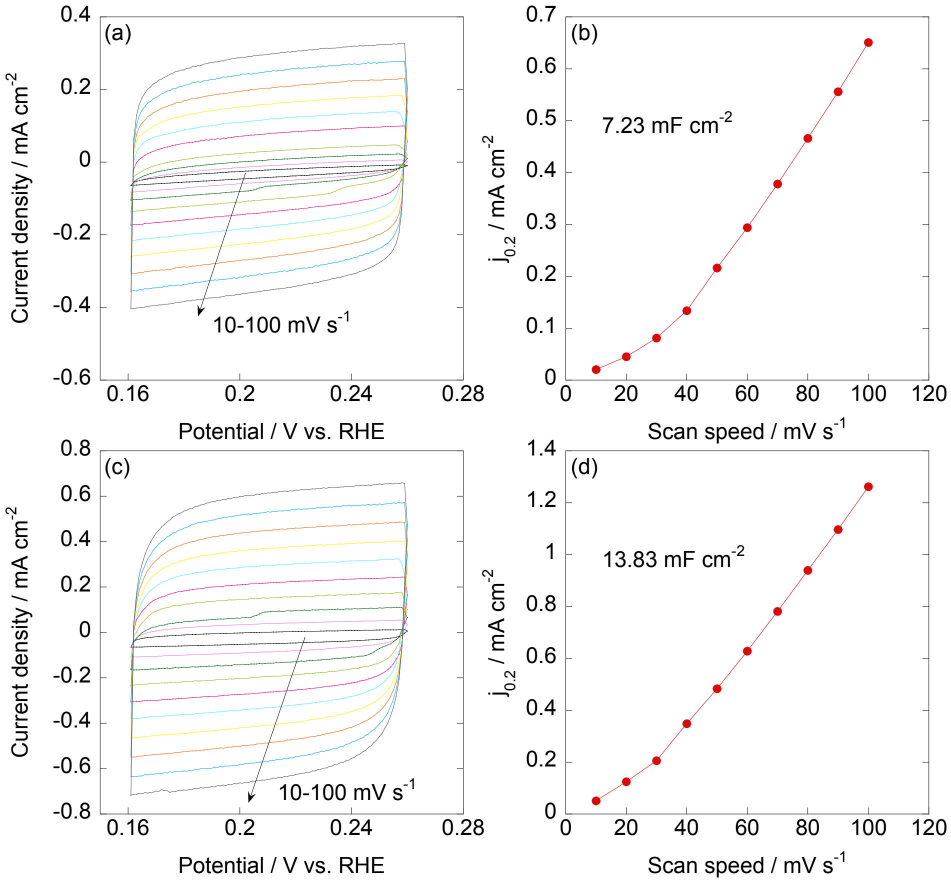

Figure S10 CV curves of CB (a) and CB@C_3N_4 (c) with various scan speed. Capacitive current@0.2V versus RHE as a function of scan rate for CB (b) and CB@C_3N_4 (d).

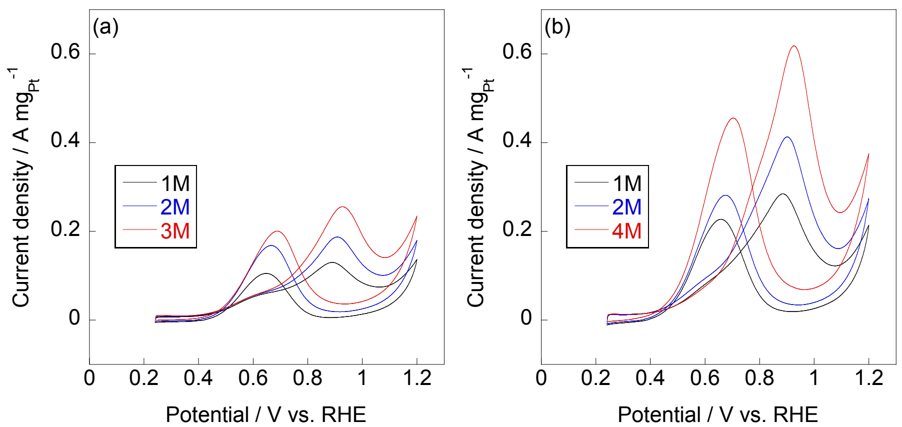

Figure S11 Methanol oxidation reaction curves of commercial Pt/CB (a) and Pt/CB@C_3N_4 (b) measured with 1M, 2M and 4M methanol in 0.5M H_2SO_4 electrolyte.

References

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