

**Supporting Information**

**Unveiling the Origin of High catalytic Activity of  
WO<sub>3</sub>/MWCNTs Nanocomposites for Hydrogen Evolution  
Reaction**

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**Table S1:** Intensity ratio for various synthesized composite.

Sample	$I_D$	$I_G$	$I_D/I_G$
W/C-5	481.33	586.32	0.82
W/C-10	1569.44	1873.8	0.83
W/C-14	3091.32	3664.26	0.84
W/C-18	5302.24	6140.79	0.86

## 1 Calculation of hydrogen coverage ( $\theta_H$ )

The calculation of hydrogen coverage ( $\theta_H$ ) is an important step for determining the rate-limiting step. It is well predicted from the previous studies if hydrogen coverage is high i.e.,  $\theta_H \approx 1$ , the reaction proceeds through the Volmer-Tafel mechanism and the recombination (Tafel) step is the rate-limiting step.[1, 2] While for low adsorption of hydrogen on the active sites, value of  $\theta_H=0$  and Volmer is the rate determining step [3]. When  $\theta_H \rightarrow 1$ , reaction proceeds through Volmer-Heyrovsky step and Heyrovsky is rate determining step [4]. The hydrogen surface coverage is calculated by following the procedure given by Elhamid et. al. [5]. In Tafel region, the rate of proton discharge ( $i_c$ ) is given by:

$$i_c = Fk_1C_{H^+}(1 - \theta_H) \exp\left(\frac{-F}{RT}\alpha\eta\right) \quad (S1)$$

$$= i'_o(1 - \theta_H) \exp\left(\frac{-F}{RT}\alpha\eta\right) \quad (S2)$$

Here,  $i'_o = Fk_1C_{H^+} = i_o/(1-\theta^e_H)$ , where  $i_o$  is defined as as exchange current density in an equilibrium, here  $\theta^e_H = 0$ ,  $C_{H^+}$  is concentration of hydrogen ions,  $\alpha$  is transfer coefficient of HER,  $F$  is Faraday's constant ( $C \text{ mol}^{-1}$ ),  $k_1$  is rate constant and  $\eta$  is overpotential. The rate equation for recombination step and desorption step can be written by taking an assumption of  $i_r = i_c$

$$i_r = i_c = Fk_2\theta_H^2 \quad (\text{for recombination}) \quad (S3)$$

$$\theta_H = \sqrt{\frac{i_c}{Fk_2}} \quad (S4)$$

$$i_r = i_c = Fk_1\theta_H \quad (\text{for desorption}) \quad (S5)$$

$$\theta_H = \frac{i_c}{Fk_1} \quad (S6)$$

After rearranging the equation number S5 and S6 we get [2, 6]

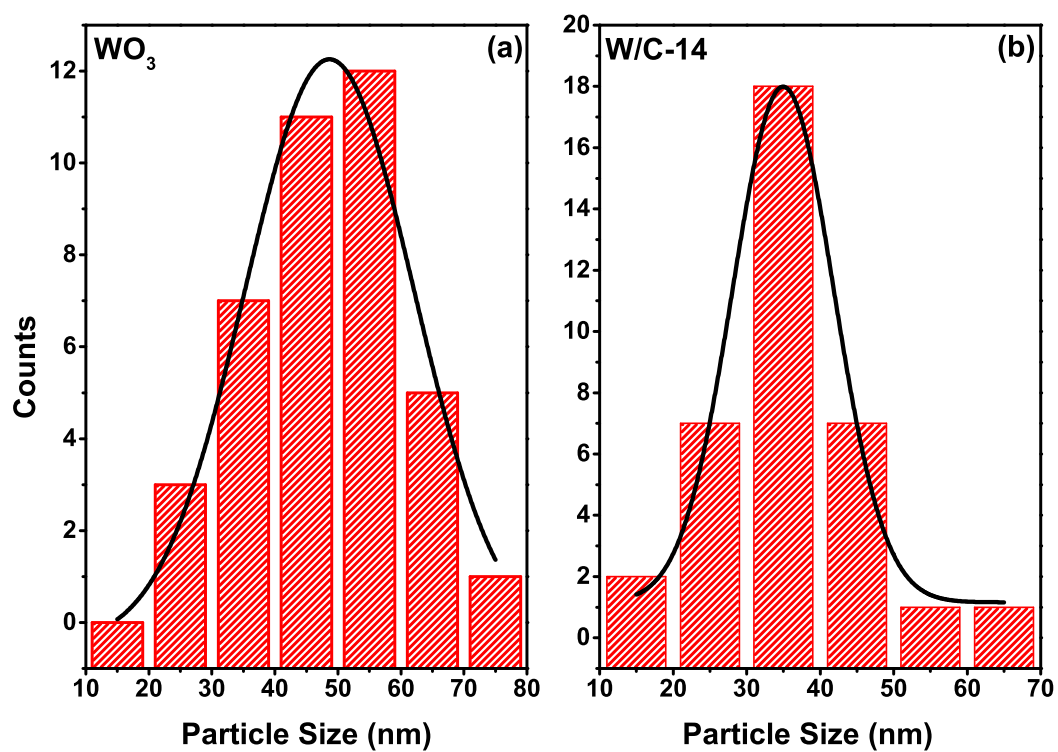
$$i_c \exp\left(\frac{F}{RT}\alpha\eta\right) = i'_o(1 - \theta_H) \quad (S7)$$

From Equations S8 and S9, we obtain

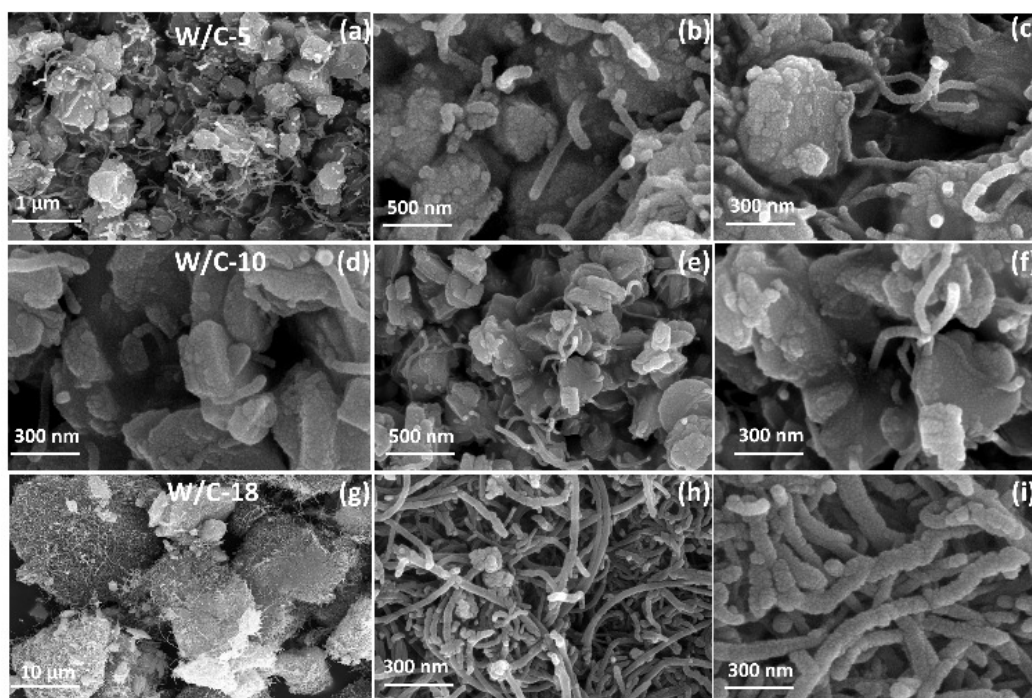
$$i_c \exp\left(\frac{F}{RT}\alpha\eta\right) = i'_o\left(1 - \sqrt{\frac{i_c}{Fk_2}}\right) \quad (S8)$$

$i_c \exp\left(\frac{F}{RT}\alpha\eta\right)$  is termed as a charging function. Figure S4, panel (a) describes the behavior of the charging function with the square root of charging current ( $\sqrt{i_c}$ ) for the W/C-14 composite. Here, for

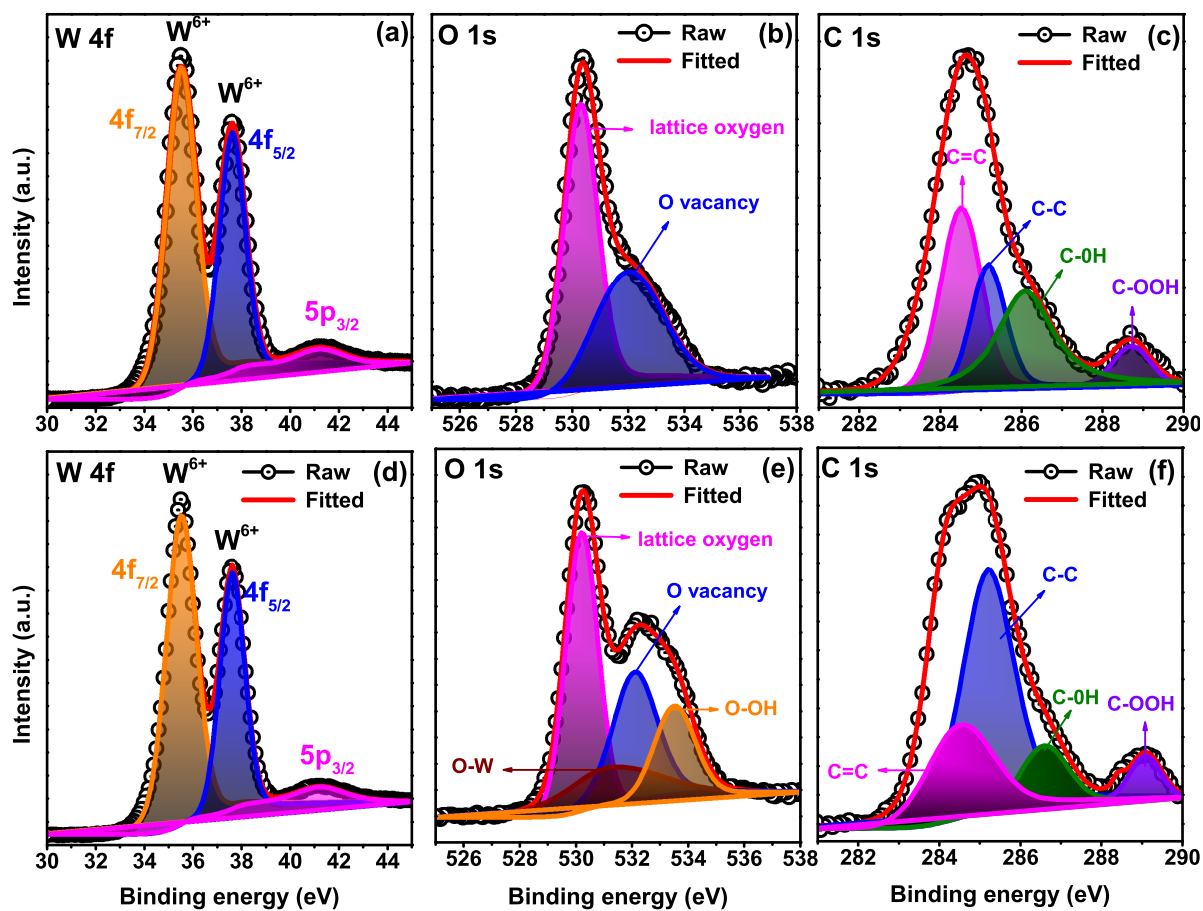
simplicity value of  $\alpha$  is to be taken as 0.5. The slope and intercept helps to find the values of  $i_o$ ,  $k_1$  and  $k_2$  and the obtained values of  $i_o = 1.17 \times 10^{-5}$  (A),  $k_1 = 1.16 \times 10^{-6}$  cm s<sup>-1</sup> and  $k_2 = 1.3 \times 10^{-7}$  mol cm<sup>-2</sup> s<sup>-1</sup>. After calculating the values of  $k_1$  and  $k_2$ , the variation of hydrogen surface coverage ( $\theta_H$ ) with the potential for desorption and recombination step was shown in panel (b). It is also predicted that hydrogen coverage  $\theta_H$  increase with the potential [3, 5]. As seen from the results, the value of  $\theta_H \rightarrow 1$  corresponds to intermediate state and hence, it is clear that reaction will proceeds through Volmer-Heyrovsky and Heyrovsky is the rate determining step.



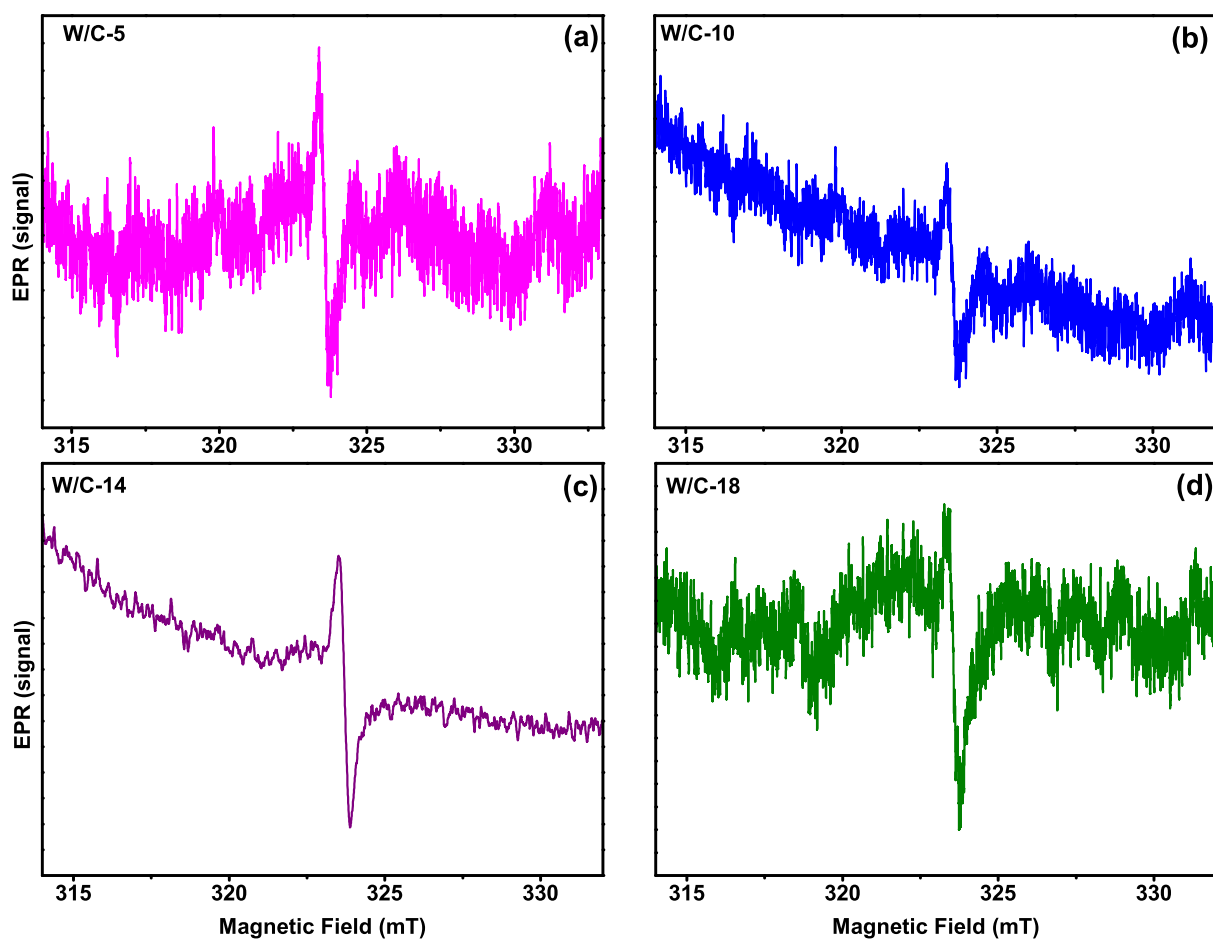
**Figure S1:** Particle size distribution histogram for (a)  $WO_3$  and (b) W/C-14 composite.



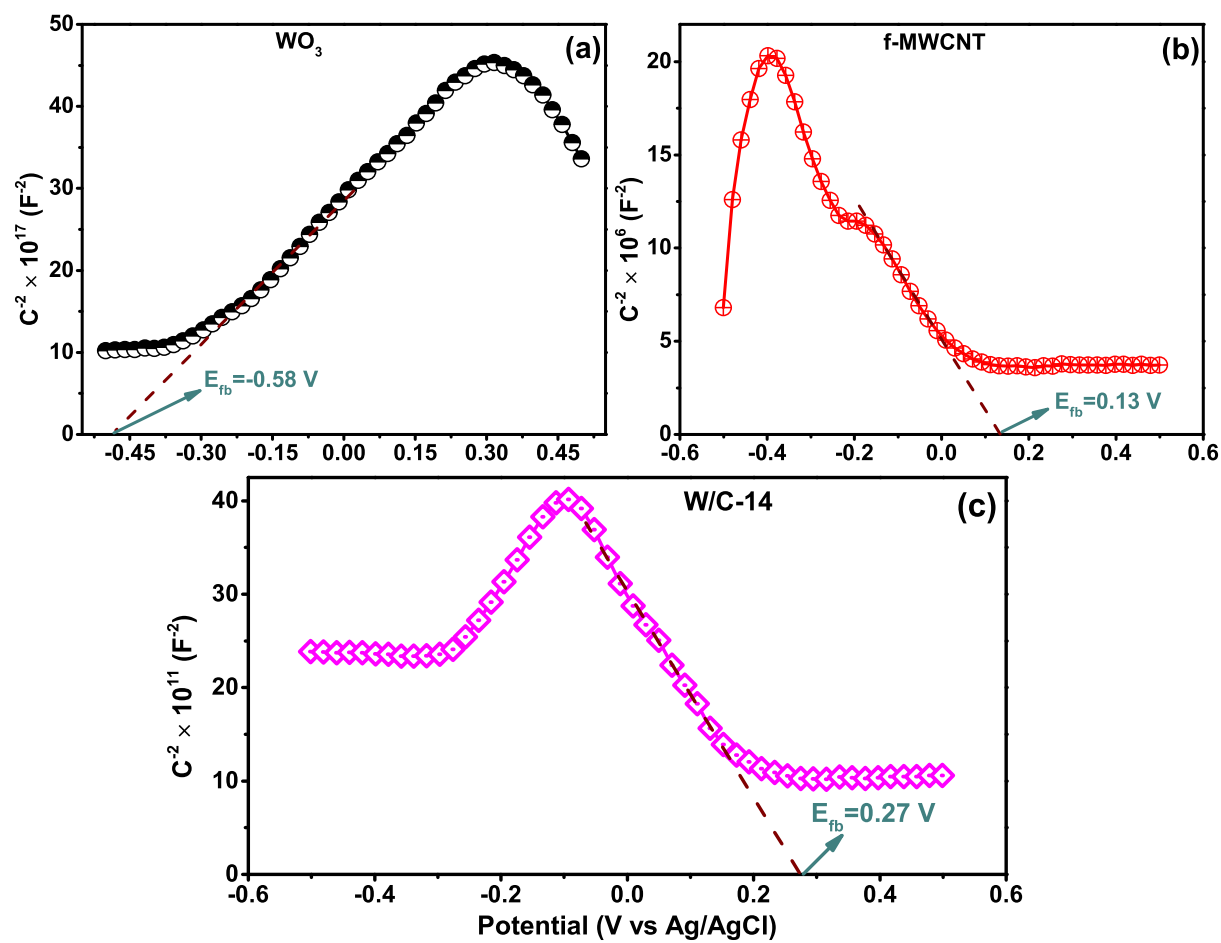
**Figure S2:** Scanning electron microscope images at different magnifications ((a)-(c)) for W/C-5, ((d)-(f)) for W/C-10 and ((g)-(i)) for W/C-18.



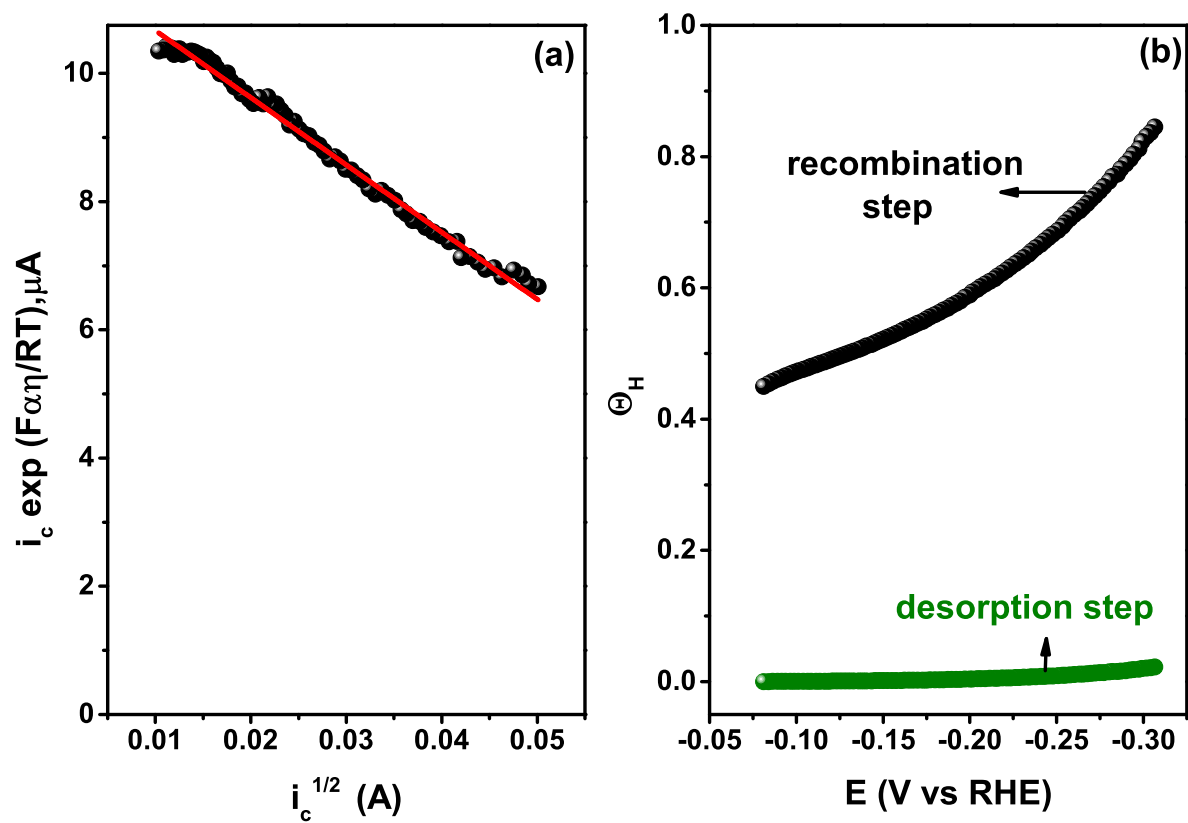
**Figure S3:** High-resolution XPS spectra for W/C-5 sample (a) W 4f, (b) O1s, (c) C 1s and W/C-18 sample (d) W 4f, (e) O1s and (f) C 1s, respectively.



**Figure S4:** EPR spectra for composites. (a) W/C-5, (b) W/C-10, (c) W/C-14 and (d) W/C-18.

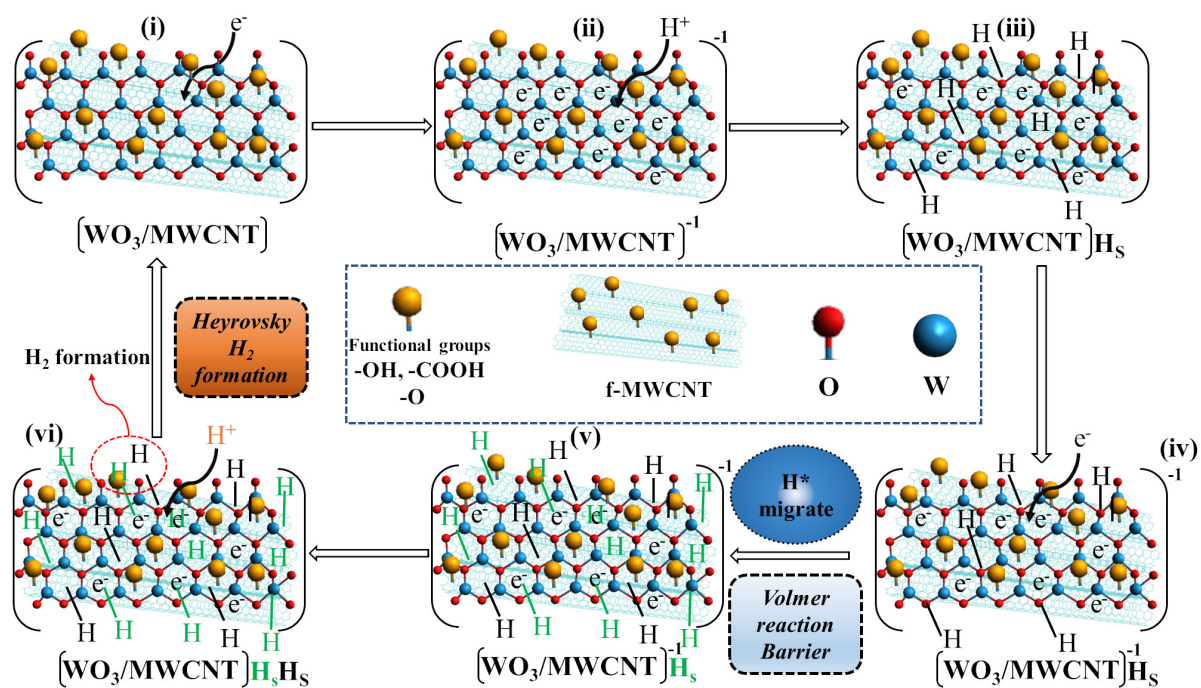


**Figure S5:** Mott-Schottky plots for different samples. (a)  $\text{WO}_3$ , (b) f-MWCNT and (d)  $\text{WO}_3/\text{MWCNT}$  composite (W/C-14).



**Figure S6:** (a) The relationship between the charging function and the square root of the cathodic current and (b) Relation between the hydrogen surface coverage ( $\theta_H$ ) and the electrode potential.

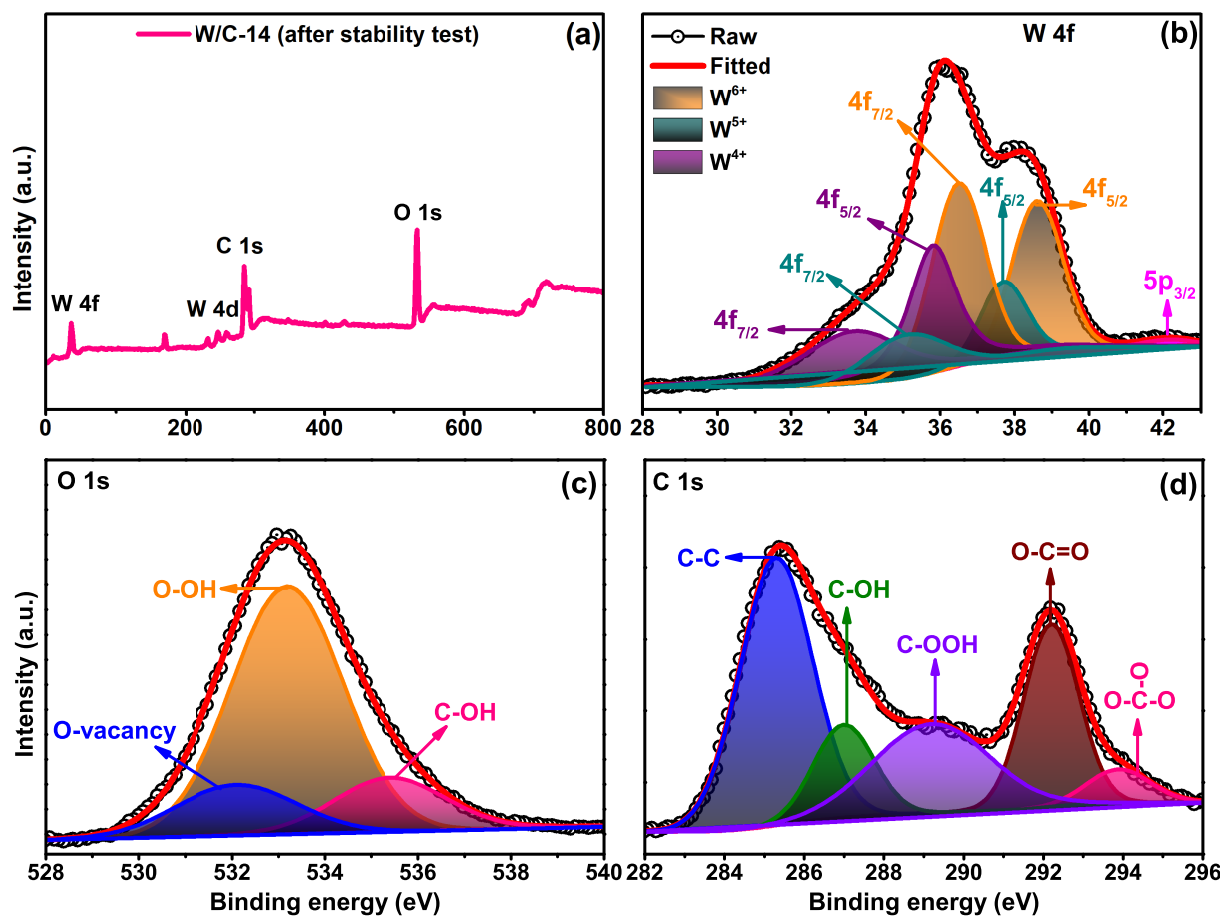




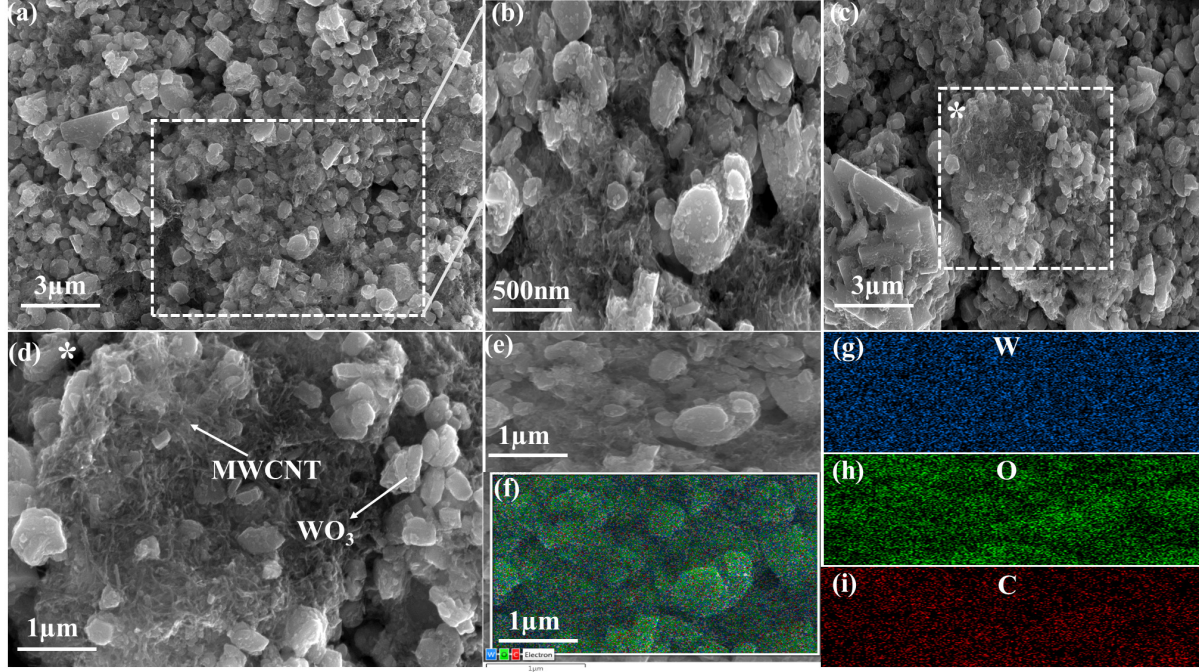
**Figure S7:** Detailed HER mechanism for  $\text{WO}_3/\text{MWCNT}$  based composites.

**Table S2:** Comparison of electrochemical properties of various samples before and after performing the stability test.

Sample ID	$\eta_{10}$ (V)	$\eta_{10}$ (V)	$\eta_{50}$ (V)	$\eta_{50}$ (V)	Tafel slope (mV/dec)	Tafel slope (mV/dec)
	Before	After	Before	After	Before	After
$\text{WO}_3$	-0.64	-0.66	-	-	347	391
W/C-5	-0.5	-0.58	-	-	241	221
W/C-10	-0.4	-0.46	-0.51	-0.55	179	200
W/C-14	-0.20	-0.29	-0.30	-0.33	70	85
W/C-18	-0.36	-0.43	-0.47	-0.53	125	138



**Figure S8:** High-resolution XPS spectra for W/C-14 sample after stability test. (a) XPS survey scan, (b) W 4f, (c) O 1s and (d) C 1s.



**Figure S9:** Scanning electron microscopic images of W/C-14 at different magnification after performing the stability test.

## 2 TOF and number of active site calculation

The TOF calculation is done by assuming the oxygen atom as an active site and the general formula is described below:

$$TOF = \frac{\text{Number of total hydrogen turnovers/cm}^2}{\text{Number of active sites/cm}^2} \quad (\text{S9})$$

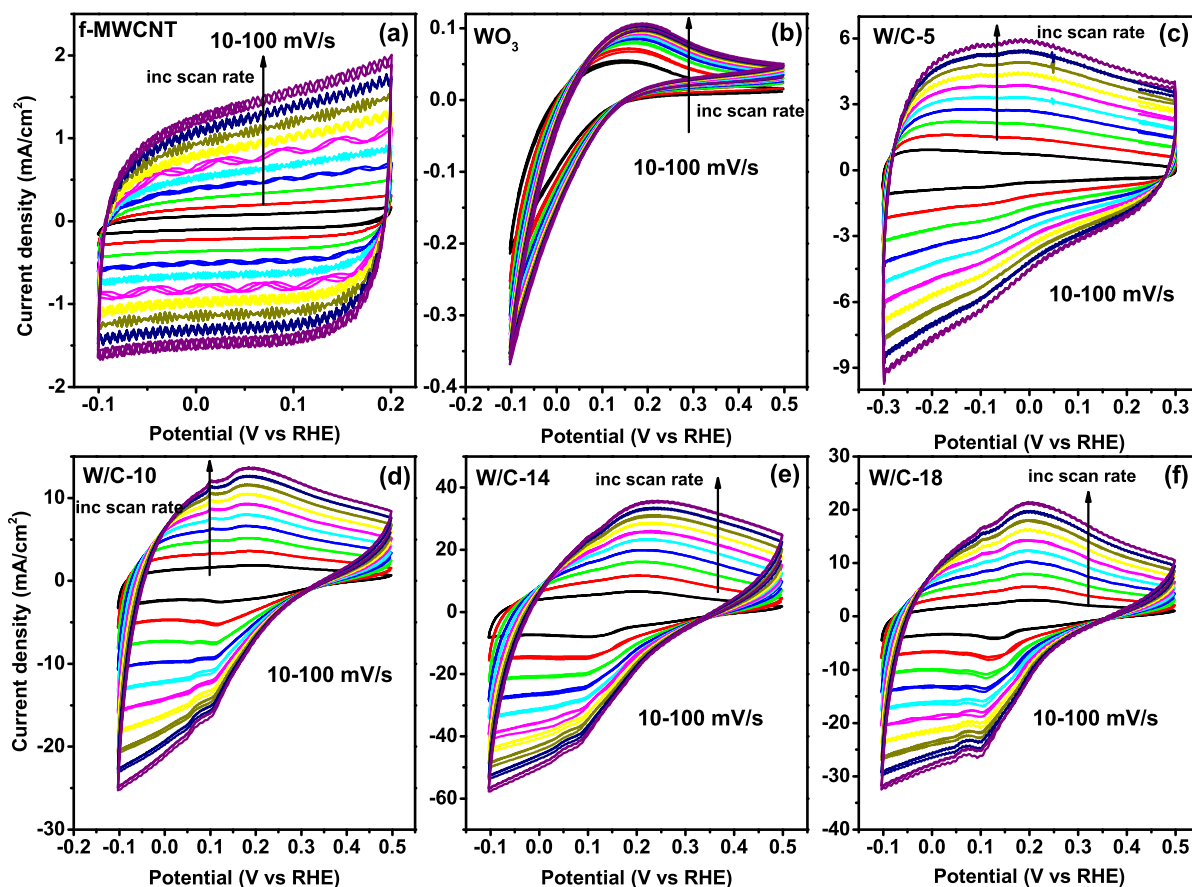
With the current density, total number of hydrogen turnovers was calculated as:

$$\begin{aligned} \text{Number of } H_2 &= \left( j \frac{\text{mA}}{\text{cm}^2} \right) \left( \frac{1 \text{ C s}^{-1}}{1000 \text{ mA}} \right) \left( \frac{1 \text{ mol } H_2}{2 \text{ mol } e^-} \right) \left( \frac{6.022 \times H_2 \text{ molecules}}{1 \text{ mol } H_2} \right) \\ &= 3.12 \times 10^{15} \frac{H_2/s}{\text{cm}^2} \text{ per } \frac{\text{mA}}{\text{cm}^2} \end{aligned} \quad (\text{S10})$$

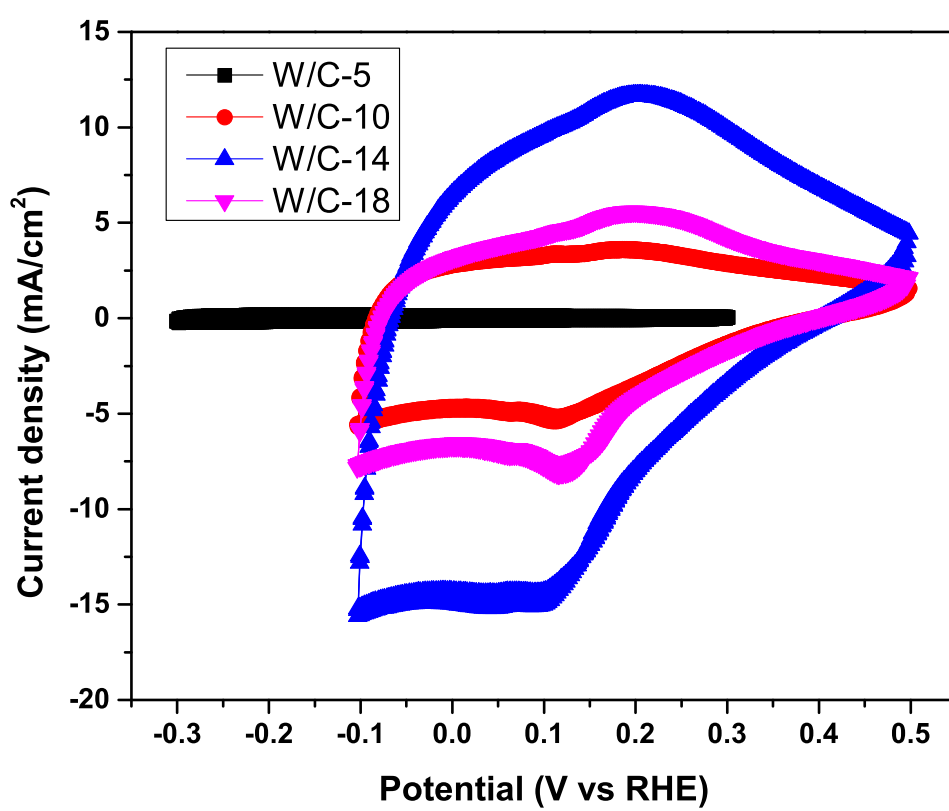
The number of oxygen atom per unit ECSA was calculated as:

$$\begin{aligned} \frac{\text{No. of O active sites in } WO_3/\text{MWCNT}}{\text{ECSA cm}^2} &= \frac{(\text{wt\% of O in } WO_3/\text{MWCNT}) \text{ mg}}{\text{per 1 mg of catalyst wt}} \times \frac{(\text{catalyst}) \text{ mg}}{\text{ECSA cm}^2} \\ &\times \frac{1 \text{ mmol}}{16 \text{ mg}} \times \frac{6.022 \times 10^{22} \text{ sites}}{1 \text{ mmol}} \end{aligned} \quad (\text{S11})$$

$$TOF(\text{s}^{-1}) = \frac{\left( \frac{3.12 \times 10^{15} H_2}{\text{cm}^2 \text{ s}} \text{ per } \frac{\text{mA}}{\text{cm}^2} \right) \times |\text{current density}| \frac{\text{mA}}{\text{cm}^2}}{\frac{\text{Number of O active site in } WO_3/\text{MWCNT}}{\text{ECSA cm}^2}} \quad (\text{S12})$$



**Figure S10:** Cyclic Voltammetry (CV) plots for various electrocatalyst in the potential range of -0.1 V to 0.5 V at scan rate of 10-100 mV/s. (a) f-MWCNT, (b) WO<sub>3</sub>, (c) W/C-5, (d) W/C-10, (e) W/C-14 and (f) W/C-18.



**Figure S11:** Comparison of CV at fixed scan rate of 20 mV/s for WO<sub>3</sub>/MWCNT composites.

## References

- [1] A. Kahyarian, B. Brown and S. Nevsic, *Journal of The Electrochemical Society*, 2017, **164**, year.
- [2] N. Dogra, P. Agrawal, S. Pathak, R. Saini and S. Sharma, *International Journal of Hydrogen Energy*, 2023, **48**, 26210–26220.
- [3] F. Bao, E. Kemppainen, I. Dorbandt, R. Bors, F. Xi, R. Schlattmann, R. van de Krol and S. Calnan, *ChemElectroChem*, 2021, **8**, 195–208.
- [4] H. Prats and K. Chan, *Phys. Chem. Chem. Phys.*, 2021, **23**, 27150–27158.
- [5] M. H. A. Elhamid, B. G. Ateya, K. G. Weil and H. W. Pickering, *Journal of The Electrochemical Society*, 2000, **147**, 2148.
- [6] R. N. Iyer and H. W. Pickering, *Annual Review of Materials Research*, 1990, **20**, 299–338.