## **Supporting Information**

## Origin of enhancement of electrocatalytic activity and durability of

## Pt-Ru alloy prepared from hetero bi-nuclear Pt-Ru complex for

## methanol oxidation reaction

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Fig. S1 (a) CVs of the 32-Pt-Ru/Au (blue, A), Pt-Ru<sub>mix</sub>/Au (O<sub>2</sub>) (red, B) and Pt-Ru<sub>mix</sub>/Au (H<sub>2</sub>) (black, C) in 0.1 M HClO<sub>4</sub> solution with 1 M methanol. Scan rate = 50 mV s<sup>-1</sup>. (b) Current decay curves of the 32-Pt-Ru/Au (blue, A), Pt-Ru<sub>mix</sub>/Au (O<sub>2</sub>) (red, B) and Pt-Ru<sub>mix</sub>/Au (H<sub>2</sub>) (black, C) at 0.4 V vs. Ag/AgCl in 0.1 M HClO<sub>4</sub> solution with 1 M methanol. The current was normalized by the surface area of Au before foreign metals modification.

Surface fraction of Pt was estimated from charge of hydrogen UPD as follows:

	32-Pt-Ru/Au		Pt-Ru <sub>mix</sub> /Au	
	$ heta_{Pt}$	$\theta_{PtRu}$	$ heta_{Pt}$	$\theta_{PtRu}$
Coverage	0.18	0.49	0.29	0.52
$\theta_{Pt}/\theta_{PtRu}$	0.37		0.56	

 $Q_{Au}(bareAu)$ : charge of Au oxide reduction at bare Au electrode

 $Q_{Au}(Pt - Ru/Au)$ : charge of Au oxide reduction at Pt-Ru modified Au electrode (exposed area of bare Au)

 $Q_{Pt}(Pt - Ru / Au)$ : charge of UPD of hydrogen on Pt at Pt-Ru modified Au electrode

$$\theta_{Pt} = \frac{Q_{Pt} (Pt - Ru / Au)}{Q_{Au} (bareAu)}: \text{ surface coverage of Pt at Pt-Ru modified Au electrode}$$

$$\theta_{PtRu} = \frac{Q_{Au} (bareAu) - Q_{Au} (Pt - Ru / Au)}{Q_{Au} (bareAu)}: \text{ surface coverage of Pt-Ru alloy at Pt-Ru modified Au electrode}$$

$$\theta_{PtRu} = \frac{Q_{Au} (bareAu) - Q_{Au} (Pt - Ru / Au)}{Q_{Au} (bareAu)}: \text{ surface coverage of Pt-Ru alloy at Pt-Ru modified Au electrode}$$

 $\frac{\sigma_{Pt}}{\theta_{PtRu}}$ : surface fraction of Pt in Pt-Ru alloy

Surface fraction of Pt was also estimated from peak intensities of XPS and relative sensitivity factor of each atom as follows:

	32-Pt-Ru/Au		Pt-Ru <sub>mix</sub> /Au	
	Pt 4f <sub>7/2</sub>	Ru 3p <sub>3/2</sub>	Pt 4f <sub>7/2</sub>	Ru 3p <sub>3/2</sub>
Peak area	2474	2874	4100	2047
$\theta_{Pt}/\theta_{PtRu}$	0.30		0.51	

 $\frac{\theta_{P_{t}}}{\theta_{P_{t}R_{u}}} = \frac{I_{P_{t}} / R_{P_{t}}}{I_{P_{t}} / R_{P_{t}} + I_{R_{u}} / R_{R_{u}}}:$  surface fraction of Pt in Pt-Ru alloy at Pt-Ru modified Au electrode

*I*: XP peak area

*R*: relative sensitivity factor of each atom

Thus, surface fraction of Pt estimated from hydrogen UPD is in reasonable agreement with that obtained from peak intensities of XPS and relative sensitive factors.