

## Supporting Information

### **Enhanced indirect atomic H<sup>\*</sup> reduction at a hybrid Pd/graphene cathode for electrochemical dechlorination under low negative potentials**

Ran Mao<sup>a</sup>, Huachun Lan<sup>b, d, \*</sup>, Li Yan<sup>e</sup>, Xu Zhao<sup>a, c</sup>, Huijuan Liu<sup>b, c</sup> and Jiuhui Qu<sup>a, c</sup>

<sup>a</sup>Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, P.R. China

<sup>b</sup>School of Environment, State Key Joint Laboratory of Environment Simulation and Pollution Control, Tsinghua University, Beijing, 100084, P.R. China

<sup>c</sup>University of Chinese Academy of Sciences, Beijing, 100049, P.R. China

<sup>d</sup>Center for Water and Ecology, Tsinghua University, Beijing 100084, China

<sup>e</sup>State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, P.R. China

\*Corresponding author: Tel.: +86-10-62849160; fax: +86-10-62849160; e-mail: hclan@tsinghua.edu.cn.

## Calculation results:

Cartesian coordinates for Pd-H and Pd/rGO-H reported in the manuscript.

<b>Table S1.</b> Cartesian coordinates for Pd-H			
Atomic Types	Coordinates (Angstroms)		
	X	Y	Z
H	1.161325	2.30293	0
Pd	-1.61411	-0.8661	-1.42289
Pd	-1.61411	-0.8661	1.42289
Pd	-0.53113	-2.93329	0
Pd	1.213315	-1.22766	1.446583
Pd	1.213315	-1.22766	-1.44658
Pd	-2.63395	1.252678	2.645655
Pd	-2.63395	1.252678	-2.64566
Pd	-2.56935	1.433586	0
Pd	0.049919	1.055869	0
Pd	0.009337	1.120237	2.64086
Pd	2.634229	0.707594	2.651885
Pd	0.009337	1.120237	-2.64086
Pd	2.634229	0.707594	-2.65189
Pd	2.671602	0.773266	0

<b>Table S2.</b> Cartesian coordinates for Pd/rGO-H			
Atomic Types	Coordinates (Angstroms)		
	X	Y	Z
C	-4.05372	-3.07696	-0.37752
C	-1.95027	-4.36288	-0.73347
C	-4.74518	-1.86812	-0.50943
C	-4.07223	-0.6628	-0.95075
C	-2.64087	-3.16276	-0.6861
C	-1.92964	-1.90973	-0.88238
C	0.198061	-5.6035	-0.87886
C	2.352195	-6.83719	-0.95191
C	-0.52512	-4.40917	-0.82223
C	0.196466	-3.16223	-0.77626
C	1.61599	-5.63115	-0.85795
C	2.338045	-4.40093	-0.72038
C	3.746078	-6.82573	-0.91557

C	4.452464	-5.62863	-0.76985
C	-4.75188	0.521828	-1.18512
C	-4.06339	1.764013	-1.30064
C	-2.62788	-0.6913	-1.03733
C	-1.91599	0.539351	-1.11828
C	-4.73535	2.985659	-1.41842
C	-4.0629	4.226552	-1.30294
C	-2.62983	1.761837	-1.16073
C	-1.95346	2.998439	-0.94197
C	-4.73693	5.469048	-1.40021
C	-4.05383	6.667126	-1.20009
C	-2.65894	4.229112	-1.00956
C	-1.97322	5.463826	-0.76437
C	-2.6932	6.673176	-0.8796
C	-0.49997	-1.92414	-0.854
C	0.222624	-0.67946	-0.87966
C	1.620922	-3.17314	-0.65228
C	2.326406	-1.92613	-0.50686
C	-0.49132	0.543672	-0.96446
C	0.189335	1.768854	-0.69386
C	1.630809	-0.68066	-0.66476
C	2.324364	0.556453	-0.47667
C	3.770442	-4.39621	-0.66244
C	4.451251	-3.16401	-0.46064
C	3.772398	-1.95155	-0.34873
C	4.434104	-0.70067	-0.06052
C	-0.55893	2.988309	-0.59929
C	0.103085	4.235114	-0.27106
C	1.604724	1.768043	-0.45495
C	2.260761	2.999498	-0.05425
C	-0.60417	5.4296	-0.37975
C	1.489203	4.18029	0.137674
C	3.743656	0.540606	-0.1552
C	4.441224	1.807767	-0.039
C	3.711638	3.017654	0.029917
Pd	2.399282	-1.3791	4.25677
Pd	-0.34097	-1.09415	4.241321
Pd	1.145675	0.178064	6.21226
Pd	-0.2297	1.843814	4.260005

Pd	2.671397	1.44901	4.15302
Pd	-3.77039	-1.83359	1.585118
Pd	1.848245	-2.25874	1.737364
Pd	-0.92176	-1.80914	1.634488
Pd	0.844576	0.305424	2.259167
Pd	-2.25658	0.230214	2.876386
Pd	-1.02769	2.323759	1.600023
Pd	3.69395	-0.26301	2.041327
Pd	4.258887	2.451802	2.11737
Pd	1.555246	3.111733	2.158351
H	1.209399	1.684778	5.309346

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**Table S3.** XPS analysis of Pd component obtained from the Pd 3d spectrum.

Electrode	Components	Pos. (eV)	FWHM (eV)	%Area
Pd/CFP	Pd <sup>0</sup> 3d <sub>5/2</sub>	335.07	1.05	53.80
	Pd <sup>0</sup> 3d <sub>3/2</sub>	340.33	1.05	35.84
	PdO <sub>x</sub> 3d <sub>5/2</sub>	336.54	2.05	6.22
	PdO <sub>x</sub> 3d <sub>3/2</sub>	341.82	2.05	4.14
Pd/rGO/CFP	Pd <sup>0</sup> 3d <sub>5/2</sub>	335.07	0.93	42.30
	Pd <sup>0</sup> 3d <sub>3/2</sub>	340.33	0.93	28.18
	PdO <sub>x</sub> 3d <sub>5/2</sub>	336.54	1.67	17.72
	PdO <sub>x</sub> 3d <sub>3/2</sub>	341.82	1.67	11.81

**Table S4.** XPS analysis of C component obtained from the C 1s spectrum.

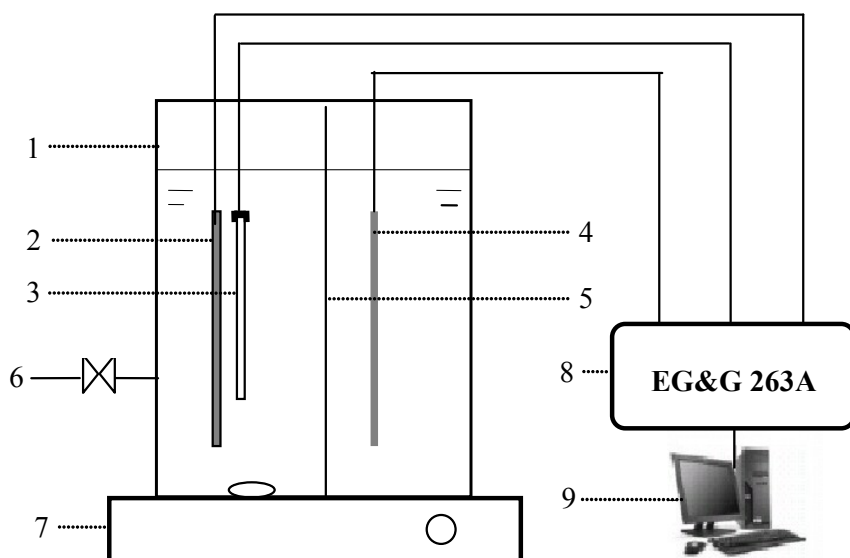
Electrode	Components	Pos. (eV)	FWHM (eV)	%Area
rGO/CFP	C-C/C=C	284.80	1.52	57.37
	C-O	286.13	1.52	15.79
	O-C=O	288.62	2.59	26.84
Pd/rGO/CFP	C-C/C=C	284.80	1.38	70.53
	C-O	286.18	1.38	11.44
	O-C=O	288.90	2.28	18.03

**Table S5.** Comparison of TCAA dechlorination performance of different electrodes.

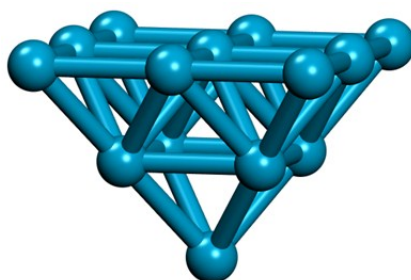
Cathode materials	Initial TCAA concentration	$E_{\text{CAT}}$ (V vs SCE)	Removal efficiency (%)	Refs.
Pd/Fe-C	500 $\mu\text{g/L}$	-1.5	90.0 (40 min)	[1]
Cu tubing	100 mg/L	-1.0	65.2 (25 min)	[2]
Graphene/Cu foam	500 $\mu\text{g/L}$	-1.2	99.6 (40 min)	[3]
MoS <sub>2</sub> /carbon felt	1.6 mg/L	-1.1	36.0 (10 min)	[4]
Co-MoS <sub>2</sub> /carbon felt	1.6 mg/L	-1.1	100.0 (10 min)	[4]
Pd/rGO/CFP	500 $\mu\text{g/L}$	-0.5	81.5 (40 min)	This work

## References

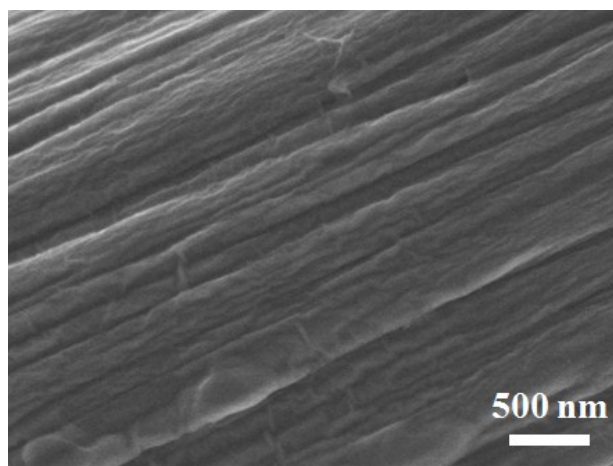
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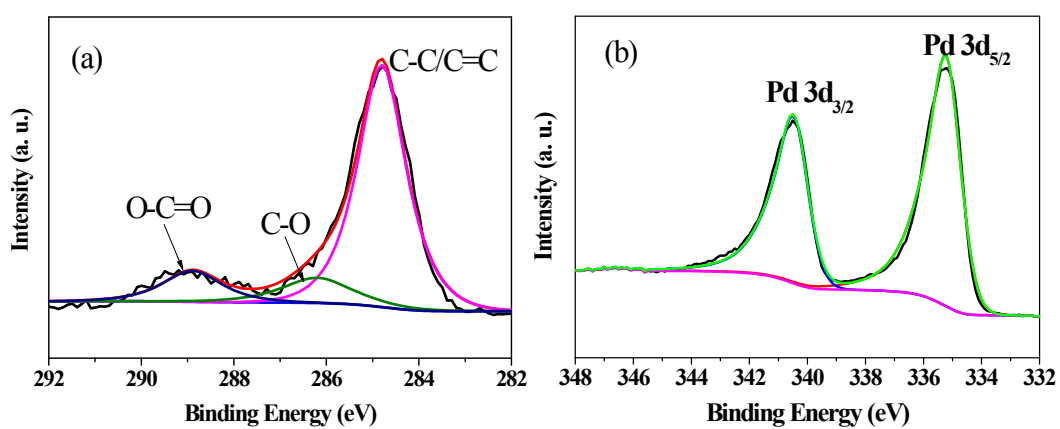
**Figure S1.** Schematic diagram of the experimental set-up. (1) reactor; (2) cathode; (3) reference electrode (SCE); (4) anode: platinum wire; (5) proton-exchange membrane; (6) sampling port; (7) magnetic stirrer; (8) electrochemical workstation; (9) Computer.



**Figure S2.** Pd<sub>14</sub> cluster, showing four {111} and one {100} faces.



**Figure S3.** SEM image of GO on CFP.



**Figure S4.** (a) XPS C 1s spectrum and (c) Pd 3d spectrum of the Pd/rGO/CFP electrode after electrochemical reduction process .