Supporting Information

A Novel Nanostructured Zn Electrode for Selective Electroreduction of CO_2 to Formate in Aqueous Solutions

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A field emission scanning electron microscopy (FESEM) was used to observe the morphology of the D-Zn. As shown in Figure S1 d, the rock like texture consists of thin layer plates, which lie on each other. It has been proved that the current density during the deposition can significantly influence the growth direction of platelets.[1] In our paper, during the deposition process of Zn, the cathode polarization effect was reduced due to low deposition current density. This results in lower nucleation rate, larger grain size, and planes with low surface energy which tends to increase their surface area.[2] The basal {00.2} plane have the lowest surface free energy in zinc crystal due to its compactness. As a consequence, oriented polycrystalline growth of zinc trends to develop a {00.2} fiber texture component.[3]

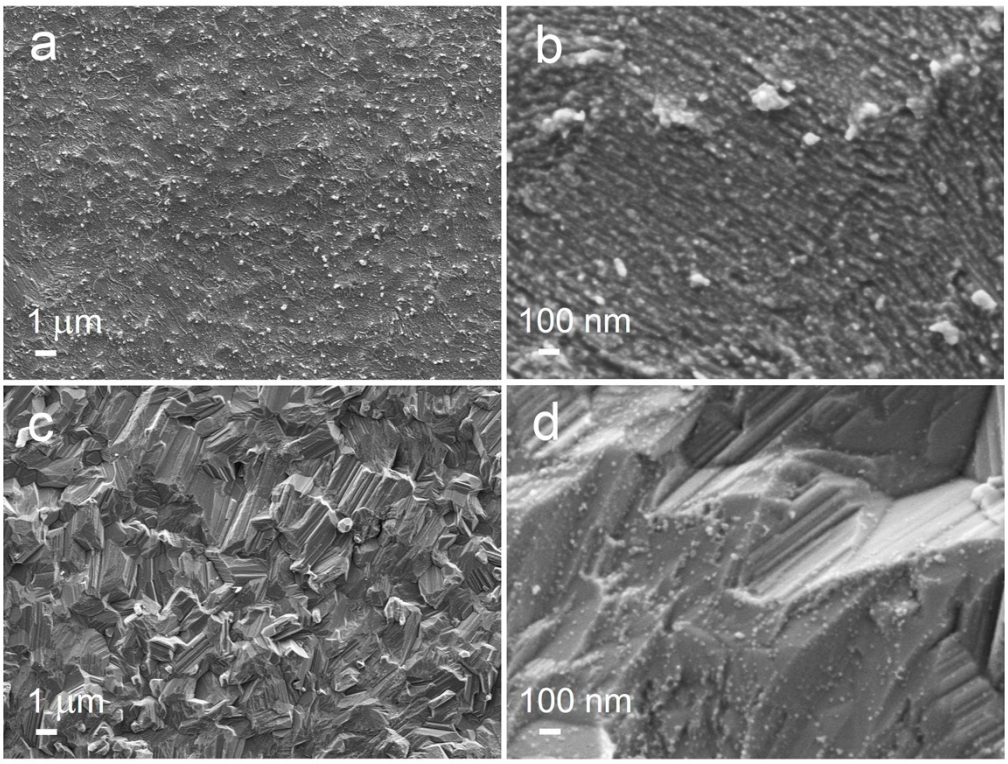

Figure S1. Low-resolution SEM and high-resolution SEM images of Zn-foil (a) (b) and D-Zn (c) (d).

The roughness measurement of the electrodes were conducted in N_2 purged 0.5 M $NaHCO_3$ aqueous solution at various scan rates. The scanning potential ranges from −0.5 to -0.3 V, because no active redox peak was observed in this regime. The double-layer width of the CV is thereby directly related to the capacitance and proportional to roughness of the electrodes. Figure S2 shows the CVs for the Zn foil and RAD-Zn, the linear regression of the double layer and the roughness factor of each material obtained from the electrochemical studies. This analysis shows that the RAD-Zn presents the highest roughness, about 4 times rougher than Zn foil (Table S1).

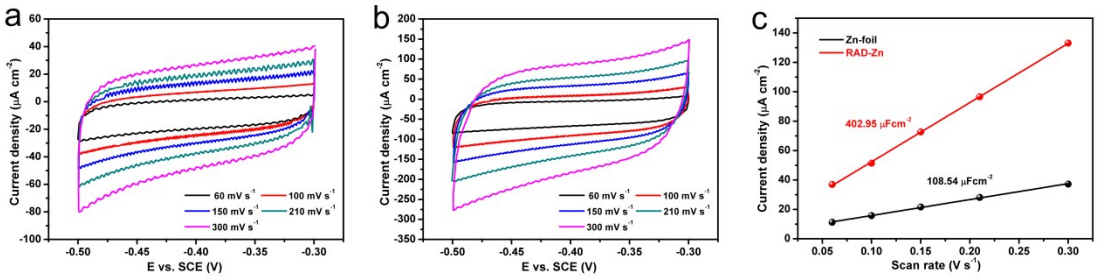

Figure S2. Capacitive behaviors on the prepared Zn electrodes：The CVs of (a) Zn-foil and (b) RAD-Zn with a potential range from –0.5 to -0.3 V (vs SCE) in a N_2-bubbled 0.5 M NaHCO3 electrolyte. (c) Current density plots at various CV scan rates. The linear regression of the double layer capacitances and the roughness factor of each material were noted in the figure.

Table S1. The capacitances and surface roughness factors of the electrodes.

Sample	Capacitance (μF cm^{-2})	Surface roughness factor
Zn-foil	108.54	1
RAD-Zn	402.95	3.7

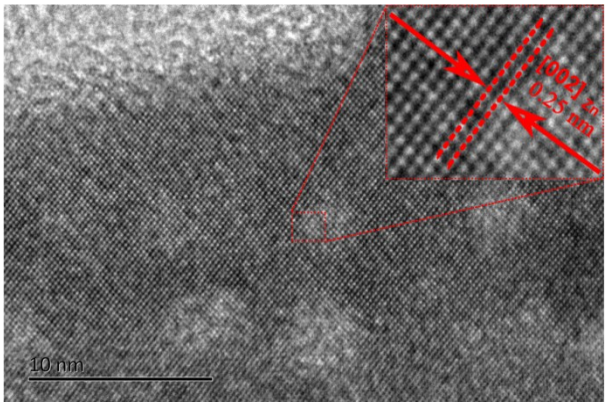

Figure S3. A typical HRTEM image of the internal slice under the surface of AD-Zn.

Table S2. XPS results for different samples.

	Peak Area / RSF		atomic ratio	Components of O 1s						
				a		b		c		atomic ratio
Sample	Zn 2p	O 1s	Zn/O	Binding Energy(ev)	Peak Area(P)	Binding Energy(ev)	Peak Area(P)	Binding Energy(ev)	Peak Area(P)	a/b/c
Zn-foil	3835.8	6815.7	0.56	532.4	2976.44	531.7	13992.7	530.4	3037.43	1.0/4.7/1.0
D-Zn	4013.5	6129.2	0.65	532.2	6679.19	531.5	5064.35	530.3	6601.65	1.0/0.8/1.0
AD-Zn	5725.8	6527.0	0.88	532.3	3273.48	531.5	4928.54	530.3	11665.2	1.0/1.5/3.6
RAD-Zn	3754.8	7989.3	0.47	532.5	7579.83	531.7	10114.9	530.6	6285.56	1.0/1.3/0.8

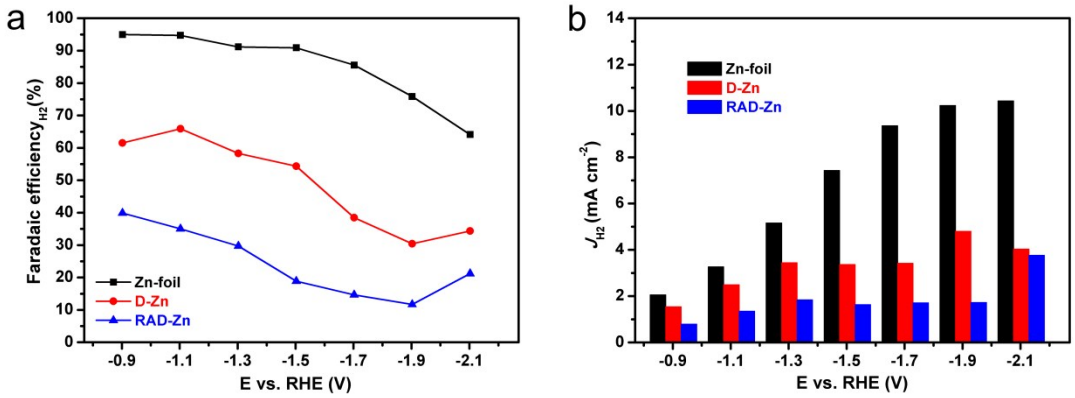

Figure S4. Comparison of (a) hydrogen faradaic efficiency, (b) hydrogen current density for Zn-foil, D-Zn and RAD-Zn at −0.93 V to −2.13 V (vs RHE) in CO_2 saturated 0.5 M $NaHCO_3$ solution.

References

1. K. Raeissi, A. Saatchi, M. A. Golozar and J. A. Szpunar, *Surface and Coatings Technology*, 2005, 197, 229-237.
2. D. Y. Li and J. A. Szpunar, *Electrochimica acta*, 1997, 42, 47-60.
3. Matysina Z A, Chuprina L M, Zaginaichenko S Y, *Journal of Physics and Chemistry of Solids*, 1992, 53(1): 167-174.