Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Pd/TiC/Ti electrode with enhanced atomic H* generation, atomic H* adsorption and 2,4-DCBA adsorption for facilitating electrocatalytic hydrodechlorination

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Caption

Fig S1 (a-f) TEM images of TiC nanoparticles with different magnification; (g) Primary particle size distribution determined from counting primary particles from (a-f) TEM images; (h) Hydrodynamic particle size distribution of TiC suspensions (50 mg L^{-1}) with 1 mM NaCl (pH=7) measured by dynamic light scattering.

Fig. S2 C_t / C_0 of 2,4-DCBA as a function of time by Pd/TiC/Ti electrode at different cathode potential (a), k_{obs} for 2,4-DCBA degradation as a function of time by Pd/TiC/Ti electrode under different potential (b) ([2,4-DCBA]$_0$ = 0.2 mM, T = 25 ℃, Initial pH = 4.0).

Fig. S3 XPS survey spectra of TiC and Pd/TiC (a), XPS spectra of C 1s in Pd/TiC and Pd/C (b), XPS spectra of O 1s in Pd/TiC and Pd/C (c), XPS spectra of Ti 2p in Pd/TiC and Pd/C (d).

Fig. S4 ln (C_t / C_0) of 2,4-DCBA as a function of time by Pd/TiC/Ti, Pd/C/Ti, Pd/MWCNTs/Ti, Pd/Al_2O_3/Ti, Pd/MoS_2/Ti electrode (a), BA generation by different electrodes (b) ([2,4-DCBA]$_0$ = 0.2 mM, cathode potential = −0.8 V vs Ag/AgCl, T = 25 ℃, Initial pH = 4.0).

Fig. S5 Mass balance during degradation of 2,4-DCBA by Pd/MoS_2/Ti (a), Pd/Al_2O_3/Ti (b), Pd/MWCNTs/Ti (c), Pd/C/Ti (d), Pd/TiC/Ti (e), generation of BA as a function of time (f).

Fig. S6 Open circuit potential (OCP) curve of ITO, Pd/C/ITO and Pd/TiC/ITO.

Fig. S7 k_{obs} of 2,4-DCBA degradation during 10 cycles.

Fig. S8 SEM images of bare Ti (× 10k) (a), bare Ti (× 40k) (b), fresh Pd/TiC/Ti (× 10k) (c), fresh Pd/TiC/Ti (× 40k) (d), used Pd/TiC/Ti (× 10k) (e), used Pd/TiC/Ti (× 40k) (f), EDS of Pd/TiC/Ti before reaction (g), EDS of Pd/C/Ti after cycles (h).

Fig. S9 XRD pattern of bare Ti sheet.

Fig. S10 Contact angle of DI water on bare Ti sheet.

Fig. S11 Quantity of electric charge as a function of time during ECH process of 2,4-DCBA by Pd/TiC/Ti electrode.

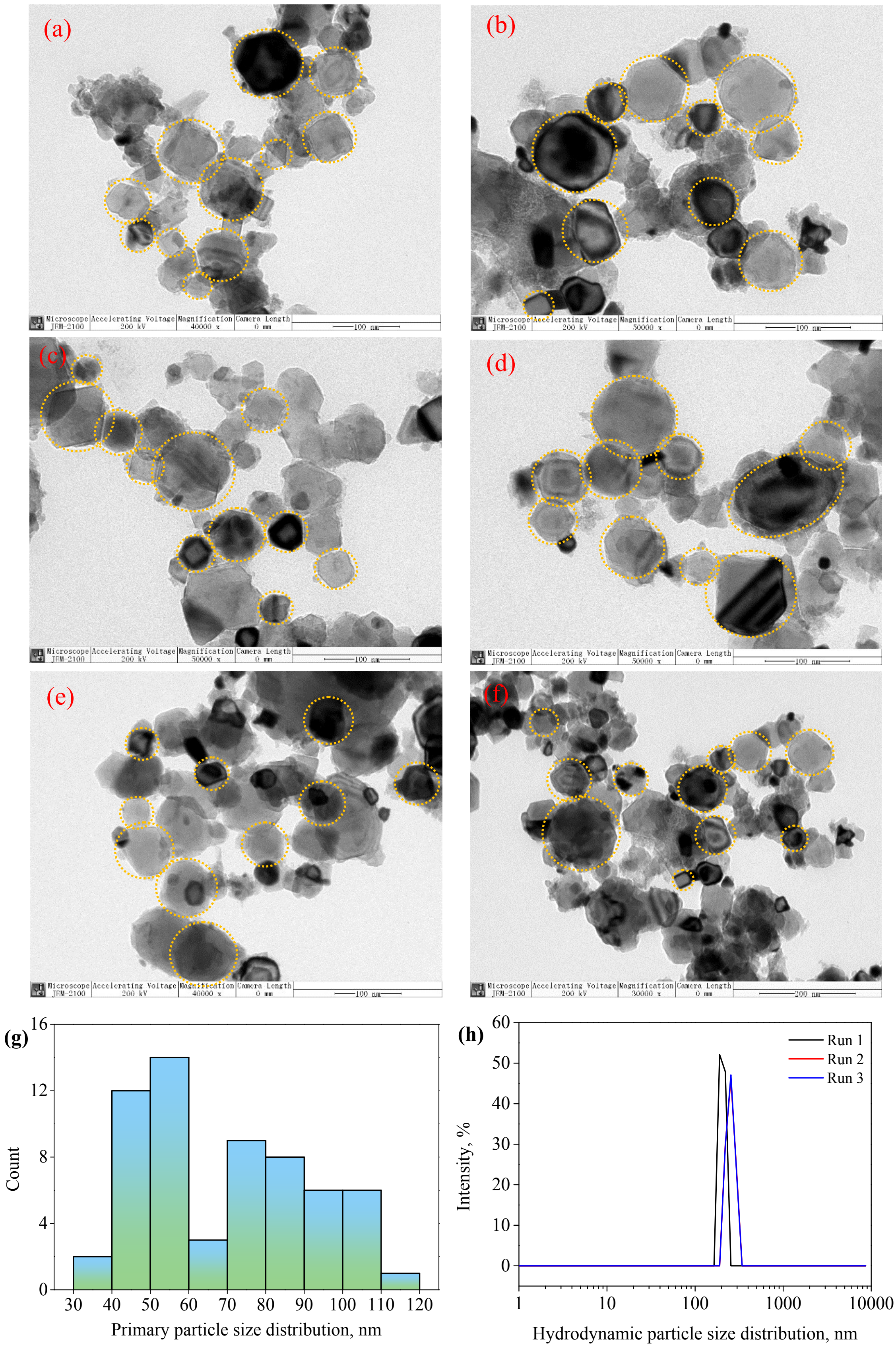
Table S1 Background values of water samples from Qizhen lake and Yuhangtang river.

Table S2 Energy consumption comparison of Pd/TiC/Ti electrode and selected studies.

Table S3 Toxicological parameters of 2,4-DCBA, CBA and BA.

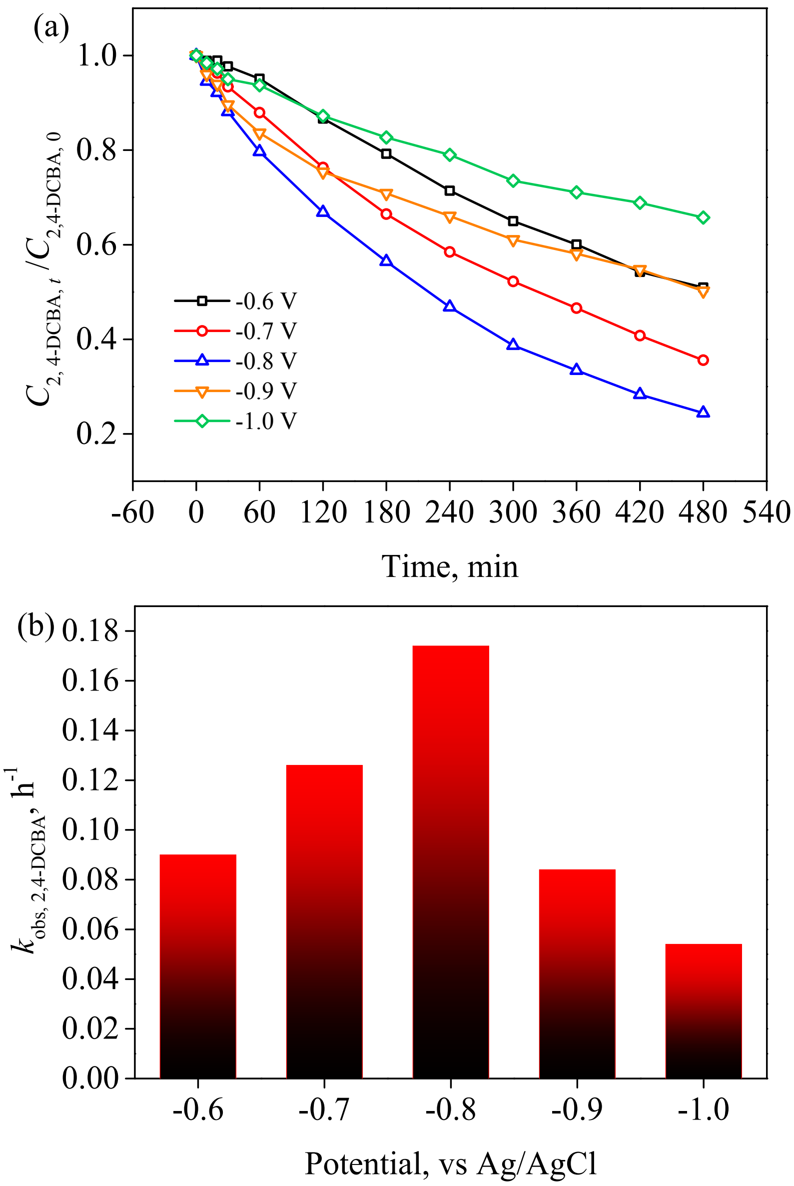
Text S1 Calculation process to predict the onset potential of HER.

Fig. S1



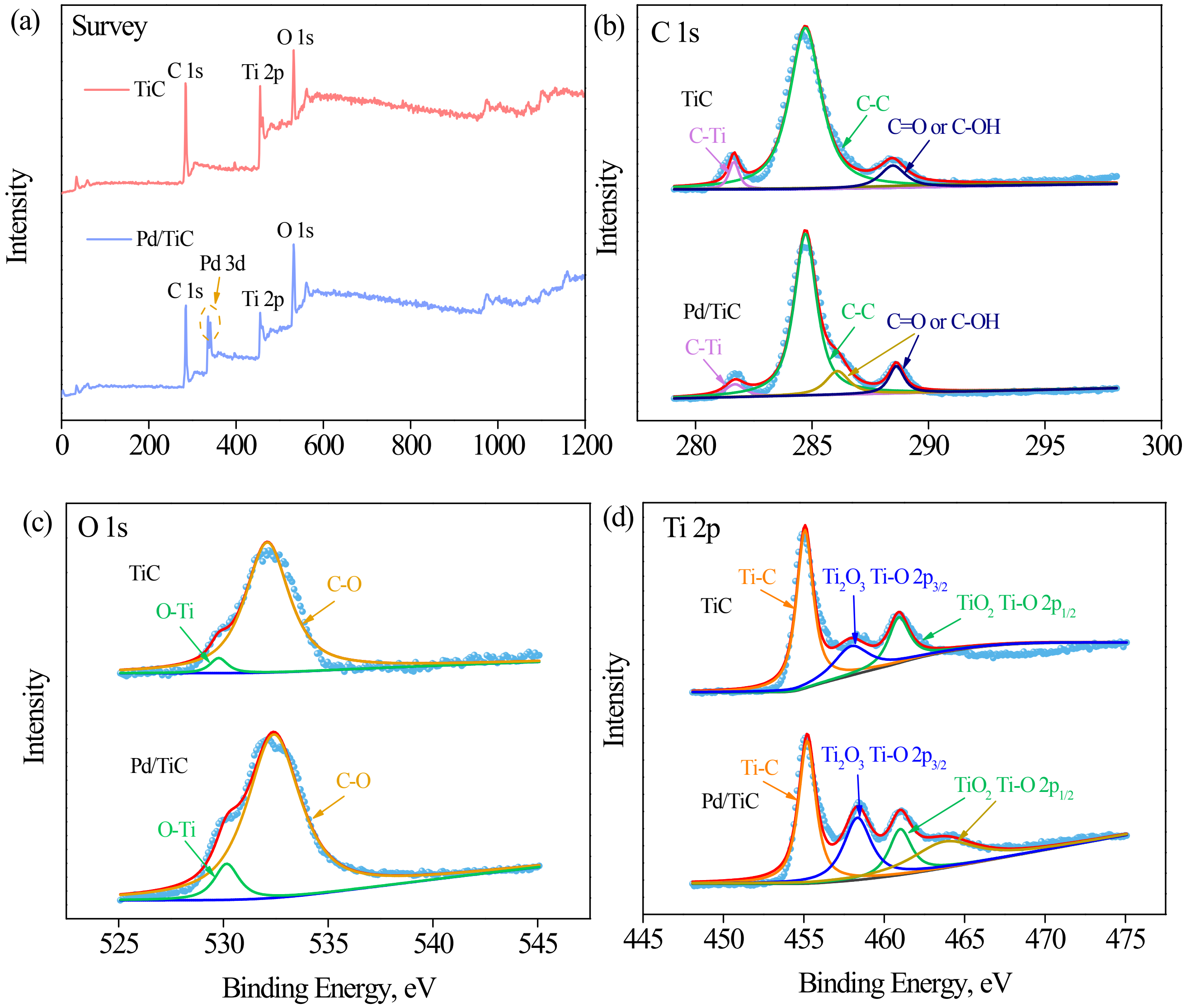
(a)
(b)
(c)
(d)
(e)
(f)
(g)
Count
Primary particle size distribution, nm
(h)
Intensity, %
Hydrodynamic particle size distribution, nm
Run 1
Run 2
Run 3

Fig. S2



(a)
1.0
0.8
0.6
0.4
0.2
$C_{2,\ 4\text{-DCBA},\ t}\ /C_{2,4\text{-DCBA},\ 0}$
-0.6 V
-0.7 V
-0.8 V
-0.9 V
-1.0 V
-60 0 60 120 180 240 300 360 420 480 540
Time, min
(b)
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
$k_{obs,\ 2,4\text{-DCBA}}$, h^{-1}
-0.6 -0.7 -0.8 -0.9 -1.0
Potential, vs Ag/AgCl

Fig. S3



(a)
Survey
TiC
C 1s
Ti 2p
O 1s
Pd/TiC
Pd 3d
Intensity
0
200
400
600
800
1000
1200
(b)
C 1s
TiC
C-Ti
C-C
C=O or C-OH
Pd/TiC
280
285
290
295
300
(c)
O 1s
O-Ti
C-O
525
530
535
540
545
Binding Energy, eV
(d)
Ti 2p
Ti-C
Ti_2O_3 Ti-O $2p_{3/2}$
TiO_2 Ti-O $2p_{1/2}$
445
450
455
460
465
470
475

Fig. S4

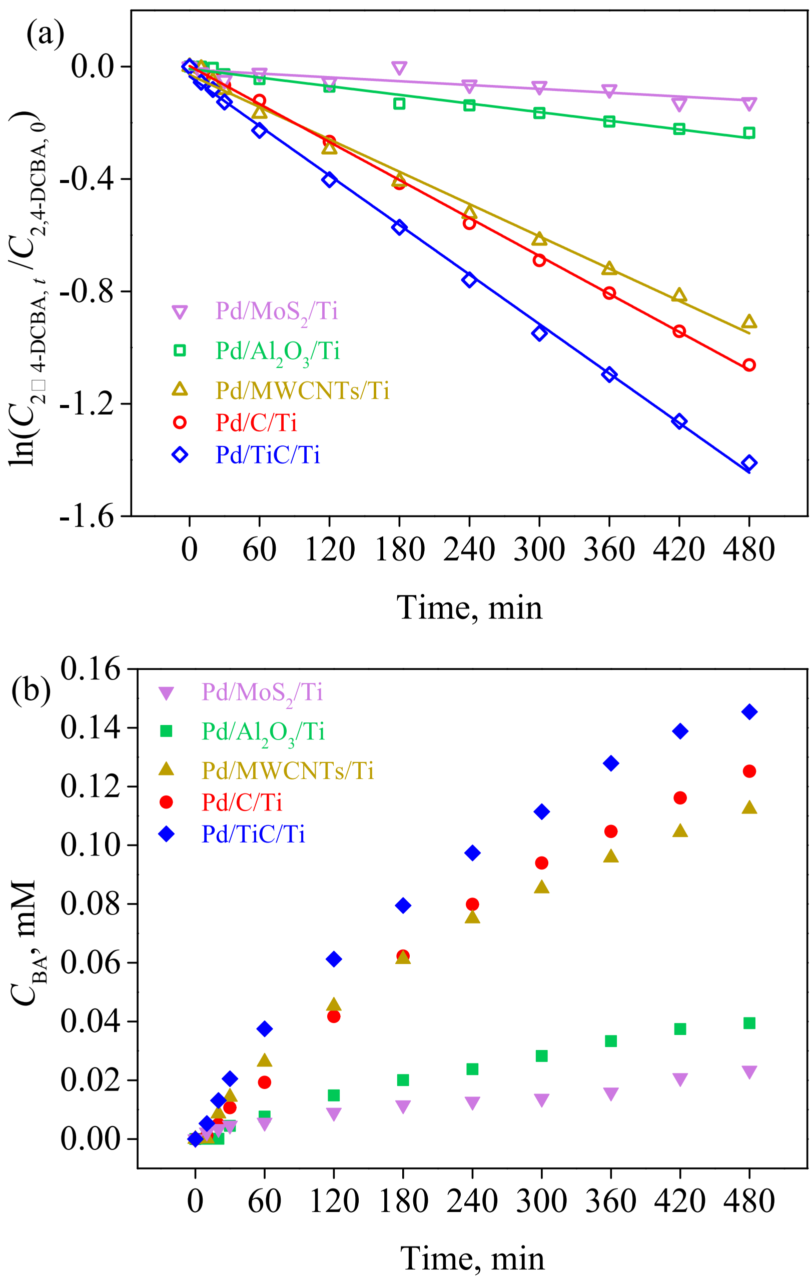
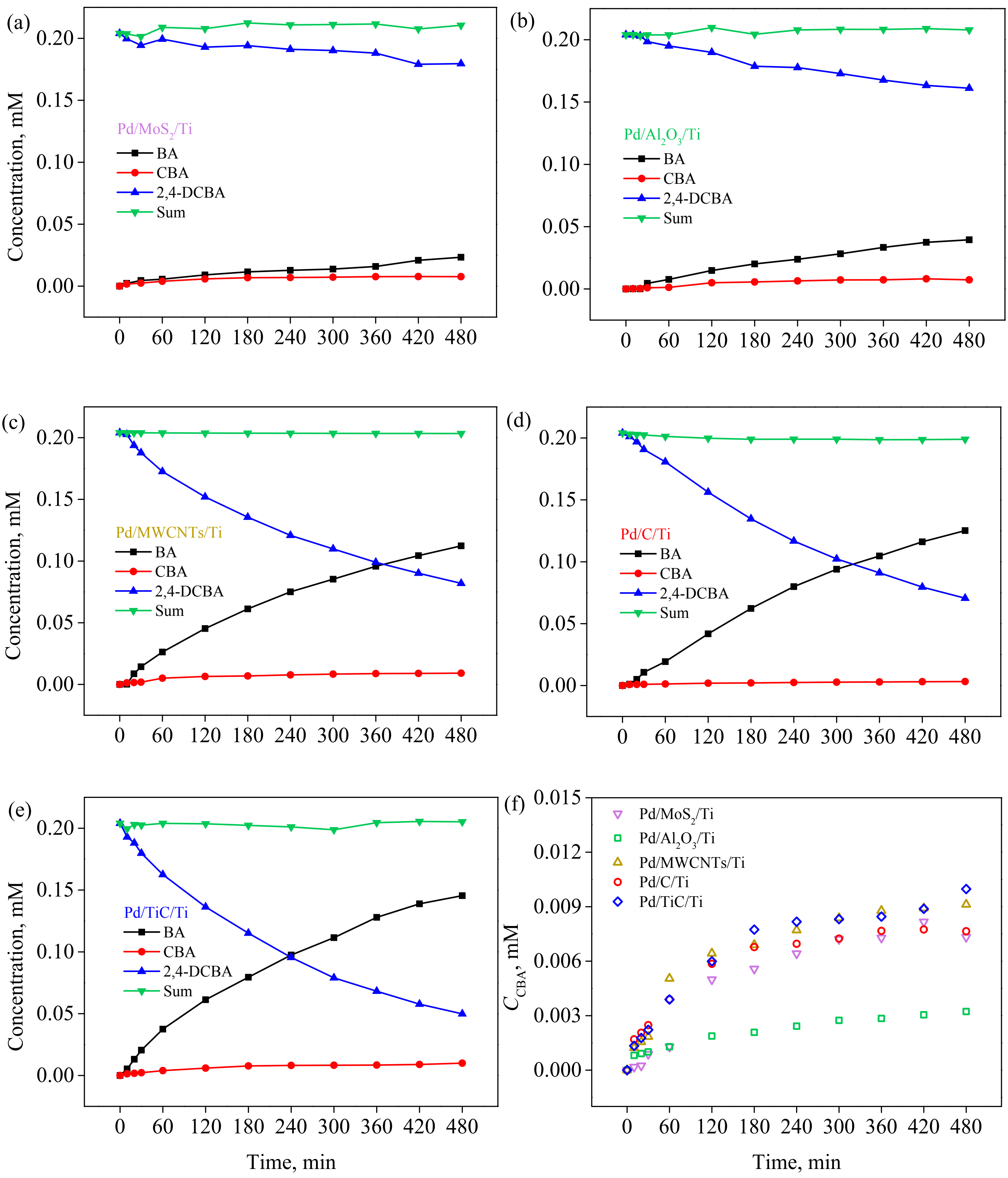
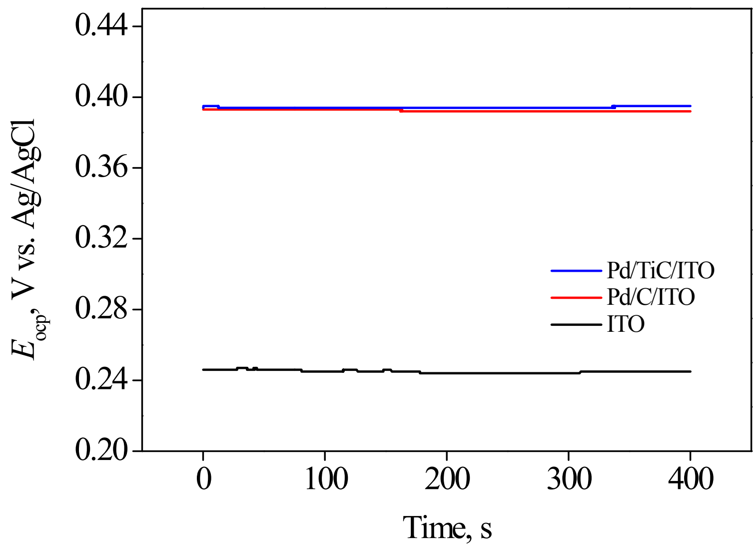

(a)
0.0
-0.4
-0.8
-1.2
-1.6
0
60
120
180
240
300
360
420
480
Time, min
Pd/MoS2/Ti
Pd/Al2O3/Ti
Pd/MWCNTs/Ti
Pd/C/Ti
Pd/TiC/Ti
(b)
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Time, min
Pd/MoS2/Ti
Pd/Al2O3/Ti
Pd/MWCNTs/Ti
Pd/C/Ti
Pd/TiC/Ti

Fig. S5



(a)
Pd/MoS2/Ti
BA
CBA
2,4-DCBA
Sum
Concentration, mM
0.20
0.15
0.10
0.05
0.00
0 60 120 180 240 300 360 420 480
(b)
Pd/Al2O3/Ti
BA
CBA
2,4-DCBA
Sum
(c)
Pd/MWCNTs/Ti
BA
CBA
2,4-DCBA
Sum
Concentration, mM
(d)
Pd/C/Ti
BA
CBA
2,4-DCBA
Sum
(e)
Pd/TiC/Ti
BA
CBA
2,4-DCBA
Sum
Concentration, mM
Time, min
(f)
Pd/MoS2/Ti
Pd/Al2O3/Ti
Pd/MWCNTs/Ti
Pd/C/Ti
Pd/TiC/Ti
C_CBA, mM
0.015
0.012
0.009
0.006
0.003
0.000
Time, min

Fig. S6



0.44
0.40
0.36
0.32
0.28
0.24
0.20
E_{ocp}, V vs. Ag/AgCl
0
100
200
300
400
Time, s
Pd/TiC/ITO
Pd/C/ITO
ITO

Fig. S7

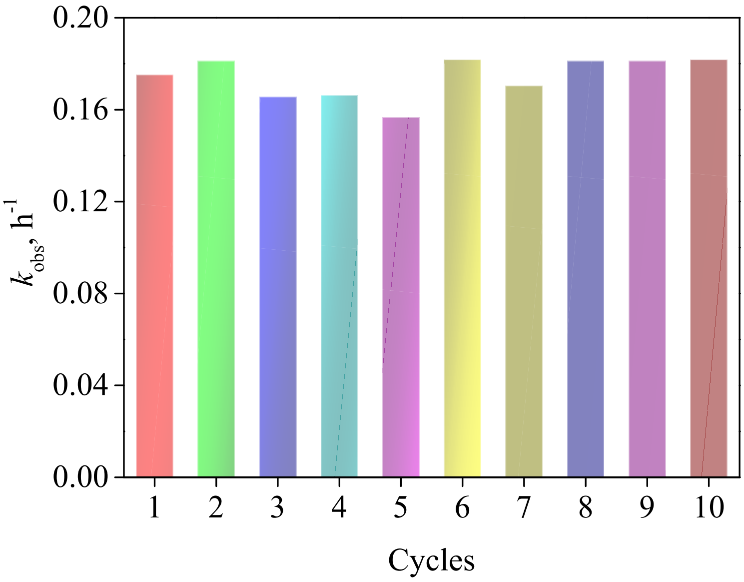
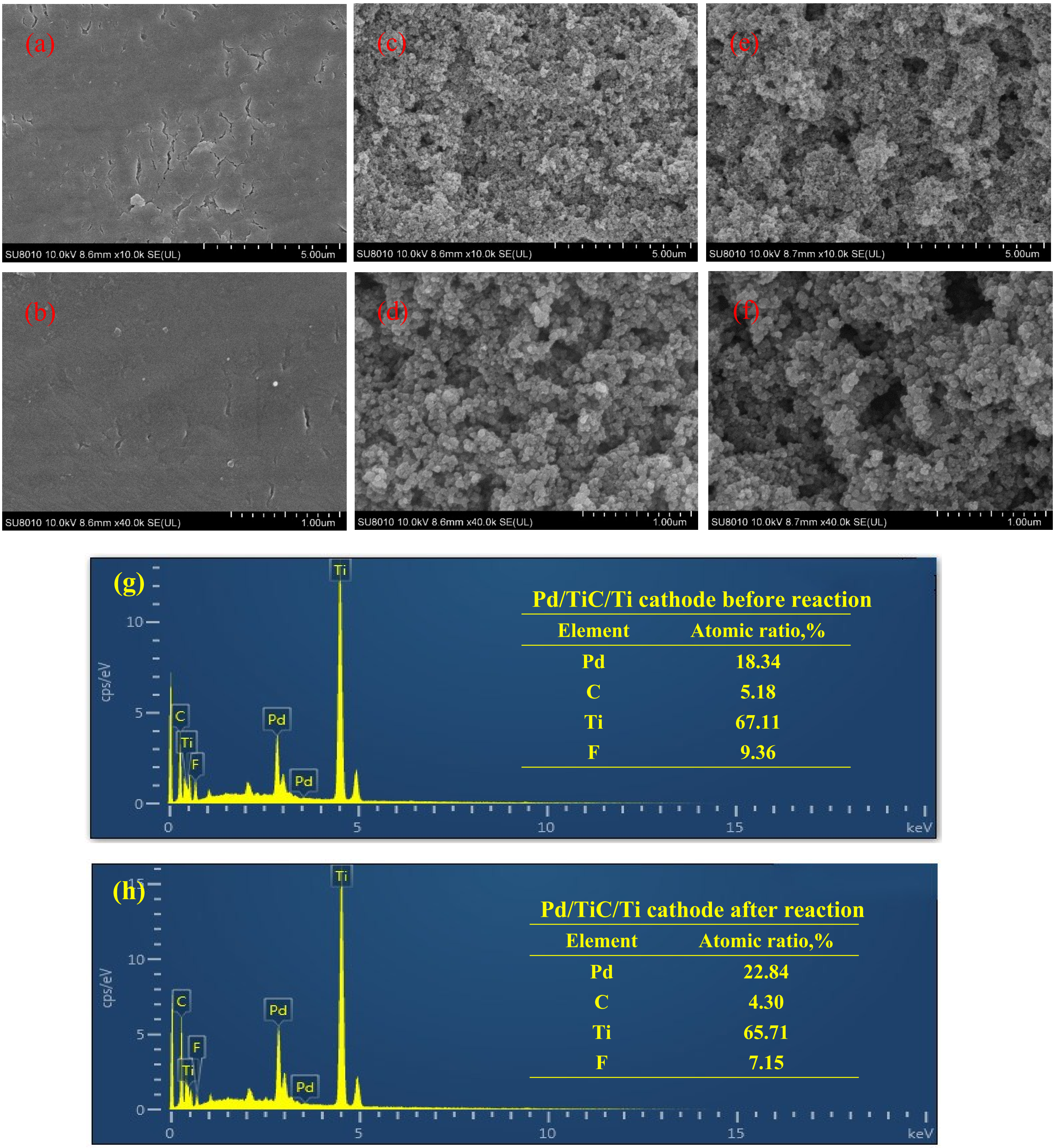
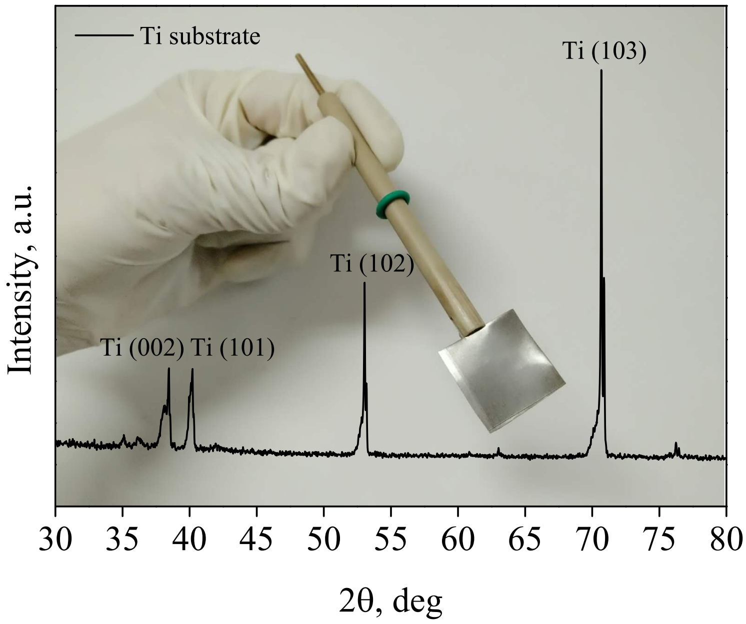


Fig. S8



(a)
SU8010 10.0kV 8.6mm x10.0k SE(UL) 5.00um
(c)
SU8010 10.0kV 8.6mm x10.0k SE(UL) 5.00um
(e)
SU8010 10.0kV 8.7mm x10.0k SE(UL) 5.00um
(b)
SU8010 10.0kV 8.6mm x40.0k SE(UL) 1.00um
(d)
SU8010 10.0kV 8.6mm x40.0k SE(UL) 1.00um
(f)
SU8010 10.0kV 8.7mm x40.0k SE(UL) 1.00um
(g)
Pd/TiC/Ti cathode before reaction
Element Atomic ratio,%
Pd 18.34
C 5.18
Ti 67.11
F 9.36
cps/eV
keV
C
Ti
F
Pd
Pd
Ti
(h)
Pd/TiC/Ti cathode after reaction
Element Atomic ratio,%
Pd 22.84
C 4.30
Ti 65.71
F 7.15
cps/eV
keV
C
F
Ti
Pd
Pd
Ti

Fig. S9



Ti substrate
Ti (103)
Ti (102)
Ti (002)
Ti (101)
Intensity, a.u.
30
35
40
45
50
55
60
65
70
75
80
2θ, deg

Fig. S10

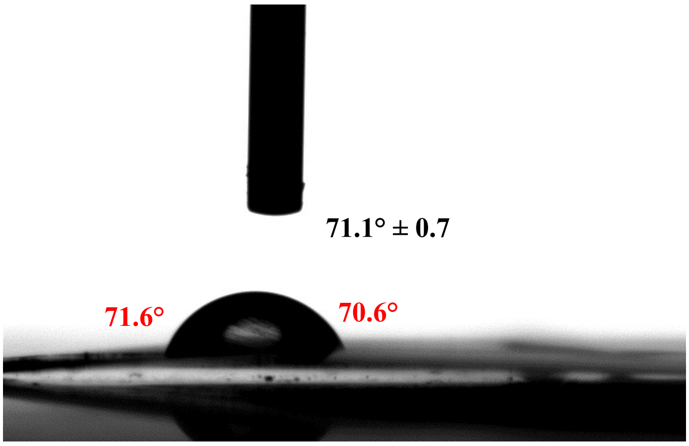
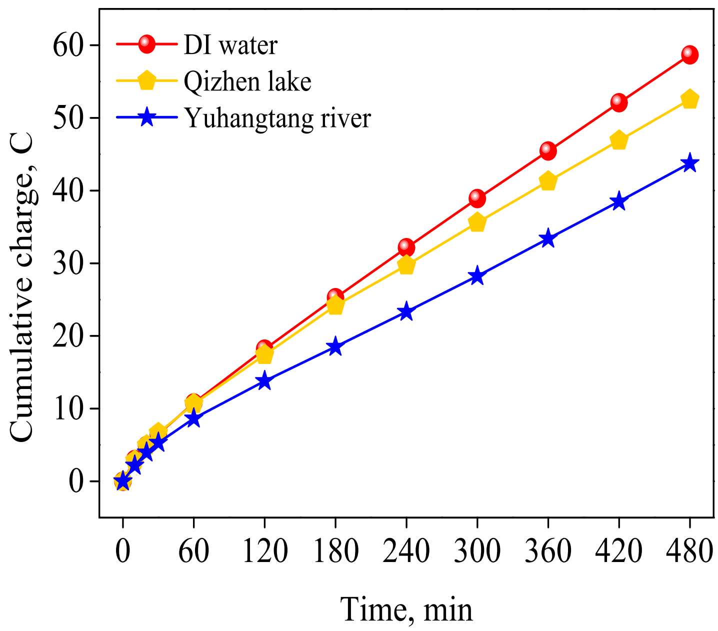


Fig. S11



DI water
Qizhen lake
Yuhangtang river
Cumulative charge, C
Time, min
0
10
20
30
40
50
60
0
60
120
180
240
300
360
420
480

Table S1

Samples [a]	Qizhen Lake	Yuhangtang river
pH	7.42	7.09
DO	8.09	8.02
Turbidity	16.01	23.21
Conductivity	365.0	284.0
Salinity	0.01	0.01
Na^{+}	14.87	10.15
K^{+}	6.72	5.49
Ca^{2+}	50.43	37.79
Mg^{2+}	7.85	5.51
F^{-}	0.34	0.33
Cl^{-}	16.32	22.7
NO_3^{-}	6.96	2.25
SO_4^{2-}	54.85	33.58
PO_4^{3-}	0.33	0.41

a: Cited from, J.S. Zhou, X.X. Zhou, K.L. Yang, Z. Cao, Z.N. Wang, C.C. Zhou, S.A. Baig, X.H. Xu, Adsorption behavior and mechanism of arsenic on mesoporous silica modified by iron-manganese binary oxide ($FeMnO_x$/SBA-15) from aqueous systems, *Journal of Hazard Materials*, 2020, **384**, 121229.

Table S2

Cathode materials	Model pollutant	Area	Energy consumption	Citation
Pd/TiC/Ti	2,4-DCBA	4 cm^2	0.37 kwh g^{-1}	This study
rGO/CFP [a]	Trichloroacetic acid	10 cm^2	0.313 kwh g^{-1}	[1]
Ni_2P/Ni foam	Trichloroacetic acid	2 cm^2	0.663 kwh g^{-1}	[2]

a: rGO/CFP refers to reduced graphene oxide hybrid grown on carbon fiber paper.

[1] R. Mao, H.C. Lan, L. Yan, X. Zhao, H.J. Liu, J.H. Qu, Enhanced indirect atomic H* reduction at a hybrid Pd/graphene cathode for electrochemical dechlorination under low negative potentials, *Environmental Science: Nano*, 2018, **5**, 2282–2292.

[2] Q.F. Yao, X.F. Zhou, S.Z. Xiao, J.B. Chen, I.A. Abdelhafeez, Z.J. Yu, H.Q. Chu, Y.L. Zhang, Amorphous nickel phosphide as a noble metal-free cathode for electrochemical dechlorination, *Water Research*, 2019, **165**, 114930.

Table S3

Target organic/ product	2,4-DCBA	*o*-CBA	*p*-CBA	BA
CAS number	50-84-0	118-91-2	74-11-3	65-85-0
Type of test [a]	LD50 – Lethal dose, 50 percent kill			
Route of exposure	Oral			
Species observed	Rodent – rat			
Dose/duration ($mg\ kg^{-1}$)	830	>500	1170	1700

a: All the acute toxicity data listed in Table S2 were cited from Chemical Toxicity database (www.drugfuture.com/toxic/).

Text S1

The onset potential of HER in theory can be estimated via Nernst equation. The Nernst equation can be described as:

$E = E^0 + RT/nF*\ln(C_o/C_R)$,

For a HER reaction, $E^0(H^+/H_2)$ is 0 V vs SHE. Since the concentration of reduction state species ($[H_2]$) is 0, the equation can be converted into:

$E = -0.059*pH$,

The pH of solution is around 5.8, so E can be obtained as −0.342 V vs SHE. Meanwhile, the potential should be revised because the reference electrode used here is Ag/AgCl:

$E(SHE) = E(Ag/AgCl) + 0.198$ V,

Lastly, the HER overpotential of Pd should be taken into consideration. When the reduction current is 0.1 A dm^{-2}, the HER overpotential of Pd is around 0.12 V, so the onset potential of HER in this case could be predicted as −0.66 V vs Ag/AgCl.