Electronic Supplementary Information (ESI)

Directional Oxygen Activation by Oxygen-Vacancy-Rich WO₂ Nanorods for Superb Hydrogen Evolution via Formaldehyde Reforming

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Fig. S1 (a) TEM and (b) HRTEM images of WO_x -precursors.



Fig. S2 XPS spectrum in the W 4f region of WO_x -precursors.



Fig. S3 (a) XRD and (b) XPS in the W 4f region patterns of WO₃.



Fig. S4 (a) solid EPR spectra, (b) XPS spectrum in the W 4f region, and (c) XRD patterns of the WO₂ NRs before and after treated by H_2O_2 .



Fig. S5 In-situ XRD of the calcined WO_x precursor from 25 to 700 °C under N_2 atmosphere.



Fig. S6 In-situ Raman of the phase transformation from WO_{2.92} to WO₂.



Fig. S7 XPS spectrum in the O 1s of WO₂ NRs and WO₃.



Fig. S8 The effect of NaOH concentration on the rate of H₂ evolution within 3 h reaction; reaction temperature =25 °C, HCHO concentration = 1 M and p_{O2} = 1 atm.



Fig. S9 (a) XRD patterns of the commercial WO₂ NPs, (b) comparison of H₂ production performance of WO₂ NRs and commercial WO₂ NPs; reaction temperature =25 °C, NaOH concentration = 0.6 M, HCHO concentration = 1 M and p_{O2} = 1 atm.



Fig. S10 (a) The solid EPR spectra and (b) XRD patterns of WO₂ NRs, WO₂ NRs-4h, WO₂ NRs-3h and WO₂ NRs-2h.



Fig. S11 Kinetic rate plot of initial TOF (h⁻¹) versus the OVs concentration.



Fig. S12 The O_2 content evolution within 3 hours of reaction with different initial O_2 partial pressure (p_{O2}).



Fig. S13 (a) The effect of HCHO concentration on the rate of H₂ evolution within 3 h reaction, and (b) Plot of initial TOF (h⁻¹) versus the HCHO concentration; reaction temperature = 25 °C, NaOH concentration = 0.6 M and p_{O2} = 1 atm.



Fig. S14 (a) The effect of reaction temperature on the rate of H₂ evolution within 3 h reaction. Reaction conditions: HCHO concentration = 1 M; NaOH concentration = 0.6 M; $p_{O2} = 1$ atm), and (b) Arrhenius plot (*ln(TOF)* vs. *1/T*.



Fig. S15 Reusability of (a) WO₂ NRs and (b) commercial WO₂ NPs catalyst during HCHO reforming reaction.



Fig. S16 XRD pattern of WO_2 NRs before and after reaction.



Fig. S17 (a) W 4f and (b) O 1s XPS spectra of WO_2 NRs before and after reaction.





Fig. S18 (a) TEM and (b) HRTEM images of WO_2 NRs after reaction.



Fig. S19 Solid EPR spectra of WO_2 NRs before and after reaction.



Fig. S20 UV-vis diffuse reflectance spectra of WO_2 NRs before and after reaction.



Fig. S21 Three views from (a) front, (b) side and (c) top directions of $C_{30}H_{14}/(WO_2)_{20}$ catalyst model. The carbon atoms in graphene part were fixed to the geometry in graphite during optimization.



Fig. S22 Optimized structure for O_2 adsorption on $C_{30}H_{14}/(WO_2)_{20}$. (Conf.#2)



Fig. S23 Optimized structures for elementary reaction, $O_2 + H_2O \rightarrow O_2 + H + OH$. (a) Reactant (Conf. #3), (b) TS (Conf. #4), and (c) product (Conf. #5).



Fig. S24 Three optimized structures for elementary reaction, $O_2 + H_2CO + H + OH \rightarrow OOH + HCO + H + OH$. (a) Co-adsorption of O_2 , OH, H, and H_2CO , as reactant (Conf.#6), (b) TS for H abstraction from H_2CO (Conf.#7), and (c) product (Conf.#8).



Fig. S25 Two optimized structures for elementary reaction, $OH + HCO \rightarrow HCOOH$. (a) TS (Conf.#9), and (b) product (Conf.#10). The reactant is Conf.#8 described as the product in Fig. S17(c).



Fig. S26 Optimized structures for elementary reaction, $H + HOO \rightarrow H_2 + O_2$. (a) Reactant as H(-O) and HOO(-W) (Conf.#11), (b) TS (Conf.#12), and (c) product (Conf.#13).

Entry	Catalyst	[HCHO] /M ^a	T /ºC b	TOF $/h^{-1}$ t $/h^{c}$ Additive		Refs.	
1	Pd NPs	0.5	25	47.6	1.67	NaOH	Ref.1
2	Ag NPs	0.5	25	62.6	0.83	NaOH	Ref.2
3	Cu NPs	0.5	18	1.67	3	NaOH	Ref.3
4	Au NPs	0.5	25	13.7	1.67	NaOH	Ref.3
5	Pt NPs	0.5	25	8.8	1.67	NaOH	Ref.3
6	Pd/TiO ₂	0.6	25	71	0.5	NaOH	Ref.4
7 ^d	CuO/Ag ₂ O	0.2	25	58.5	0.5	КОН	Ref.5
8	WO ₂ NRs	1	25	173	3	NaOH	This work
9	WO ₂ NRs	1	50	382	3	NaOH	This work
10	WO ₂ NRs	10	25	98	3	NaOH	This work

Table S1. Comparisons of the catalysts properties during HCHO reforming reaction into H_2 .

^a concentrations of HCHO; ^b reaction temperature; ^c reaction time; ^d operated with an applied potential at 0.15 V vs. SCE.

Entry	Initial p_{O2}	Initial	H ₂ /µmol	TOF
2	/atm	O ₂ content /mmol		/h ⁻¹
1	0	0	0	0
2	0.12	0.269	126.7	27
3	0.20	0.448	201.1	44
4	0.50	1.121	295.5	64
5	0.66	1.479	418.5	90
6	0.84	1.883	509.1	110
7	1.00	2.242	546.9	173

Table S2. Catalytic performance of WO_2 NRs at different initial O_2 concentrations and the O_2 content evolution in each reactor within 3 h reaction.

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	NaOH /M	0.2	0.4	0.6	1	2	5	10
H ₂	NaOH + WO ₂ NRs	0	0	0	0	0	0	0
/µmol	NaOH + 0 6M HCHO	0.1	02	49	42	33	1.5	03

Table S3. In different concentrations of pure NaOH solution, the H_2 production activity only exists WO₂ NRs or 0.6M HCHO.

Reference:

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