

## Supporting Information

# Boosted Photoelectrochemical Water Oxidation Performance with a Quaternary Heterostructure: CoFe<sub>2</sub>O<sub>4</sub>/MWCNT-Doped MIL-100(Fe)/TiO<sub>2</sub>

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## Figure and Table Captions

Figure S1. UV-vis absorbance spectra of CoFe<sub>2</sub>O<sub>4</sub>/MWCNTs@MIL-100(Fe)/TiO<sub>2</sub> and individual components.

Figure S2. XRD pattern of CoFe<sub>2</sub>O<sub>4</sub>/MWCNTs @ MIL-100 (Fe), CoFe<sub>2</sub>O<sub>4</sub>/MWCNTs, CoFe<sub>2</sub>O<sub>4</sub> samples with standard card JCPDS No.00-001-0646 and JCPDS No. 01-080-6487.

Figure S3. XRD pattern of CoFe<sub>2</sub>O<sub>4</sub>/MWCNTs@MIL-100(Fe)/TiO<sub>2</sub> sample before and after the reaction.

Figure S4. Raman spectrum of CoFe<sub>2</sub>O<sub>4</sub>.

Figure S5. Raman spectrum of CoFe<sub>2</sub>O<sub>4</sub>/MWCNTs.

Figure S6. Raman spectrum of CoFe<sub>2</sub>O<sub>4</sub>/MWCNTs doped MIL-100(Fe).

Table S1. Comparison of different pore size distribution of BET in CoFe<sub>2</sub>O<sub>4</sub>/MWCNT-doped MIL-100(Fe)/TiO<sub>2</sub>, CoFe<sub>2</sub>O<sub>4</sub>/MWCNTs doped MIL-100(Fe), CoFe<sub>2</sub>O<sub>4</sub>/MWCNTs and CoFe<sub>2</sub>O<sub>4</sub>.

Table S2. Photoelectrochemical parameters measured for the CoFe<sub>2</sub>O<sub>4</sub>/MWCNTs @MIL-100 (Fe) /TiO<sub>2</sub> photoanodes.

Table S3. Comparative analysis of performance of CoFe<sub>2</sub>O<sub>4</sub>/MWCNTs@MIL-100(Fe)/TiO<sub>2</sub> developed in this study against similar catalysts in photoelectrochemical (PEC) water splitting.

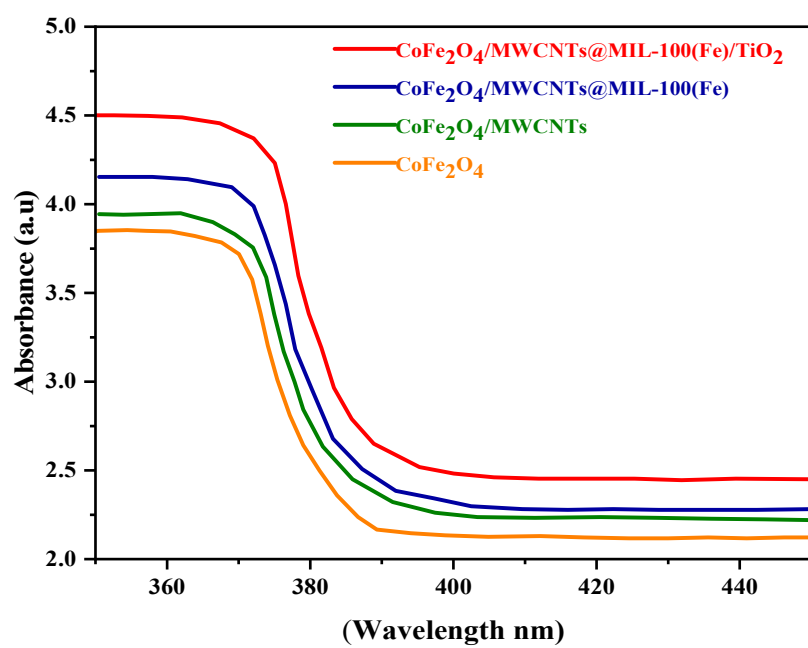


Figure S1. UV-vis absorbance spectra of  $\text{CoFe}_2\text{O}_4/\text{MWCNTs}@/\text{MIL-100}(\text{Fe})/\text{TiO}_2$  and individual components.

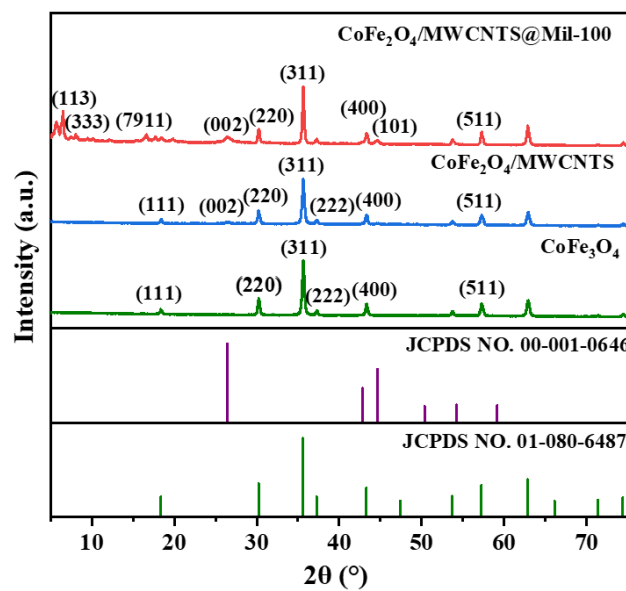


Figure S2. XRD pattern of  $\text{CoFe}_2\text{O}_4/\text{MWCNTs}@ \text{MIL-100}$  (Fe),  $\text{CoFe}_2\text{O}_4/\text{MWCNTs}$ ,  $\text{CoFe}_2\text{O}_4$  samples with standard card JCPDS No.00-001-0646 and JCPDS No. 01-080-6487.

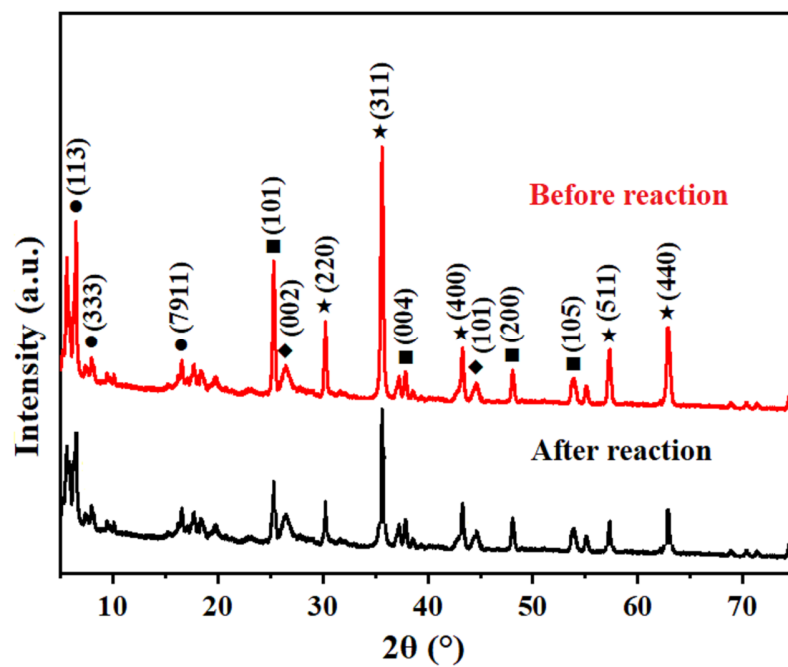


Figure S3. XRD pattern of samples before and after the reaction.

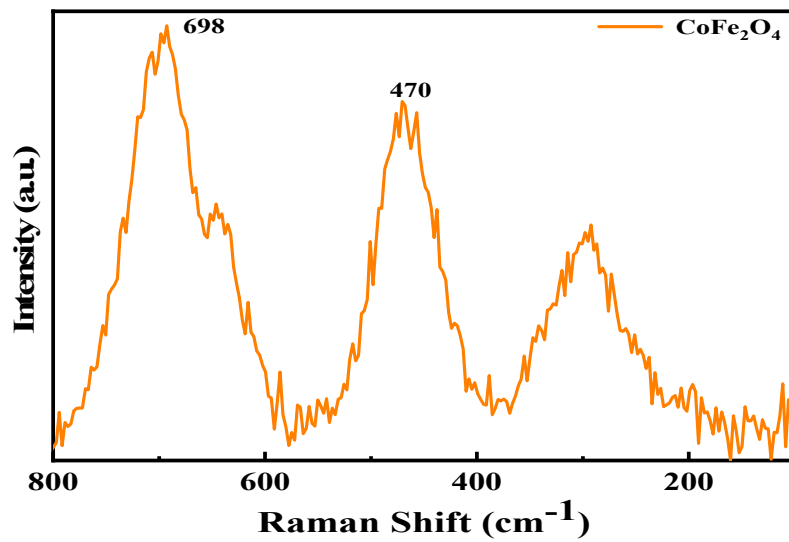


Figure S4. Raman spectrum of  $\text{CoFe}_2\text{O}_4$ .

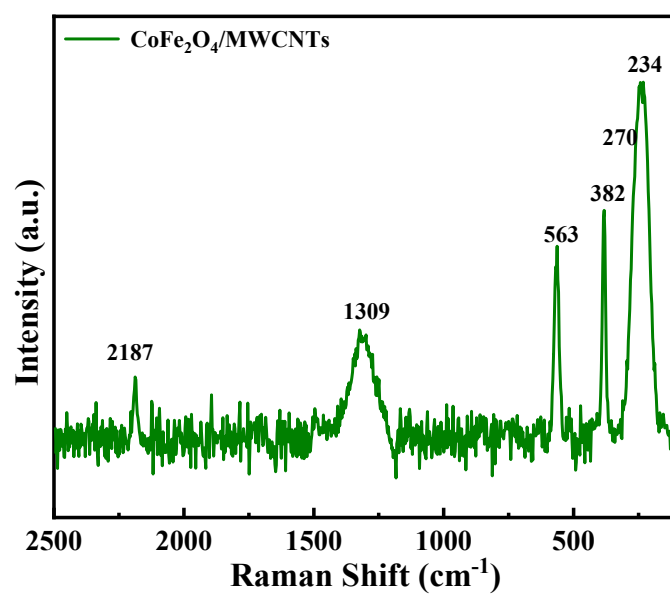


Figure S5. Raman spectrum of CoFe<sub>2</sub>O<sub>4</sub>/MWCNTs.

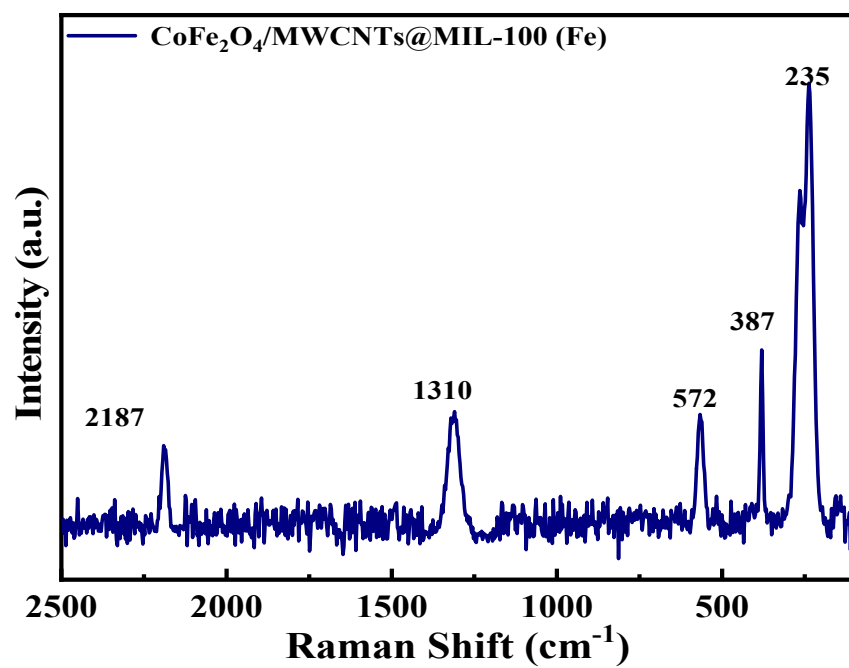


Figure S6. Raman spectrum of CoFe<sub>2</sub>O<sub>4</sub>/MWCNTs doped MIL-100(Fe).

Table S1. Comparison of different pore size distribution of BET in CoFe<sub>2</sub>O<sub>4</sub>/MWCNTs@MIL-100(Fe)/TiO<sub>2</sub>, CoFe<sub>2</sub>O<sub>4</sub>/MWCNTs doped MIL-100(Fe), CoFe<sub>2</sub>O<sub>4</sub>/MWCNTs and CoFe<sub>2</sub>O<sub>4</sub>.

Sample	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	Pore Volume (cm <sup>3</sup> g <sup>-1</sup> )	Average Pore Size (nm)
CoFe <sub>2</sub> O <sub>4</sub> /MWCNTs @MIL-100(Fe) /TiO <sub>2</sub>	1240	0.80 cm <sup>3</sup> /g.	18
CoFe <sub>2</sub> O <sub>4</sub>	71	0.27	4
MWCNTs	260	0.13	15
MIL-100(Fe)	768.5	0.62	1.7
TiO <sub>2</sub>	121	0.12	10



Table S2. Photoelectrochemical parameters measured for the CoFe<sub>2</sub>O<sub>4</sub>/MWCNTs @MIL-100 (Fe)/TiO<sub>2</sub> photoanodes.

Catalyst	$J_{ph}$ (mA/cm <sup>2</sup> ) at 1 V vs SCE	$V_{oc}$	Charge transfer resistance (Ohm)	ABPE (%)	$V_{fb}$
CoFe <sub>2</sub> O <sub>4</sub>	0.16	0.26	55.31	0.07	-0.32
CoFe <sub>2</sub> O <sub>4</sub> /MWCNTs	1.92	0.39	26.97	1.19	-0.68
CoFe <sub>2</sub> O <sub>4</sub> /MWCNTs@ Mill-100(Fe)	5.17	0.67	23.62	4.60	-0.084
CoFe <sub>2</sub> O <sub>4</sub> /MWCNTs@ Mill-100(Fe)/TiO <sub>2</sub>	6.00	0.70	20.50	5.00	-0.09

Table S3. Comparative analysis of performance of CoFe<sub>2</sub>O<sub>4</sub>/MWCNTs@MIL-100(Fe)/TiO<sub>2</sub> developed in this study against similar catalysts in photoelectrochemical (PEC) water splitting.

Catalyst Composition	Photocurrent Density (mA cm <sup>-2</sup> )	Applied Bias (V vs. RHE)	Incident Photon-to-Current Efficiency (IPCE) (%)	Stability	Reference
TiO <sub>2</sub> /CoFe <sub>2</sub> O <sub>4</sub>	1.20	1.23	10 at 350 nm	Retained 85% over 10,000 s	[1]
TiO <sub>2</sub> /MWCNTs	2.20	1.23	12 at 350 nm	Retained 90% over 11,000 s	[2]
MIL-100(Fe)/TiO <sub>2</sub>	2.20	1.23	11 at 350 nm	Retained 92% over 12,000 s	[3]
TiO <sub>2</sub> (Pristine)	0.90	1.23	8 at 350 nm	Retained 80% over 8,000 s	[4]
Fe <sub>2</sub> O <sub>3</sub> /NiOOH	2.00	1.23	9 at 400 nm	Retained 85% over 15,000 s	[5]
Cu <sub>2</sub> O/TiO <sub>2</sub>	3.00	1.23	14 at 500 nm	Retained 90% over 10,000 s	[6]
ZnO/CdS	2.50	1.23	12 at 450 nm	Retained 88% over 12,000 s	[7]
g-C <sub>3</sub> N <sub>4</sub> /NiFe-LDH	3.20	1.23	13 at 420 nm	Retained 92% over 15,000 s	[8]

MoS <sub>2</sub> /TiO <sub>2</sub>	2.80	1.23	11 at 470 nm	Retained 87% over 10,000 s	[9]
CoFe <sub>2</sub> O <sub>4</sub> /MWCNTs@MI L-100(Fe)/TiO <sub>2</sub>	3.70	1.23	13 at 350 nm	Retained 95% over 12,000 s	This Work

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