Supplementary materials

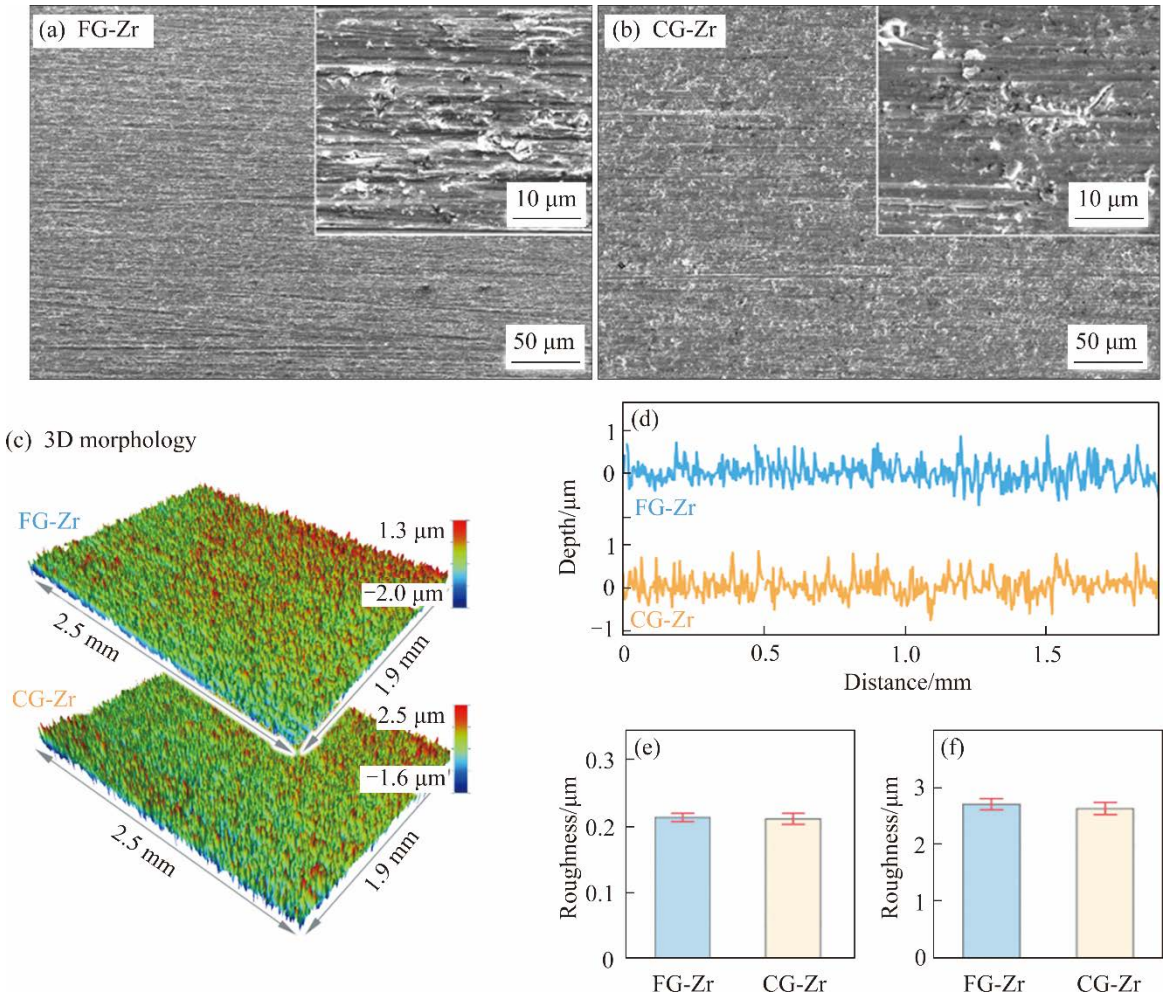

Figure S1 The microstructure (a and b), 3D morphology (c), cross-sectional profiles (d), arithmetic mean roughness (e), and average roughness (f) of Zr alloys after polishing with 2000# sandpaper

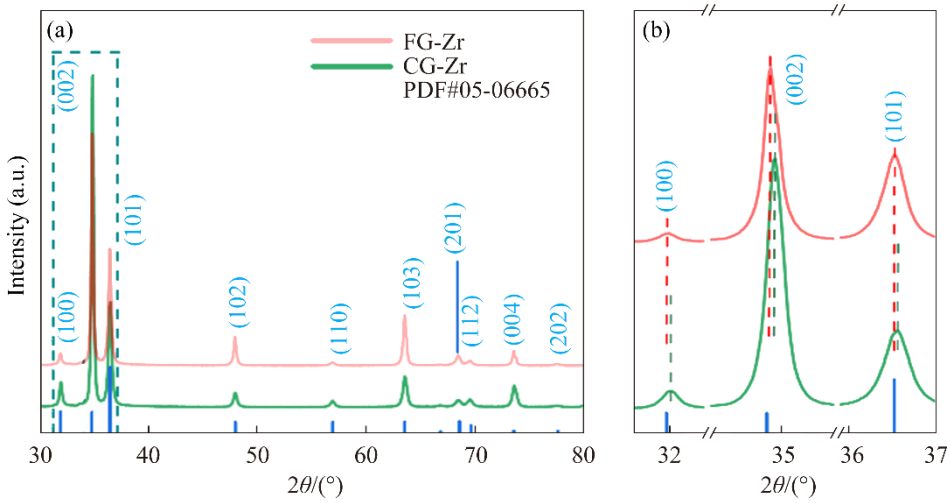

Figure S2 (a) XRD patterns of Zr alloys with fine and coarse grain; (b) Enlarged area of the peaks (100), (002) and (101)

Table S1 Electrochemical parameters calculated from PD curves evaluated in 12 mol/L HNO_3 with varying concentrations of F^-

Solution	Sample	E_{corr}/V	J_{corr}/(μA·cm^{-2})	J_p/(μA·cm^{-2})	ΔE_b/V
0 mmol/L F^-	FG-Zr	0.82±0.01	1.5±0.3	1.0	0.56
	CG-Zr	0.82±0.01	1.6±0.1	1.5	0.53
0.1 mmol/L F^-	FG-Zr	0.82±0.01	2.1±0.3	2.2	0.49
	CG-Zr	0.81±0.01	3.6±0.3	3.5	0.50
0.2 mmol/L F^-	FG-Zr	0.80±0.00	2.8±0.6	2.8	0.52
	CG-Zr	0.76±0.00	5.2±0.6	5.2	0.52
0.5 mmol/L F^-	FG-Zr	0.79±0.01	5.7±1.7	5.8	0.47
	CG-Zr	0.77±0.01	8.1±0.6	7.8	0.53
1.0 mmol/L F^-	FG-Zr	0.76±0.00	24.0±2.6	23.4	0.50
	CG-Zr	0.75±0.01	34.8±1.3	34.4	0.52
2.0 mmol/L F^-	FG-Zr	0.60±0.00	89.1±5.3	90.0	0.64
	CG-Zr	0.61±0.02	109.1±4.3	107.8	0.66

E_{corr} and J_{corr} represent the corrosion potential and corrosion current density, respectively; J_p corresponds to the passivation current density at 1.11 V; ΔE_b characterizes the passive region in the polarization curve.

Table S2 Fitting results of the impedance spectrum

Solution	Sample	R_s/(Ω·cm^2)	R_{ct}/(kΩ·cm^2)	CPE_{dl}/(μS·s^{-n}·cm^{-2})	n	χ^2
0 mmol/L F^-	FG-Zr	2.07	32.3	9.94	0.94	2.2×10^{-2}
	CG-Zr	—	30.2	10.50	0.95	4.6×10^{-4}
0.1 mmol/L F^-	FG-Zr	2.13	10.2	11.54	0.99	5.9×10^{-2}
	CG-Zr	2.13	9.4	9.52	0.99	5.7×10^{-2}
0.2 mmol/L F^-	FG-Zr	2.05	6.7	12.76	0.98	6.8×10^{-2}
	CG-Zr	2.16	5.9	7.23	0.96	8.1×10^{-2}
0.5 mmol/L F^-	FG-Zr	1.57	4.1	3.87	0.93	2.8×10^{-2}
	CG-Zr	5.99	2.9	8.43	0.97	1.6×10^{-2}
1.0 mmol/L F^-	FG-Zr	2.18	2.7	2.13	0.99	3.4×10^{-2}
	CG-Zr	2.20	1.9	4.30	0.99	4.5×10^{-2}
2.0 mmol/L F^-	FG-Zr	1.01	1.3	3.40	0.97	3.9×10^{-3}
	CG-Zr	2.14	1.2	4.16	0.98	5.1×10^{-3}

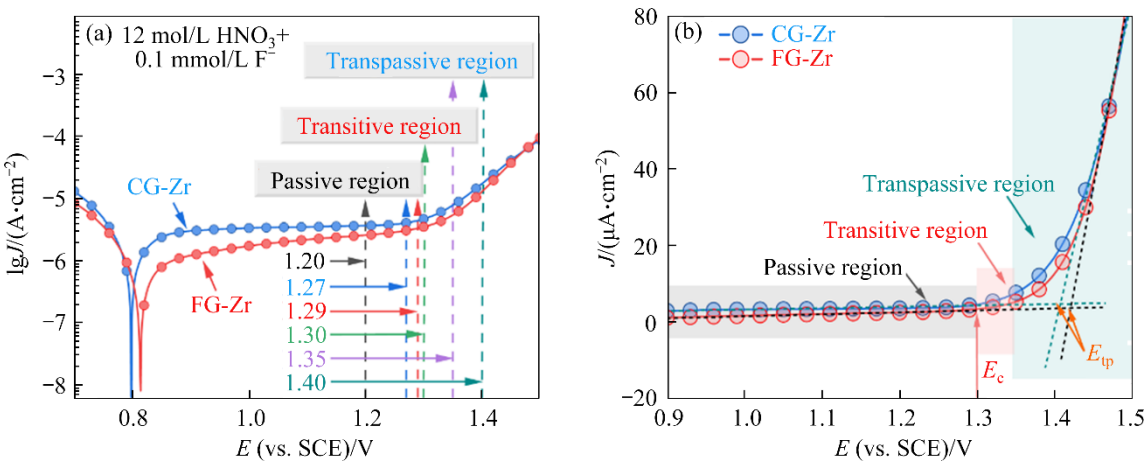

Figure S3 (a) Three types of applied potentials and corresponding polarization curves for FG-Zr and CG-Zr in 12 mol/L HNO_3 containing 0.1 mmol/L F^-; (b) Schematic diagram illustrating the definitions of the passive, transitive, and transpassive regions in the polarization curve

Figure S4 The schematic diagram illustrating the role of grain boundaries on the oxide-layer formation