Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.


Supporting Information

# Unique Sandwich Structure of Ru@$TiO_2$: Salicylic Acid Microetching from $K_2Ti_2O_5$ and High-Performance Electrocatalytic Hydrogen Evolution

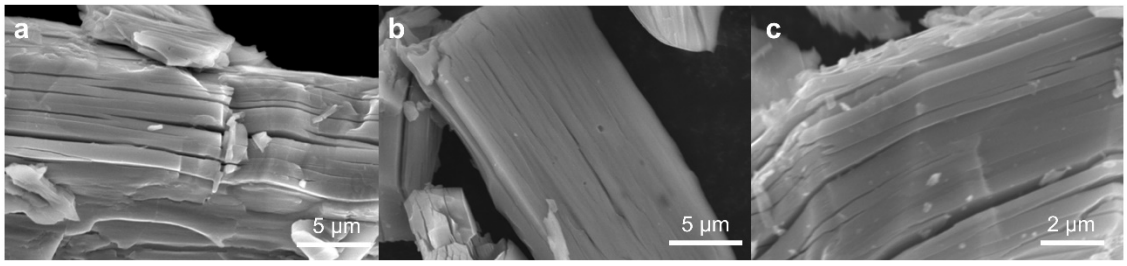


**Figure S1.** SEM image of (a) $K_2Ti_2O_5$, (b) $H_x[Ti_2O_5]$ and (c) $Ru_x[Ti_2O_5]$.

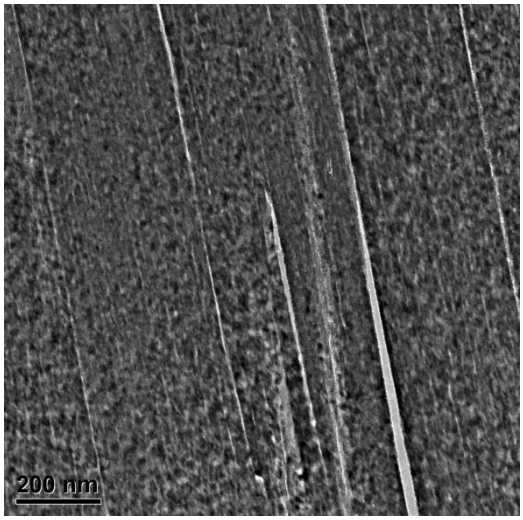


**Figure S2.** TEM image of the longitudinal section of Ru@$TiO_2$ sandwich.

**Figure S3.** (a) TEM image of Ru@$TiO_2$ sandwich. (b) Corresponding particle size distribution of Ru nanoparticle.

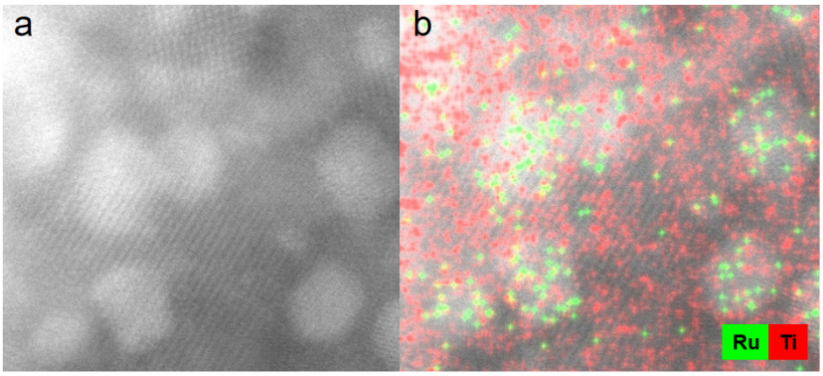


**Figure S4.** HAADF and corresponding elemental mapping of Ru@$TiO_2$ sandwich.

**Figure S5.** SAED image of Ru@$TiO_2$ sandwich.

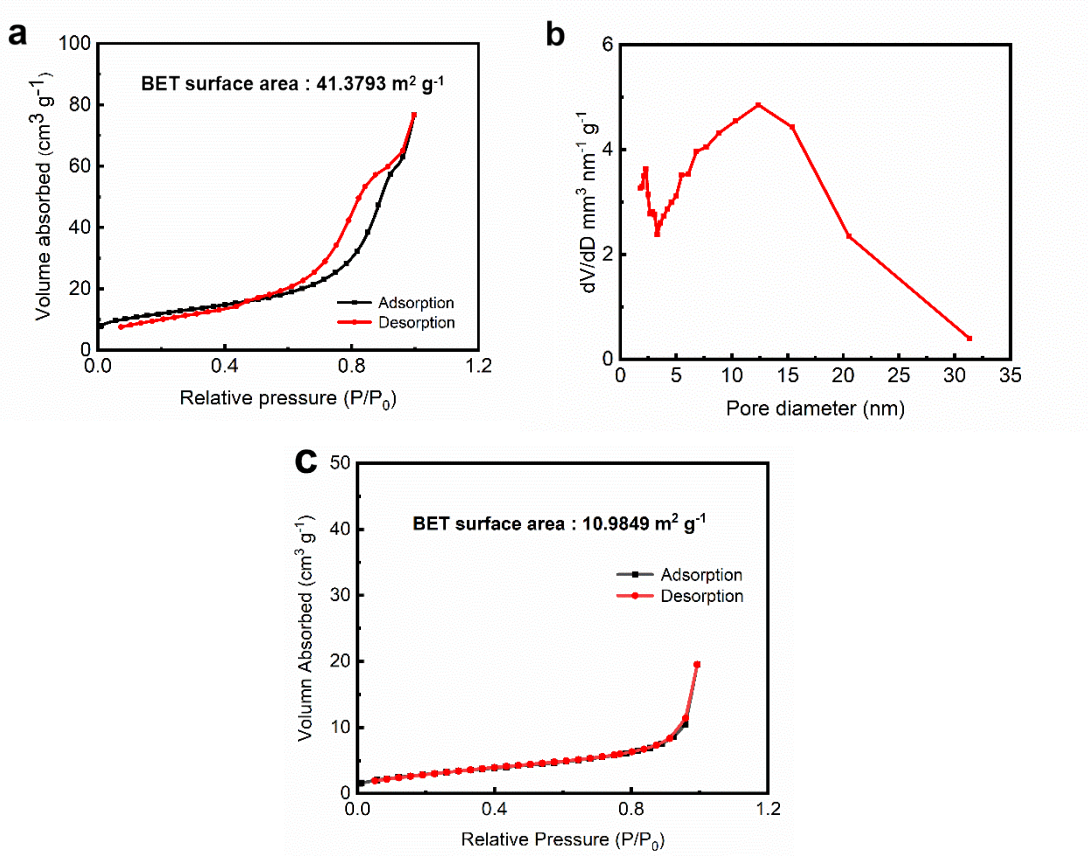


**Figure S6.** (a) Nitrogen adsorption-desorption isotherms and (b) BJH pore-diameter distribution of Ru@$TiO_2$ sandwich. (c) Nitrogen adsorption-desorption isotherms of commercial anatase nano $TiO_2$.

**Figure S7.** LSV curves for 2.54 *wt.* % Ru@$TiO_2$ sandwiches annealed at different temperatures.

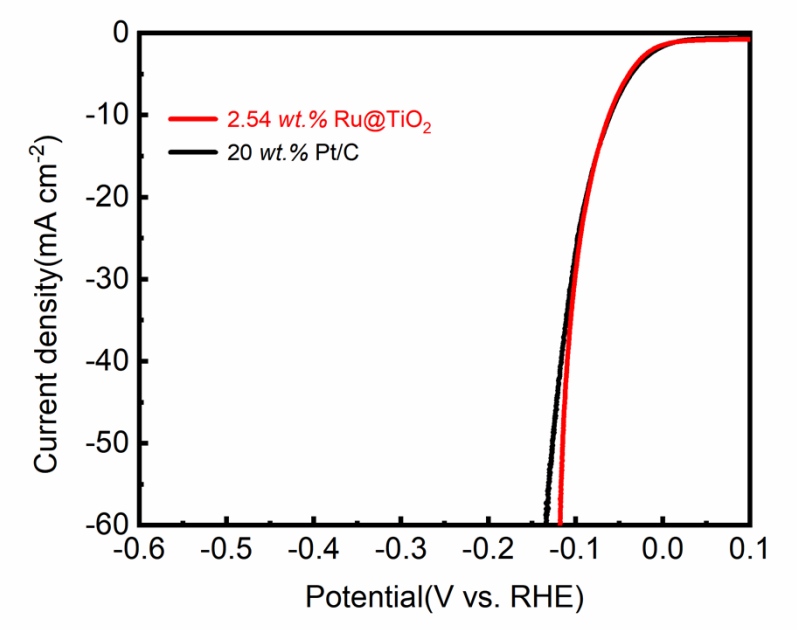


**Figure S8.** LSV curves for 2.54 *wt.* % $Ru@TiO_2$ sandwiche and 20 *wt.* % Pt/C at high current density.

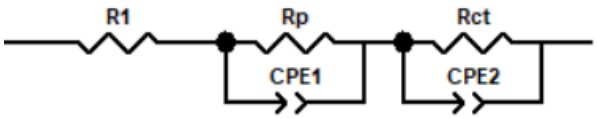


**Figure S9.** Equivalent circuit used for approximation of the EIS data: Two-CPE model. R1, Rp, Rct, CPE1, and CPE2 represent the solution resistance, electrode texture and charge transfer resistances, and constant phase elements, respectively.

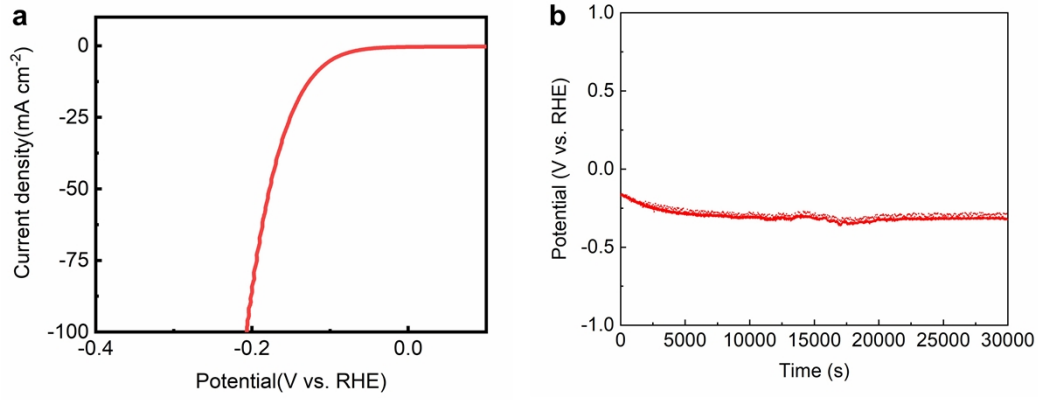


**Figure S10.** (a) LSV curve of 2.54 *wt.*% $Ru@TiO_2$ sandwich in 0.5 M $H_2SO_4$. (b) CP curve of 2.54 *wt.*% $Ru@TiO_2$ at 100 mA $cm^{-3}$ in 0.5 M $H_2SO_4$.

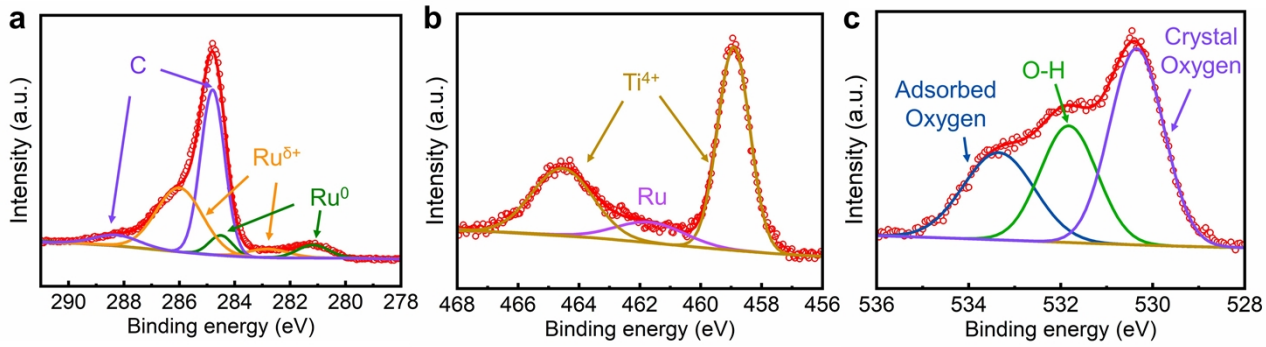


**Figure S11.** (a) Ru 3d, (b) Ru 2p and (c) O 1s XPS curves of Ru@$TiO_2$ sandwich after cycling at 10 mA $cm^{-3}$ for 12 h.

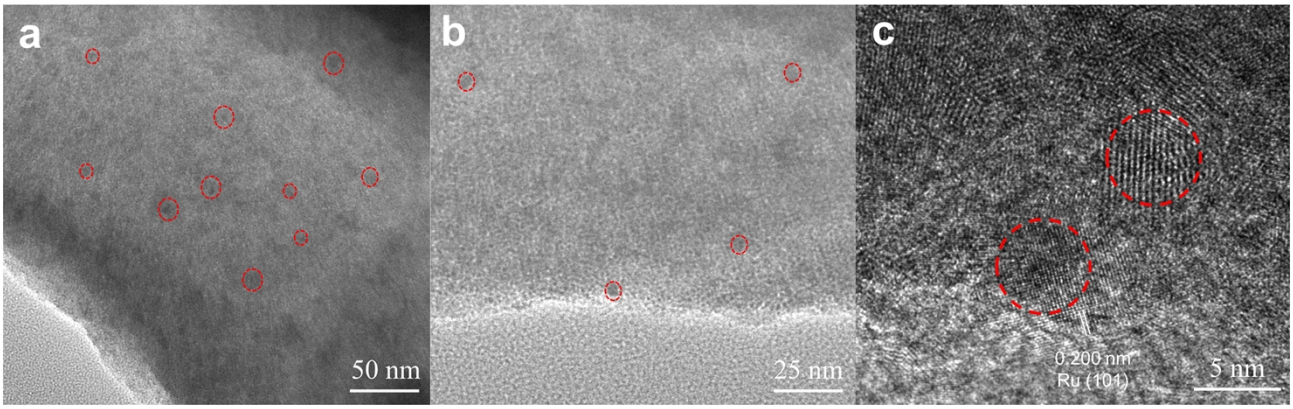


**Figure S12.** (a, b) TEM and (c) HRTEM images of Ru@$TiO_2$ sandwich after cycling at 10 mA $cm^{-3}$ for 12 h.

**Table S1.** EDX analysis of $K_2Ti_2O_5$ and $H_x[Ti_2O_5]$.

| Sample | K (at. %) | Ti (at. %) | O (at. %) |
|---|---|---|---|
| **$K_2Ti_2O_5$** | 13.4 | 20.4 | 66.2 |
| **$H_x[Ti_2O_5]$** | 0.9 | 25.4 | 73.5 |

**Table S2.** HER performance comparison between Ru@$TiO_2$ and other electrocatalysts

| Catalyst | Electrolyte | Ru content (*wt.*%) | η (mV) at 10 (mA $cm^{-2}$) | Tafel slope (mV $dec^{-1}$) | References |
|---|---|---|---|---|---|
| **Ru@$TiO_2$** | 0.1 M KOH | 2.54 | 60 | 70 | This work |

| | | | | | |
|---|---|---|---|---|---|
| **Ru-C/$TiO_2$** | 1 M KOH | 23.1 | 44 | 73.7 | 1 |
| **$Cu_{2-X}S$@Ru** | 1 M KOH | 63.8 | 82 | 48 | 2 |
| **Ru@CN** | 1 M KOH | 3.18 | 32 | 64 | 3 |
| **$Ni_5P_4$-Ru** | 1 M KOH | 3.83% | 54 | 52 | 4 |
| **Ru-CoP/NC** | 1 M KOH | 10 | 22 | 50 | 5 |
| **Ru-OCNT** | 1 M KOH | 20 | 34 | 27.8 | 6 |
| **Ru/NC@WOC** | 0.1 M KOH | 6.3 | 32 | 40.5 | 7 |

**References**


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