Role of Carbon – Dots – Derived Underlayer in Hematite Photoanodes

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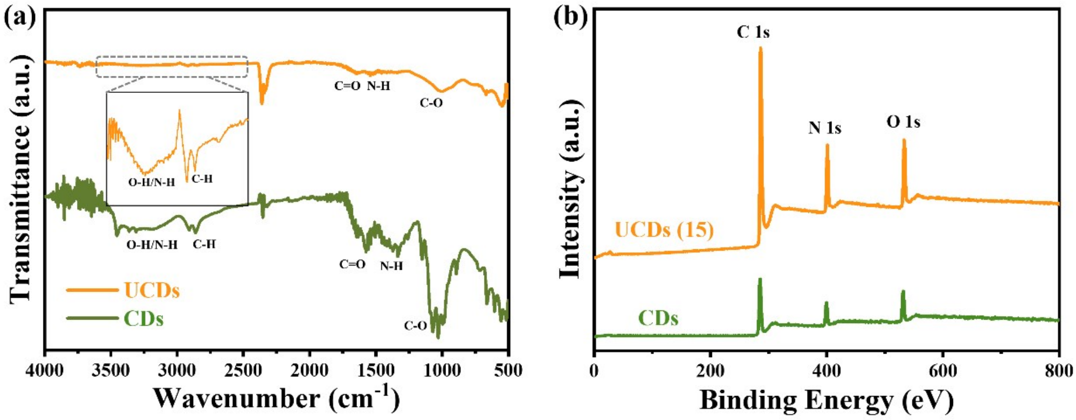

Fig.S1 (a) FTIR of CDs and UCDs (15); (b) XPS survey spectra for CDs and UCDs (15).

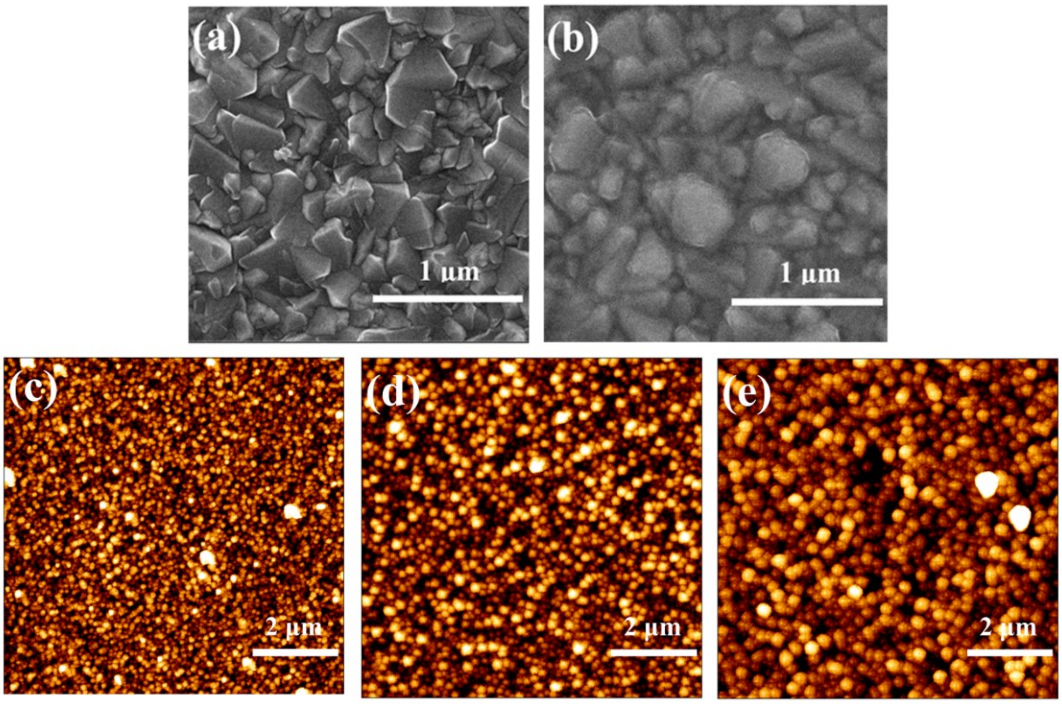

Fig. S2 SEM images of (a) FTO and (b) UCDs (10); AFM images of (c) UCDs (5), (d) UCDs (15), and (e) UCDs (20).

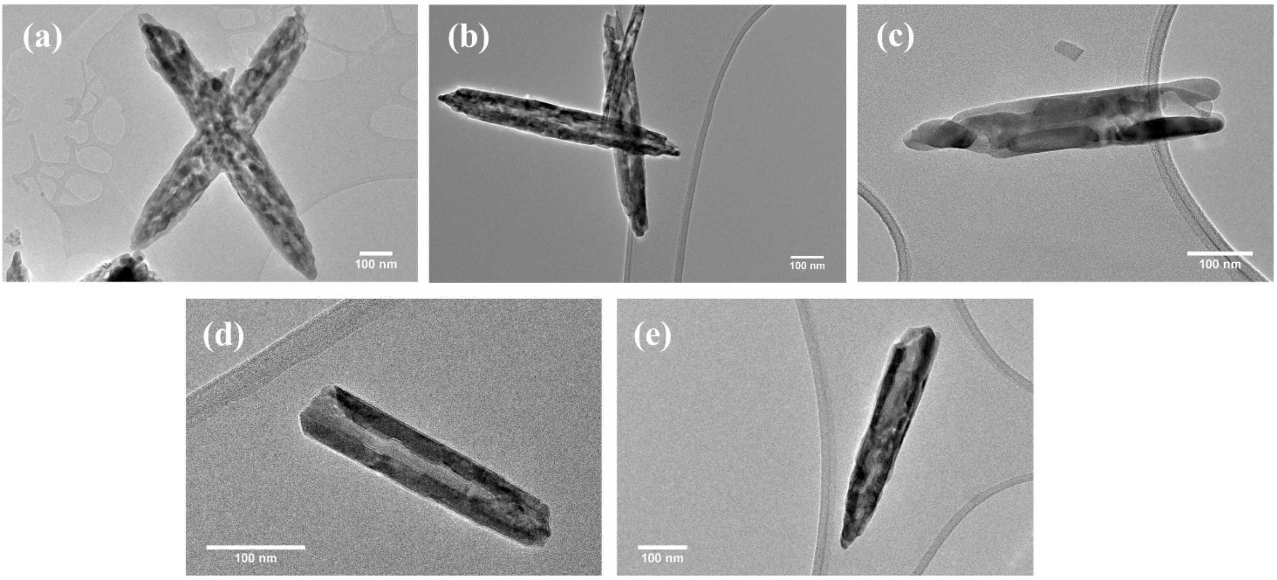

Fig. S3 TEM images of (a) pristine hematite, (b) H/UCDs (5), (c) H/UCDs (10), (d) H/UCDs (15), and (e) H/UCDs (20).

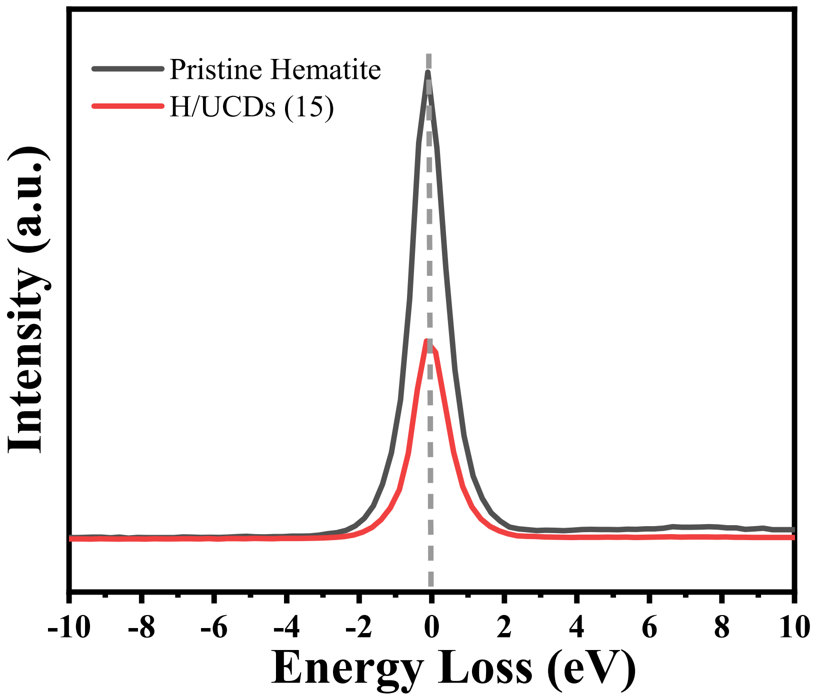

Fig. S4. Zero-loss peaks of EELS spectrum.

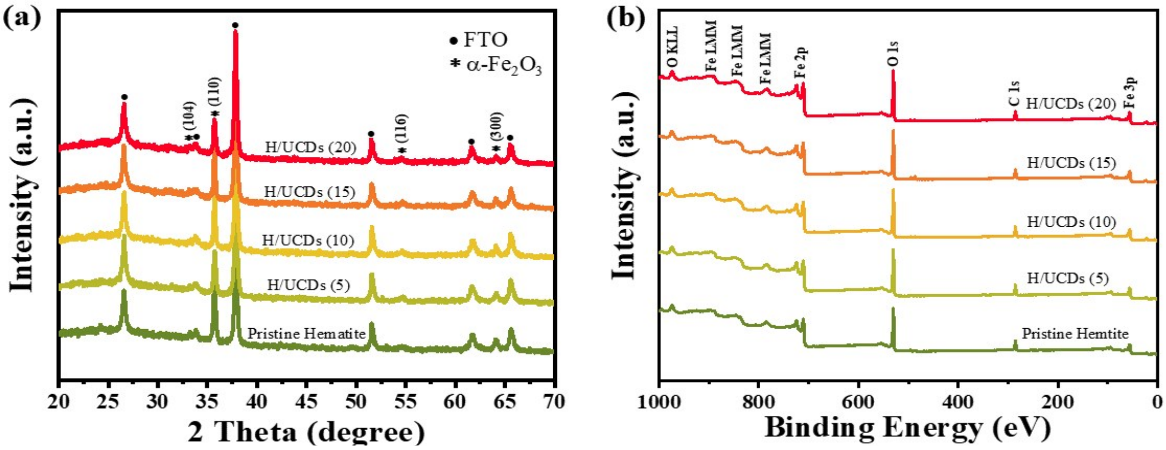

Fig. S5 (a) XRD and (b) XPS survey spectra of pristine hematite and H/UCDs photoelectrodes.

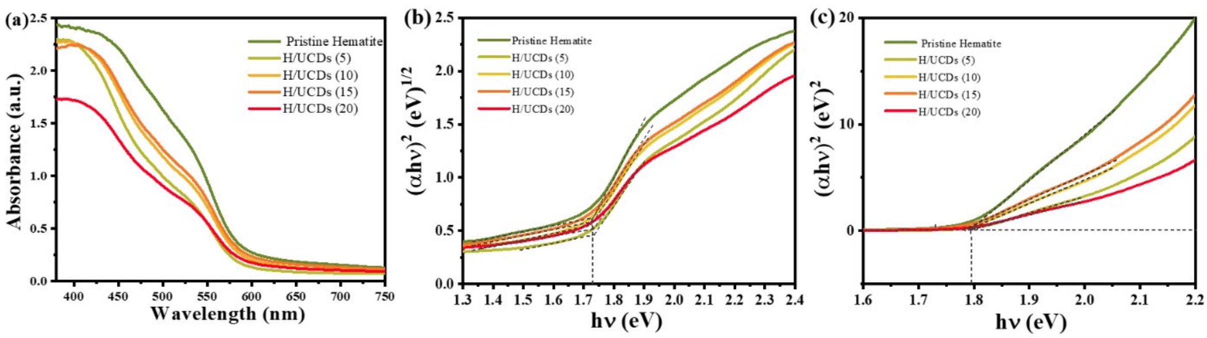

Fig. S6 (a) UV-vis absorption spectra; (b) Indirect and (c) Direct Tauc plots for pristine hematite and H/UCDs photoelectrodes.

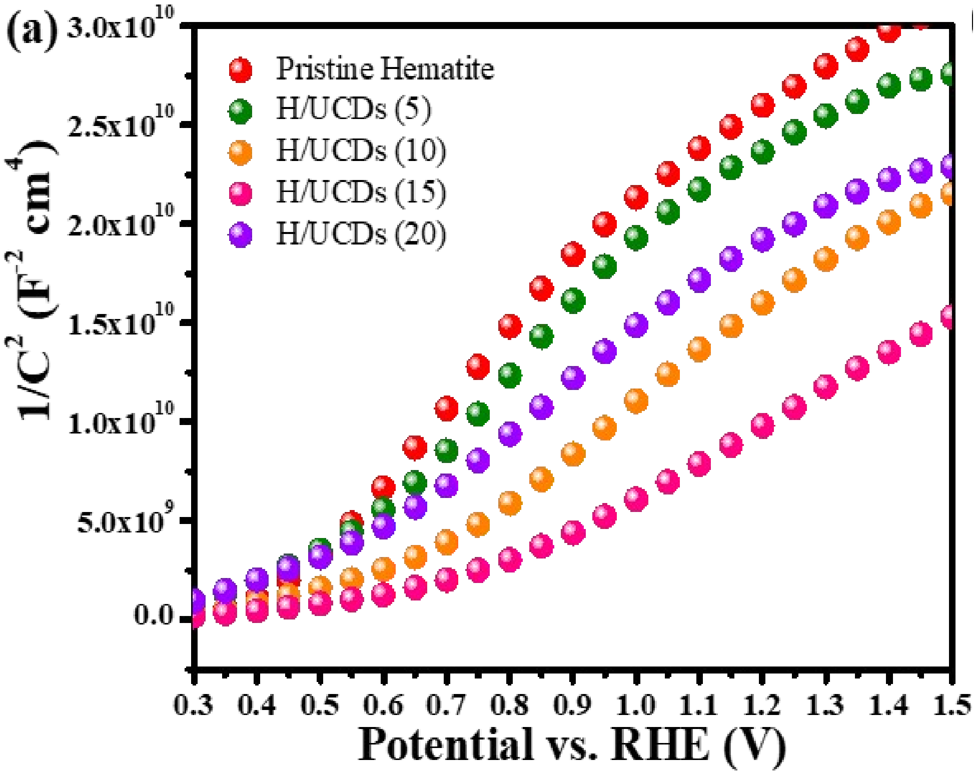

Fig. S7 Mott-Schottky plots at 10 KH_Z under dark conditions.

Table S1. Mott-Schottky, PEIS and IMPS results at 1.25 V *vs* RHE.

Sample	Mott- Schottky		PEIS					IMPS			
	E_{fb}	N_d	Rs	R_{trap}	R_{ct}	C_{bulk}	C_{ss}	K_{ct}	K_{rec}	CTE	τ_d
	V	$\times 10^{18}$	Ω cm^2	Ω cm^2	Ω cm^2	μF cm^{-2}	μF cm^{-2}	s^{-1}	s^{-1}	%	s^{-1}
Pristine Hematite	0.43	1.09	17.97	11016	40095	7.46	17.86	5.03	16.42	23.45	0.20
H/UCDs (5)	0.46	1.19	20.34	12557	61337	8.41	27.74	3.95	14.42	21.51	0.25
H/UCDs (10)	0.56	1.71	18.23	644.1	2673	17.00	180.65	20.30	11.22	64.40	0.41
H/UCDs (15)	0.67	2.30	29.27	472.8	780.6	29.66	300.70	21.16	6.30	77.07	0.62
H/UCDs (20)	0.45	1.61	22.53	3419	16733	10.79	82.95	6.40	16.69	27.70	0.29

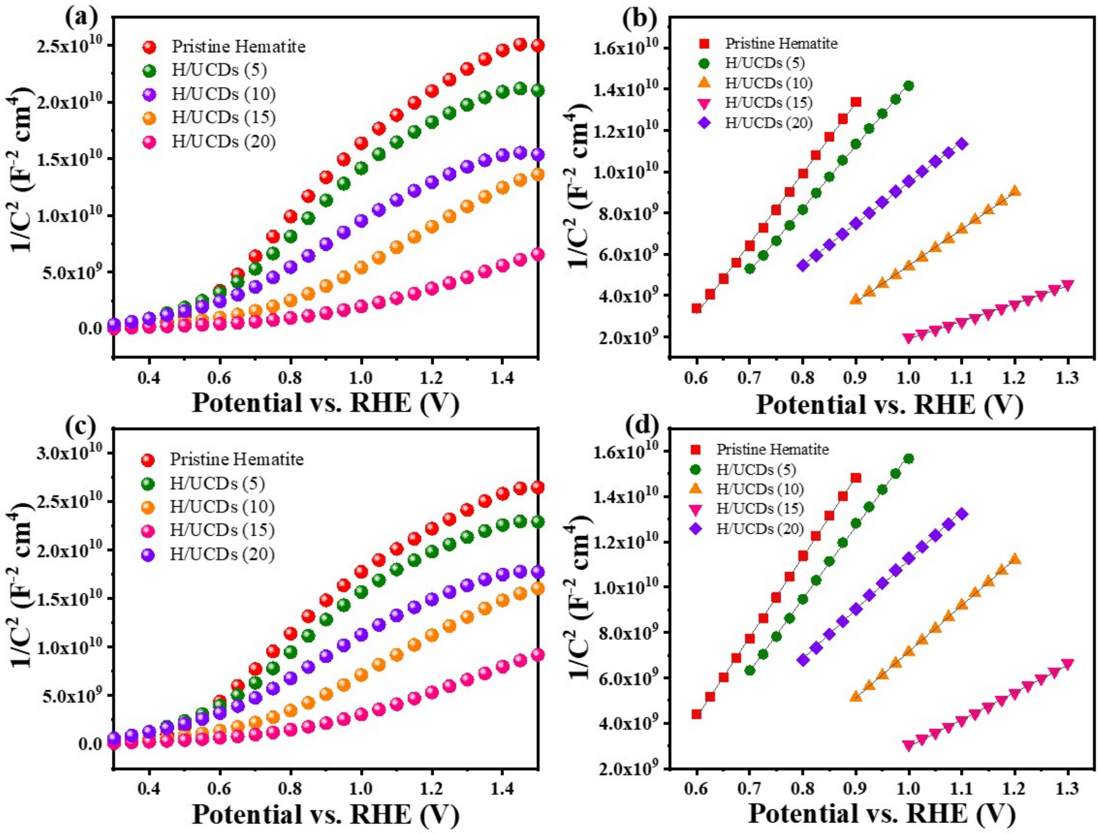

Fig. S8. Mott-Schottky plots at (a) 3 KH_Z (b) linear fitting of Mott-Schottky plots at 3 KH_Z (c) Mott-Schottky plots at 5 $KH_{Z;}$ (d) linear fitting of Mott-Schottky plots at 5 $KH_{Z.}$

Table S2. Mott-Schottky results at 3KHz and 5 KHz

Sample	3 KHz		5 KHz	
	E_{fb}	N_d	E_{fb}	N_d
	V	cm^{-3}	V	cm^{-3}
Pristine Hematite	0.51	1.26E18	0.48	1.21E18
H/UCDs (5)	0.53	1.41E18	0.50	1.34E18
H/UCDs (10)	0.69	2.43E18	0.65	2.10E18
H/UCDs (15)	0.78	5.02E18	0.75	3.57E18
H/UCDs (20)	0.52	2.15E18	0.50	1.95E18

Mott-Schottky Analysis:

The Mott-Schottky measurements have been calculated following the equation[1]:

$$\frac{1}{C^2} = (\frac{2}{\varepsilon\varepsilon_0 A N_d})(E - E_{fb} - \frac{k_B T}{e}) \qquad \text{S1}$$

where *C* and *A* are the space charge capacitance and photoelectrode area, respectively, ε is the vacuum permittivity (8.85×10^{-12} F m^{-1}), ε_0 is the relative dielectric constant of hematite ($\varepsilon_0 = 33$),[2] N_d is the charge donor density (cm^{-3}), E is the applied potential, E_{fb} is the flat band potential, k_B is the Boltzmann constant (1.38×10-23 J K^{-1}), *T* is the absolute temperature (in K), and *e* is the electronic charge. E_{fb} can be determined from the intercept on the potential axis by the extrapolation of the linear variation part of $1/C^2$ against potential *E*, and the slope of the straight line is related to N_d based on the following equation[3]:

$$N_d = \frac{2}{e\varepsilon\varepsilon_0}\left[\frac{d\left(1/C^2\right)}{dE}\right]^{-1} \qquad \text{S2}$$

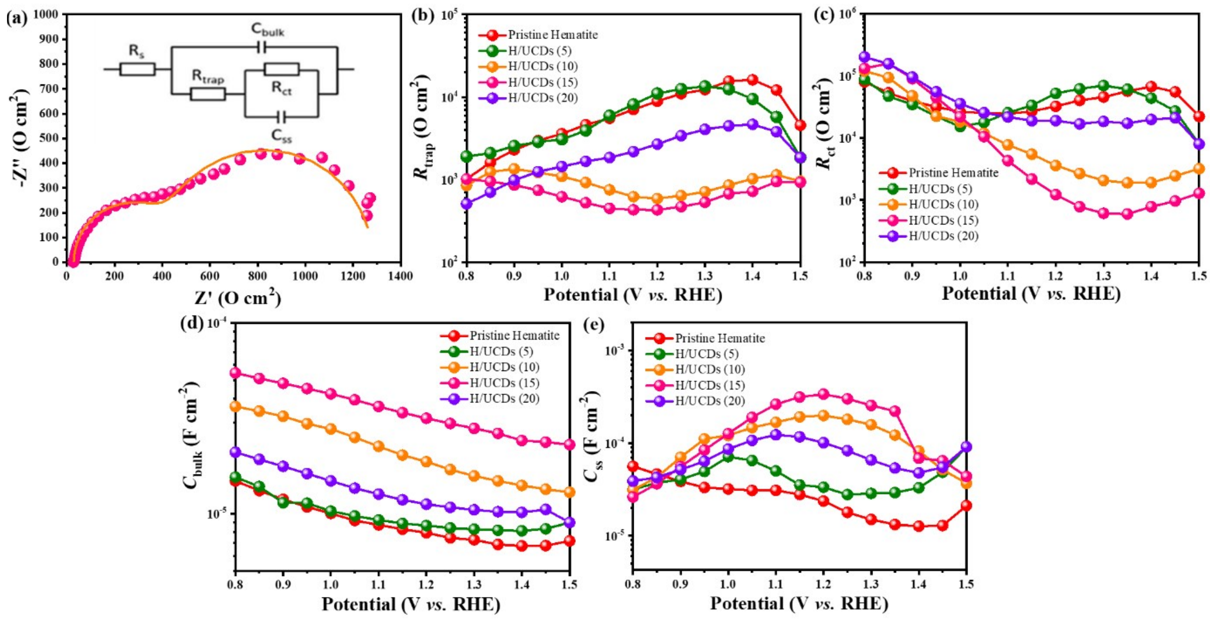

Fig. S9 (b) Nyquist plot and corresponding fitting curve of H/UCDs (15) at 1.25 v *vs.* RHE, and inset image shows equivalent circuit used; (c) R_{trap}, (d) R_{ct}, (e) C_{bulk}, and (f) C_{ss} obtained from EIS fitting as a function of applied potential for hematite and H/UCDs samples.

References

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3. X. Yang, A. Wolcott, G. Wang, A. Sobo, R. C. Fitzmorris, F. Qian, J. Z. Zhang and Y. Li, *Nano lett.*, **2009,** 9, 2331-2336.