

Supporting Information

Hexapod PtRuCu Nanocrystalline Alloy for Highly Efficient and Stable Methanol Oxidation

Shengfeng Xue,^{1†} Wentao Deng,^{2†} Fang Yang,^{1†} Jinlong Yang,¹ Ibrahim Saana

Amiin, ¹Daping He, ^{1,3} Haolin Tang, ^{1*} Shichun Mu^{1*}*

¹ State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China

² Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, U.K.

³ Hubei Engineering Research Center of RF-Microwave Technology and Application, Wuhan University of Technology, Wuhan 430070, China

*hedaping@whut.edu.cn

*tanghaolin2005@yahoo.com.cn

*msc@whut.edu.cn

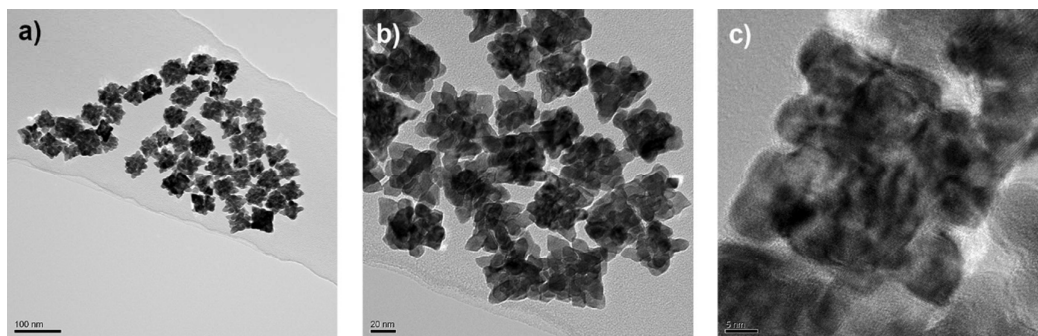


Figure S1 Representative (a, b) TEM images and (c) HRTEM image for PtRuCu dendrites synthesized by extending the reaction time to 2 h. Scale bar: (a) 100 nm; (b) 20 nm; (c) 5 nm.

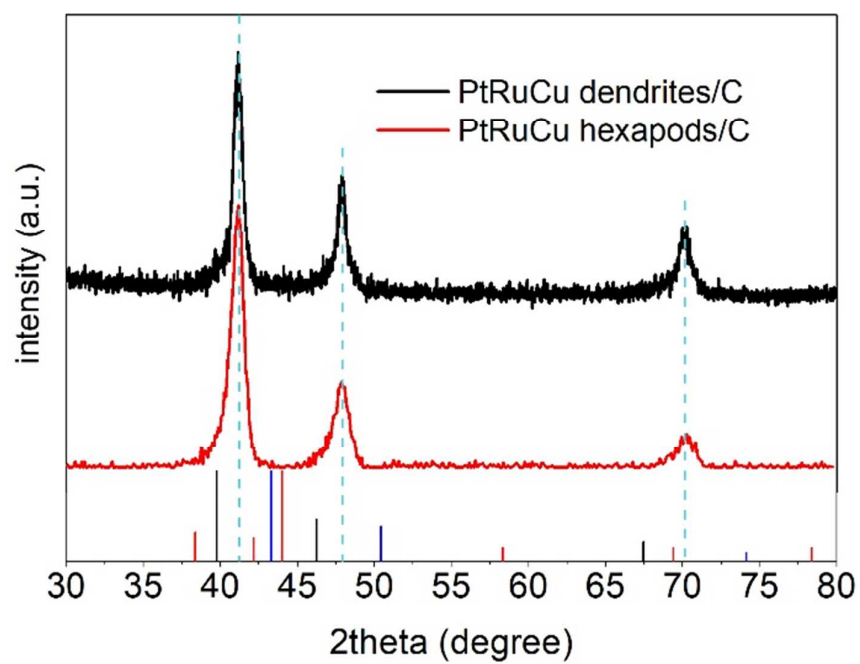


Figure S2 XRD patterns of PtRuCu (i.e. hexapods)/C and PtRuCu dendrites/C.

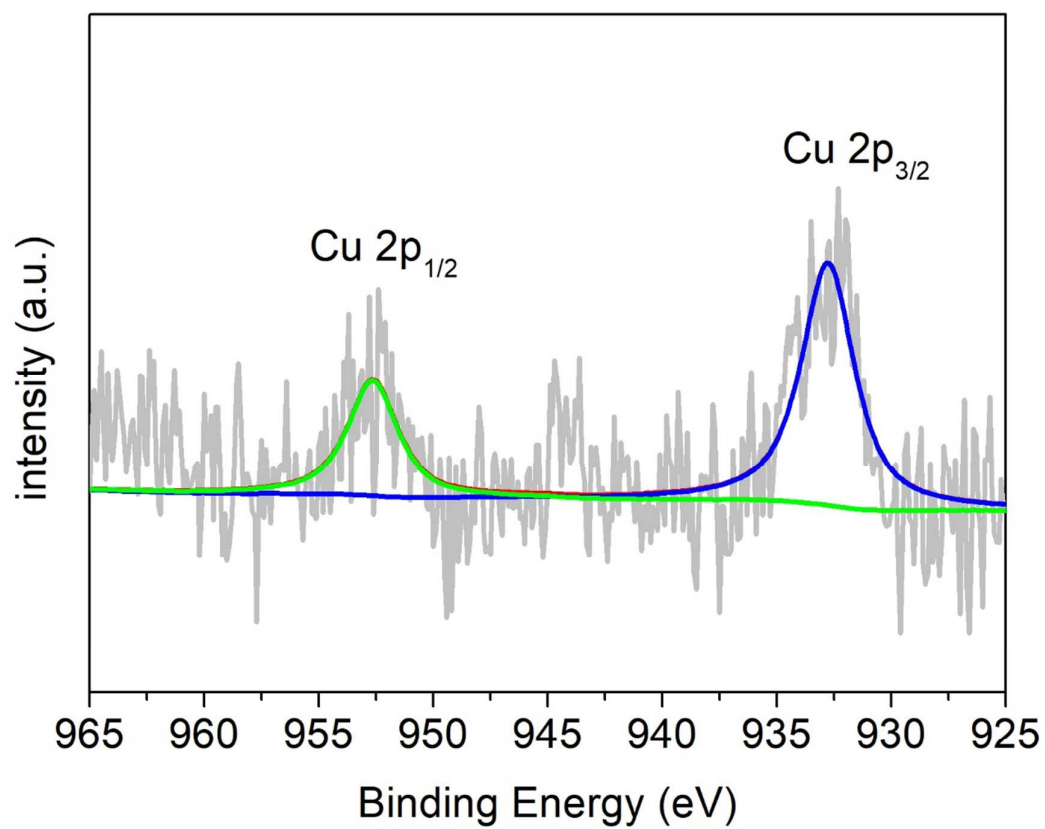


Figure S3 XPS spectrum in Cu 2p region of PtRuCu

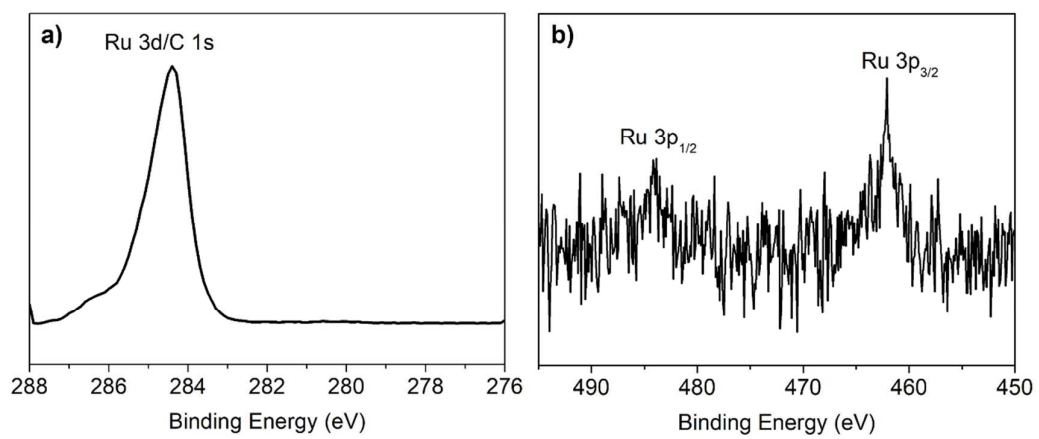


Figure S4 XPS spectra of (a) Ru 3d and C 1s regions and (b) Ru 3p region for PtRuCu.

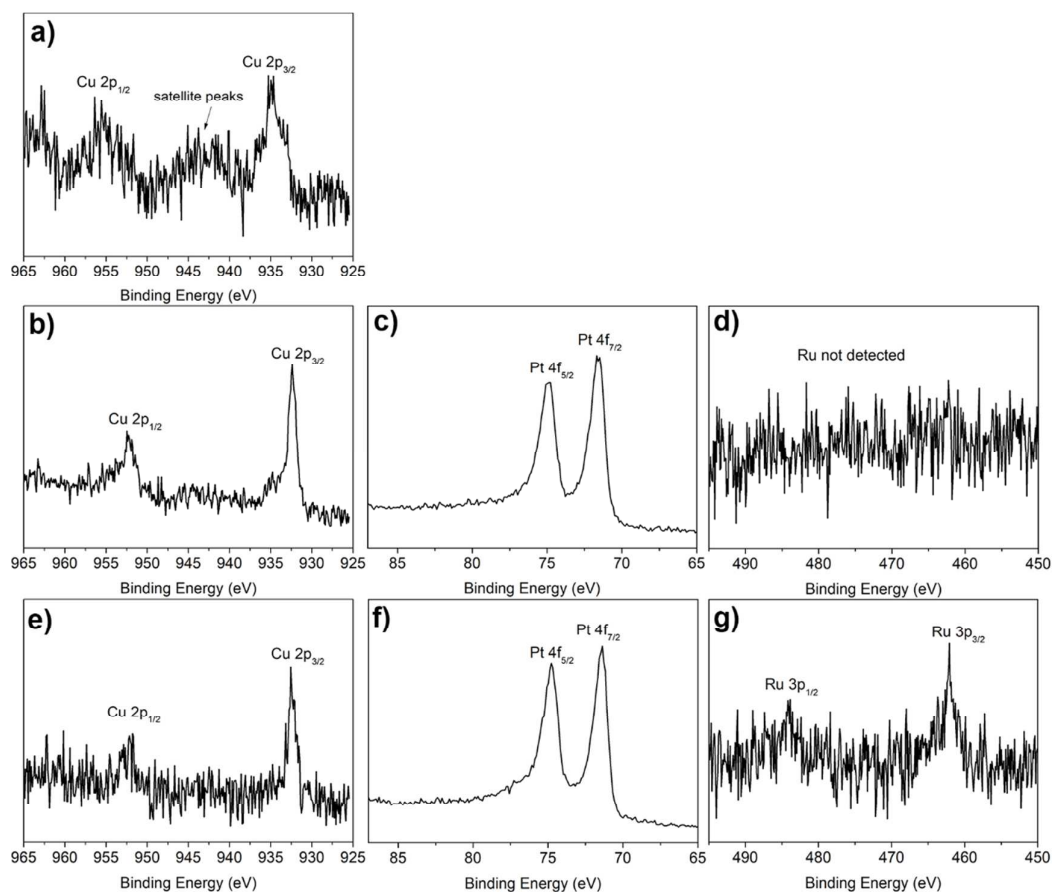


Figure S5 XPS spectra of elemental changes in Cu, PtCu and PtRuCu. a) Cu 2p region of synthesized Cu; b-d) Cu 2p, Pt 4f and Ru 3p region of PtCu octahedra; e)-g) Cu 2p, Pt 4f and Ru 3p region of PtRuCu hexapods.

Figure S5 shows the XPS spectra of the products at different stages from Cu→PtCu→PtRuCu. In Figure R5a, the satellite peaks and the main peak locate at ~935 eV, indicating that the main component of the product is CuO. The most possible reason is that as-synthesized Cu could be oxidized in air.¹ No satellite peaks are observed in the spectra of PtCu and PtRuCu (**Figure R5b** and **Figure R5e**), confirming that Cu(OAc)₂ is completely reduced to metallic Cu with the prolongation of the reaction time and the addition of Pt(acac)₂. From the spectra of Pt in PtCu and PtRuCu (**Figure**

R5c and **R5f**), ~ 0.2 eV negative shift appears in PtRuCu compared to PtCu, verifying that Pt alloys better with Cu as reaction time increased. **Figure R5d** and **Figure R5g** show the XPS spectra in Ru 3p region. Ru cannot be detected in PtCu (the product was obtained when $\text{Ru}(\text{acac})_3$ and $\text{Pt}(\text{acac})_2$ were added and heated for 30 min) but appears in PtRuCu (the product was obtained when $\text{Ru}(\text{acac})_3$ and $\text{Pt}(\text{acac})_2$ was added and heated for 60 min). This proves that $\text{Ru}(\text{acac})_3$ is barely reduced due to the insufficient reaction time, and the $\text{Pt}(\text{acac})_2$ has priority in the reduction reaction

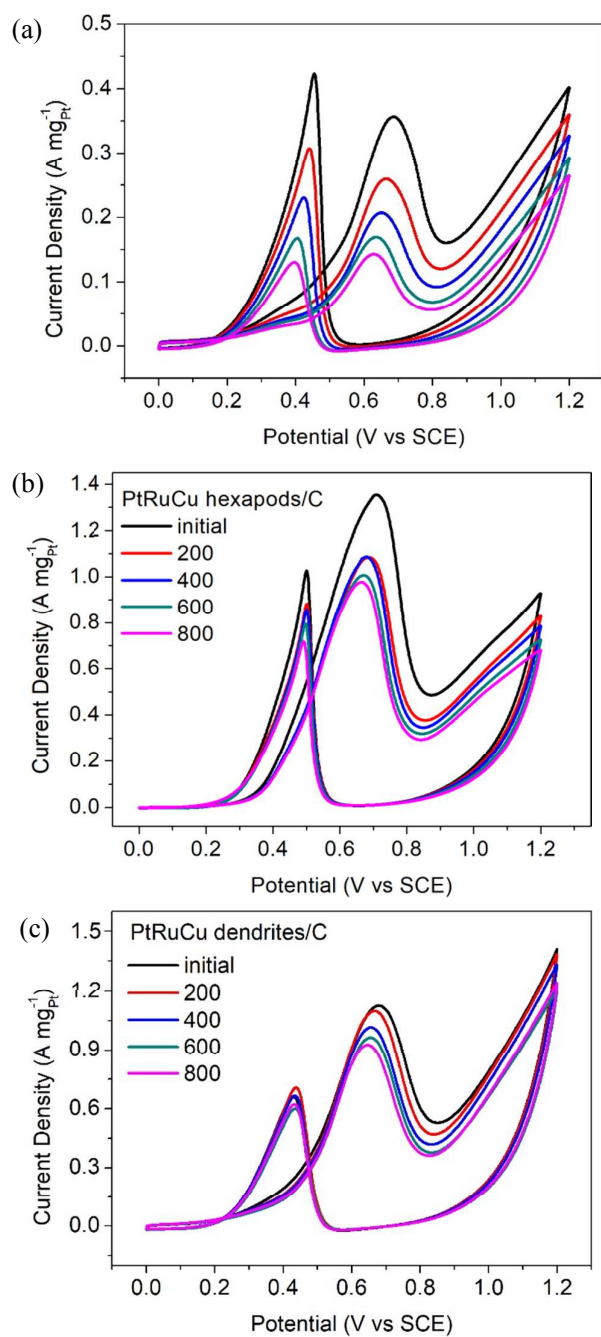


Figure S6 MOR performance of (a) Pt/C and (b)PtRuCu/C and (c)PtRuCu dendrites/C after 0, 200, 400, 600 and 800 CV cycles.

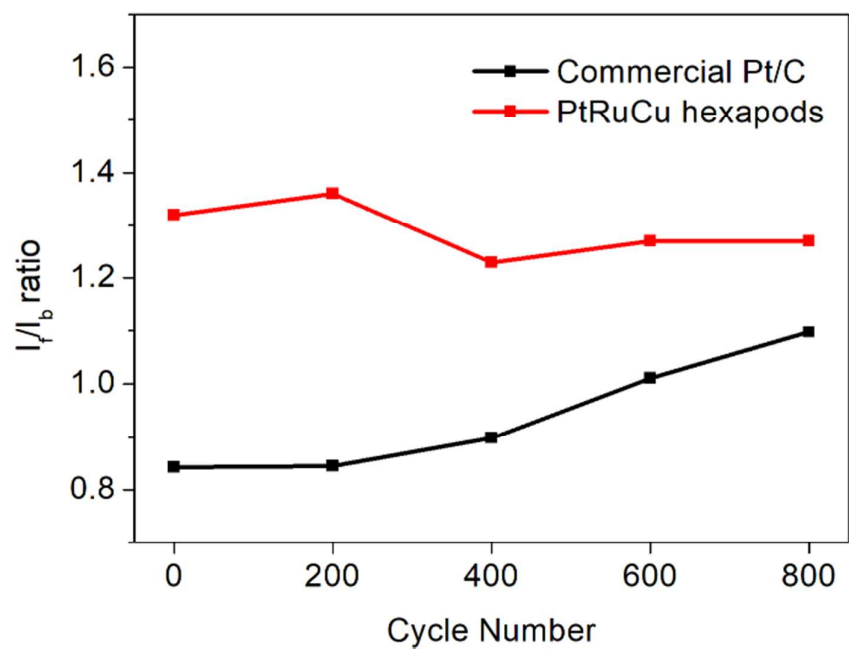


Figure S7 Ratio of I_f/I_b for commercial Pt/C and PtRuCu/C after different CV cycles in
0.1M HClO_4 +1M CH_3OH

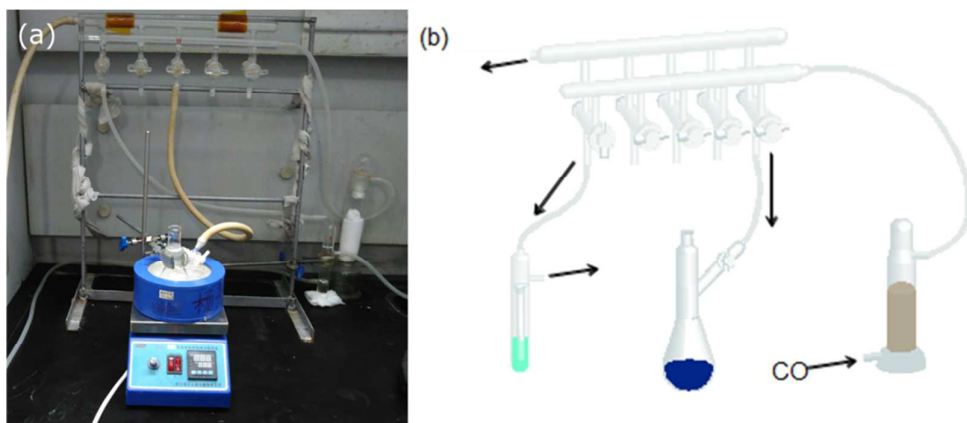


Figure S8 (a) Reaction devices used in the synthesis and (b) its sketch map.

Table S1 XPS spectrum peaks for Pt/C PtRuCu hexapods/C and Cu in different regions.

	Pt/C	PtRuCu	Cu
Pt 4f 7/2	71.50 eV *	71.10 eV *	
Pt 4f 5/2	74.80 eV *	74.59 eV *	
Pt(0) 4f 7/2	71.50 eV	71.18 eV	
Pt(0) 4f 5/2	74.90 eV	74.58 eV	
Pt(II) 4f 7/2	72.66 eV	72.98 eV	
Pt(II) 4f 5/2	76.06 eV	76.38 eV	
Cu 2p 3/2		932.80 eV	932.60 eV
Cu 2p 1/2		952.66 eV	952.20 eV

* : raw data