

## Supplementary information

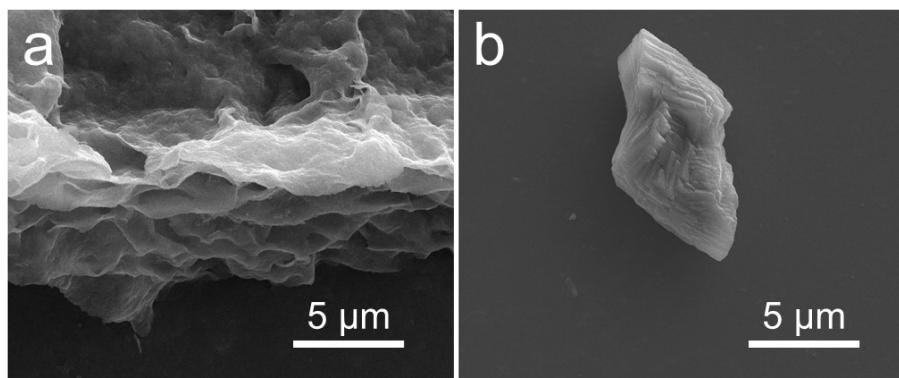
### **Gamma-rays induced strong coupling between Ru nanoparticle and cobalt-based metal organic framework nanolayer for methanol oxidation and hydrogen evolution**

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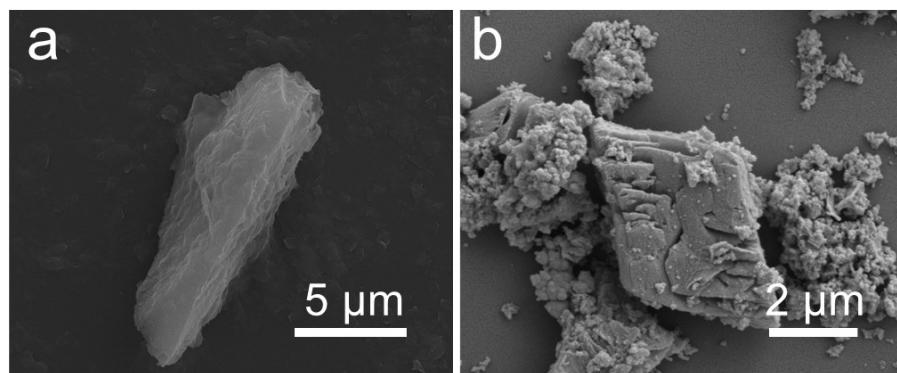
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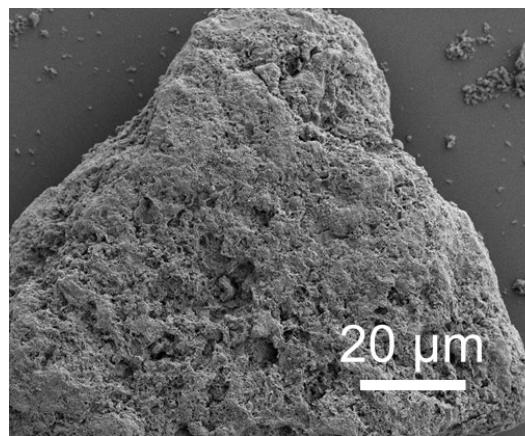
E-mail: majun0502@ustc.edu.cn



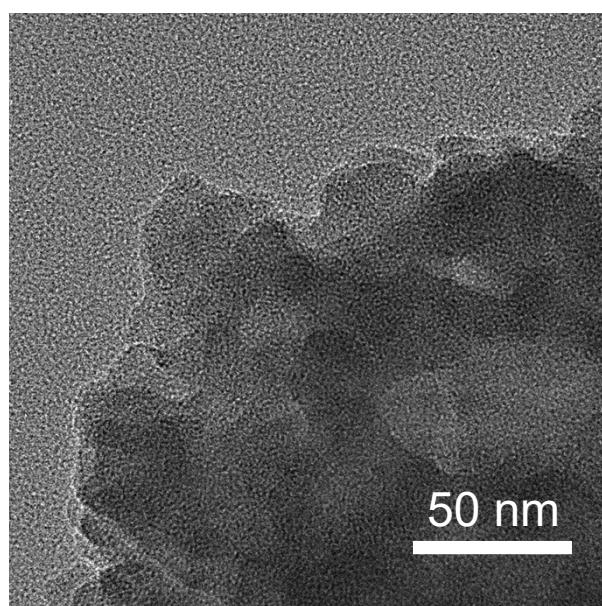
**Fig. S1** The SEM image of (a) Co MOLs, (b) bulk Co MOFs.



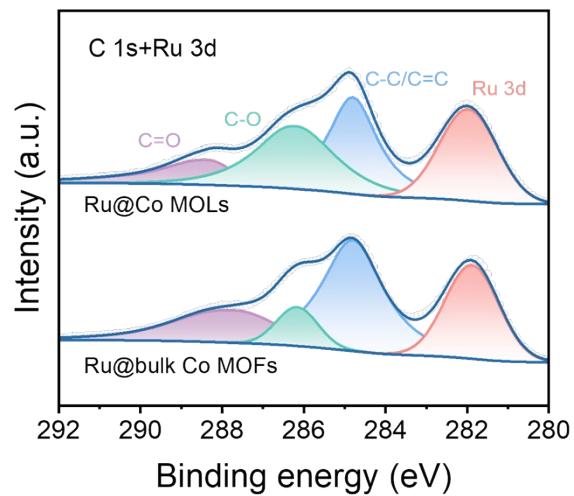
**Fig. S2** The SEM image of (a) Co MOLs-20 kGy, (b) bulk Co MOFs-20 kGy.



**Fig. S3** The SEM image of Ru@Co MOFs.

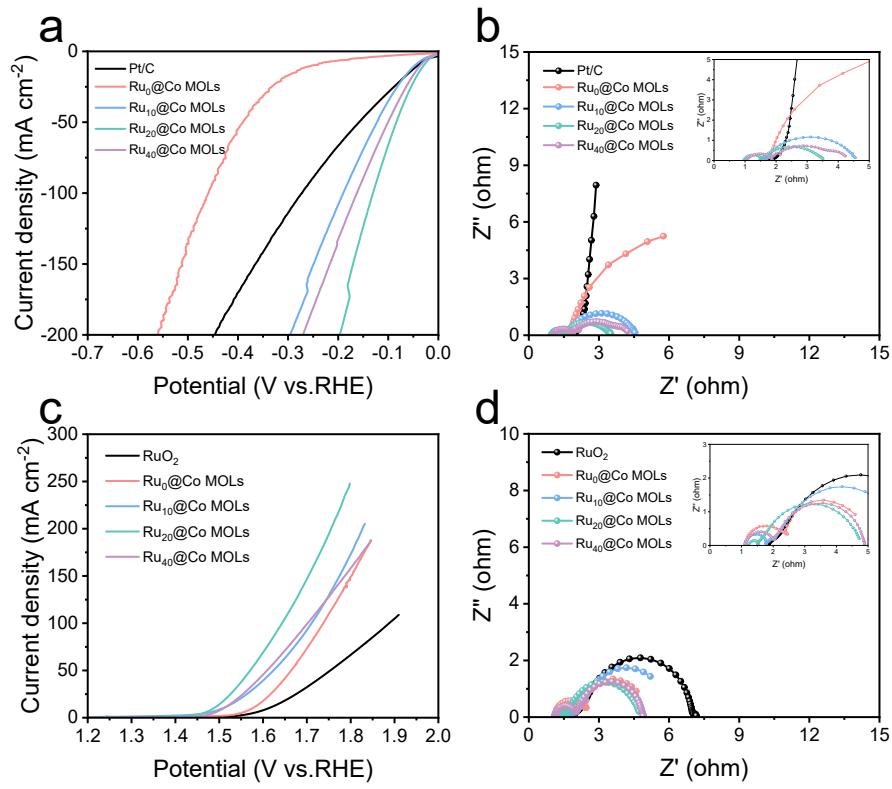


**Fig. S4** The TEM image of Ru@Co MOLs.

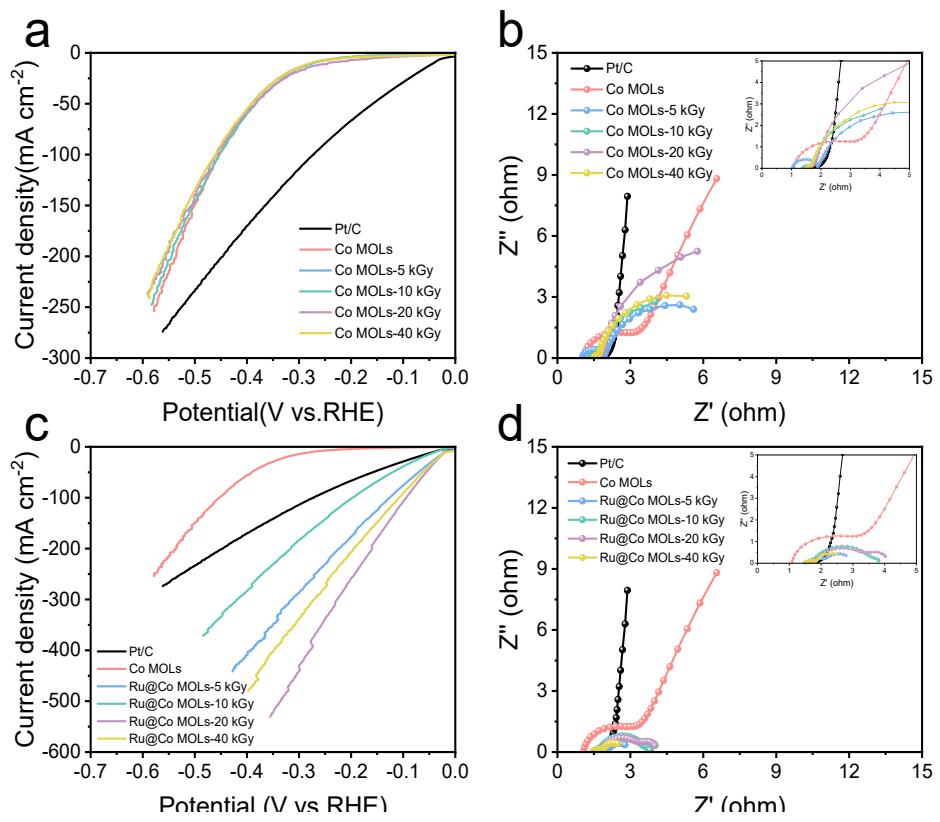


**Fig. S5** High-resolution XPS spectra of C 1s+Ru 3d for Ru@Co MOLs and Ru@Co MOFs.

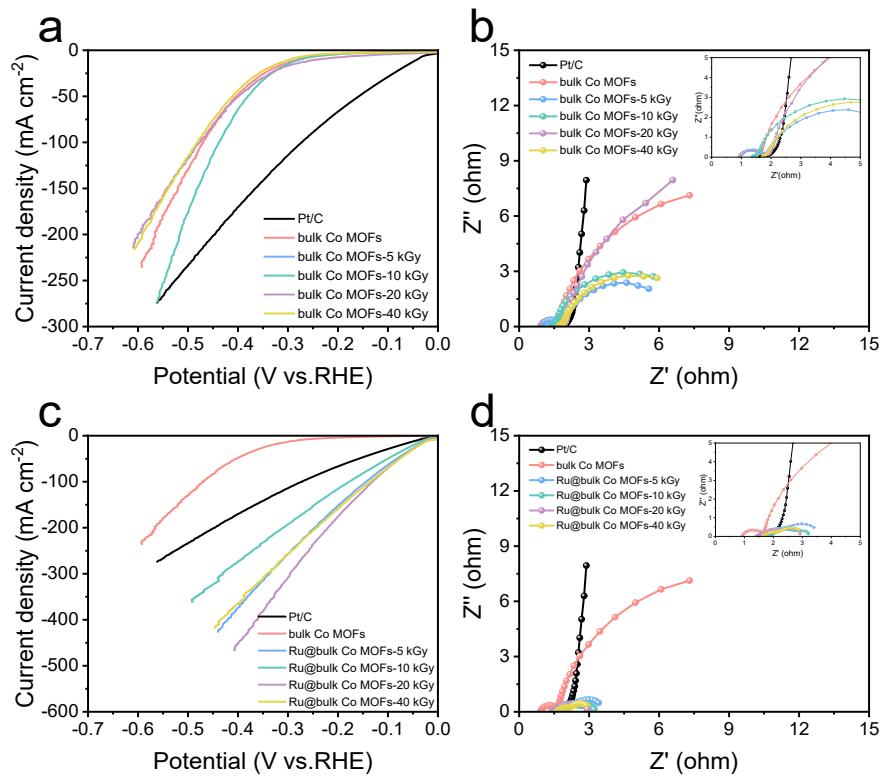
In the C 1s spectrum of Ru@Co MOLs in Fig. S4, three peaks correspond to C=O (288.35 eV), C-O (286.2 eV), and C-C/C=C (284.8 eV), while the peak at 281.97 eV corresponds to the Ru 3d<sub>5/2</sub> of oxidized Ru species.



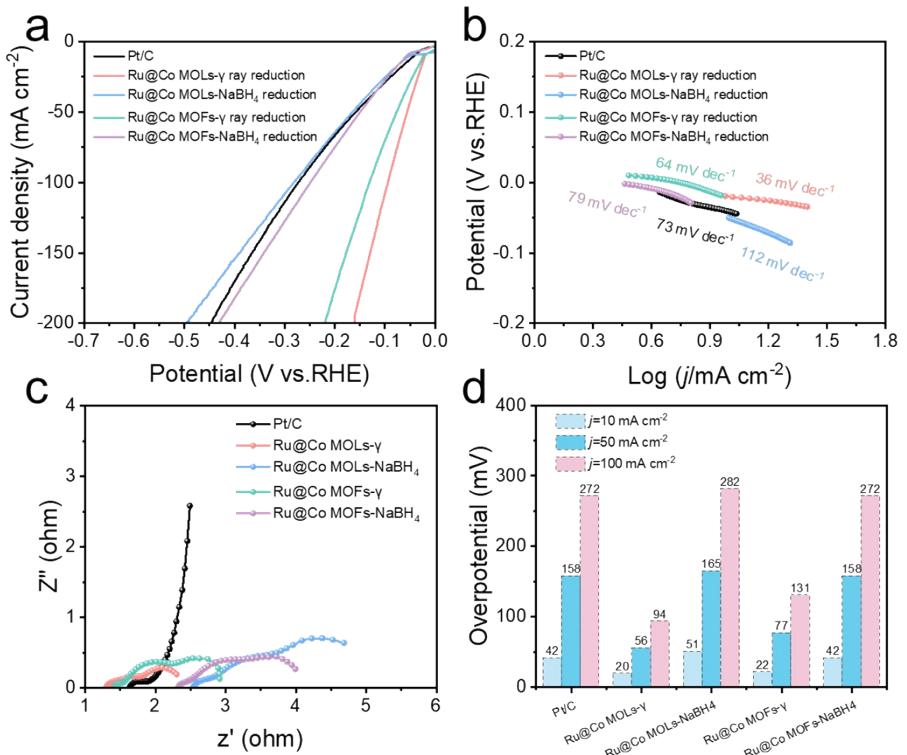
**Fig. S6** The LSV and EIS curves of HER and OER of Co MOLs and Ru@Co MOLs with different Ru loading amounts.



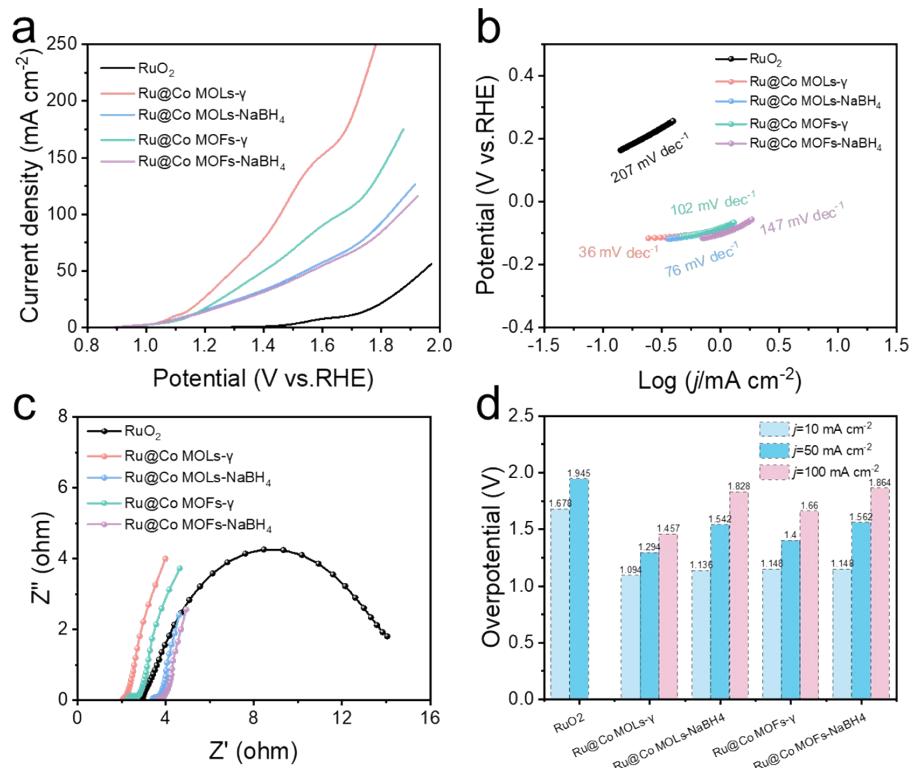
**Fig. S7** The LSV and EIS curves of Co MOLs and Ru@Co MOLs with different absorbed doses.



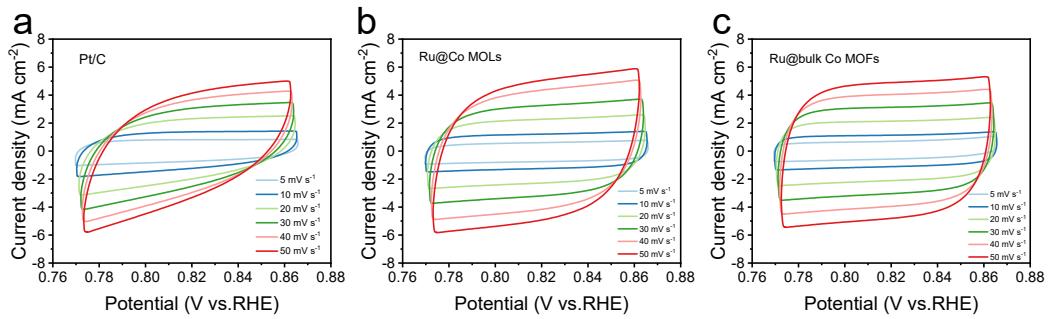
**Fig. S8** The LSV and EIS curves of bulk Co MOFs and Ru@Co MOFs with different absorbed doses.



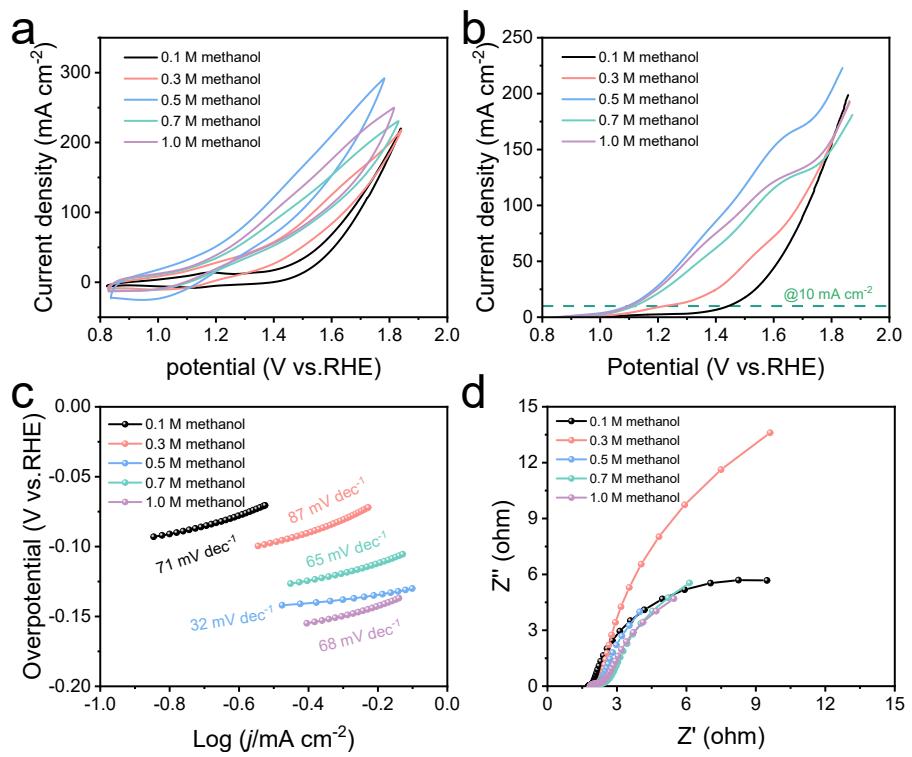
**Fig. S9** (a) The LSV curves, (b) The Tafel slope and (c) The EIS curves of Ru@Co MOLs and Ru@Co MOFs synthesized by different synthetic methods for HER. (d) The overpotential values of Ru@Co MOLs and Ru@Co MOFs synthesized by different synthesis methods at 10, 50 and 100  $\text{mA cm}^{-2}$ .



**Fig. S10** (a) The LSV curves, (b) The Tafel slope and (c) The EIS curves of  $\text{Ru@Co MOLs}$  and  $\text{Ru@Co MOFs}$  synthesized by different synthetic methods for MOR. (d) The overpotential values of  $\text{Ru@Co MOLs}$  and  $\text{Ru@Co MOFs}$  synthesized by different synthesis methods at  $10$ ,  $50$  and  $100 \text{ mA cm}^{-2}$ .



**Fig. S11** The CV curves at non-Faradaic regions with various scan rates for (a) Pt/C, (b) Ru@Co MOLs and (c) Ru@Co MOFs.



**Fig. S12** (a) The CV curves, (b) The LSV curves, (c) The Tafel slope and (d) The EIS curves of different methanol concentrations for Ru@Co MOLs.

**Table S1** Fitting results of EIS for different catalysts.

Samples	$R_s$ (ohm)	$R_{ct}$ (ohm)
Pt/C	1.510	2.284
Co MOLs	1.243	9.43
Co MOFs	1.332	18.773
Ru@Co MOLs	1.315	1.234
Ru@Co MOFs	1.523	1.797

**Table S2.** Comparison of the HER activity for Ru@Co MOLs with other reported catalysts in alkaline electrolyte.

Catalyst	Overpotential·(mV)· @10·mA·cm <sup>-2</sup>	Tafel·slope (mV·dec <sup>-1</sup> )	Reference
Ru@Co MOLs	20	35	This work
Ru SAs-SnO <sub>2</sub> /C	10	25	<sup>1</sup>
RuCo ANSs	10	21	<sup>2</sup>
$\beta$ -Ni(OH) <sub>2</sub> /Ni-Ru SAs NSAs	16	21	<sup>3</sup>
CNT-RuSx	17	35	<sup>4</sup>
Mo <sub>2</sub> C-Ru/C	22	25	<sup>5</sup>
Ru-CoP/NC	22	50	<sup>6</sup>
Ru/P-TiO <sub>2</sub>	27	28	<sup>7</sup>
Ru/NDC-4	29	21	<sup>8</sup>
Ru/MoO <sub>2-x</sub>	29	22	<sup>9</sup>
Ru/Co <sub>3</sub> O <sub>4</sub>	31	70	<sup>10</sup>
Ru/Ni(OH) <sub>2</sub>	31	30	<sup>11</sup>
Ru-CoFe <sub>2</sub> O <sub>4</sub> /NF	31	48	<sup>12</sup>
Ru <sub>NP</sub> -Ru <sub>SA</sub> @CFN-800	33	37	<sup>13</sup>
NiRu <sub>0.13</sub> -BDC	34	32	<sup>14</sup>
Ru@TiO <sub>2</sub> -V	34	35	<sup>15</sup>
Ru-MnFeP/NF	35	36	<sup>16</sup>
V <sub>O</sub> -Ru/HfO <sub>2</sub> -OP	39	29	<sup>17</sup>
Ru-G/CC	40	76	<sup>18</sup>

Ru@1T-MoS <sub>2</sub> -MXene	44	47	19
Ru-NiFe-P	44	80	20
(Ru-Co)O <sub>x</sub>	44	23	21
BPed-Ru-Gr	51	50	22
Ru <sub>0.10</sub> @2H-MoS <sub>2</sub>	51	65	23
Ni <sub>5</sub> P <sub>4</sub> -Ru	54	52	24
ECM@Ru	83	59	25
H-B/Ru-FeP	110	76	26

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**Table S3.** The cell voltage of Ru@Co MOLs||Ru@Co MOLs methanol electrolyzer at 10 mA cm<sup>-2</sup> compared with other catalysts reported in 1 M KOH.

Catalyst	Voltage <sub>MOR  HER</sub> at 10 mA cm <sup>-2</sup>	Voltage <sub>MOR  HER</sub> at 10 mA cm <sup>-2</sup>	Reference
Ru@Co MOLs	1.54	1.18	This work
NiGd@N-C/NF	1.60	1.34	<sup>27</sup>
Mo-Co <sub>4</sub> N	1.60	1.43	<sup>28</sup>
NiCoSe <sub>4</sub> @NiCo-LDH	1.633	1.38	<sup>29</sup>
MoNi/DS-dNPC/NF	1.65	1.47	<sup>30</sup>
Co(OH) <sub>2</sub> @HOS/CP	1.66	1.50	<sup>31</sup>
Ni <sub>0.33</sub> Co <sub>0.67</sub> (OH) <sub>2</sub> /NF	1.66	1.50	<sup>32</sup>
MnSe/Co <sub>0.85</sub> Se@NC	1.69	1.49	<sup>33</sup>
Ni(OH) <sub>2</sub> /NF	1.70	1.52	<sup>34</sup>
3D Sn/NF-15	1.76	1.54	<sup>35</sup>

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