Supporting Information

Sub-micrometer-thick hydrophobic zeolite corrosion-resistant coatings synthesized by solvothermal secondary growth

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1. Experimental Section

1.1 Materials

Tetrapropylammonium hydroxide (TPAOH, 25%), tetraethyl silicate (TEOS, 98%), ethylene glycol (EG, 99%), diethylene glycol (DEG, 99%), triethylene glycol (TEG, 99%) and tetraethylene glycol (tEG, 99%) were purchased from Aladdin. Stainless-steel plates (SSP, 20 mm × 20 mm) were immerged in 30 % H_2O_2 solution and heated at 90 ^oC for 3 h, then washed with copious DI water and dried at 60 ^oC.

1.2 Preparation methods

The synthesis solution with the molar composition of 1TEOS : 0.32TPAOH : 165H_2O was prepared by introducing 9.2 g TEOS into aqueous solution containing 11.26 g TPAOH and 120 g H_2O. After being aged under stirring for 4 h, the mixture was poured into a Teflon lined stainless-steel autoclave and crystallized at 175 ^oC for 2 h. Afterward, the solid products were centrifuged, washed with distilled water and dried at 60 ^oC in an oven overnight. The average size (along *c*-axis) of the MFI seed crystals is about 1 μm, as shown in Figure S1a.

MFI seed layer on SSP support was fabricated by manual assembly technique. The seeded support was vertically placed in a Teflon-lined autoclave for secondary growth. The molar composition of the synthesis solution was TEOS : TPAOH : H_2O : diols = 1 : 0.2 : 100 : x, where x = 0 - 100. After stirring for 4 hours, the solution was transferred to the autoclave and heated in an oven at 175 ^oC for 4 hours. After synthesis, the film was washed with deionized water and dried at 60 ^oC. If necessary, the obtained film was calcined at 450 ^oC for 12 h with the heating and cooling rate of 1 ^oC/min to remove structure directing agent. The MFI zeolite film prepared by adding EG with molar amount of 20 was denoted as EG-20. Other samples synthesized using diols were named by analogy.

1.3 Sample characterization

Scanning electron microscope (ZEISS Sigma 300, Hitachi TM 3030) was used to observe the surface and the cross-sectional morphology of the films. X-ray diffraction (XRD) patterns were collected on Bruker D8 Advance diffractometer with Cu Kα radiation. The ICP-OES analysis for the synthesis solution was carried out on Agilent 5110. Equilibrium water contact angle test was conducted on Chengde Dingsheng JY-82C video tester. FT-IR and XPS characterization of MFI zeolite crystals was performed on Thermo Fisher Nicolet iS10 and Thermo Scientific K-Alpha, respectively. The element content analysis was carried out on Elementar UNICUBE. The corrosion resistance of MFI zeolite films and bare SSP was characterized on a CHI660E

electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd.). The electrochemical polarization and electrochemical impedance spectroscopy (EIS) measurements were conducted in a three-electrode system. The testing solution used in the work is a 3.5 wt% sodium chloride solution, simulating the marine environment.

2. Supplementary Figures and Tables

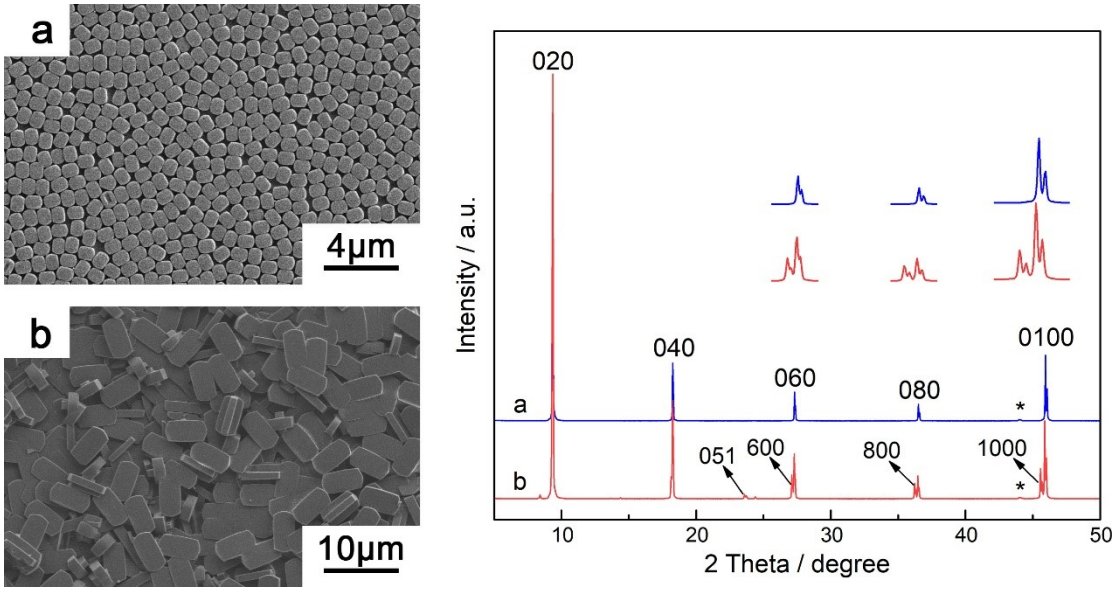

Figure S1. SEM images and XRD patterns of (a) *b*-axis-oriented MFI zeolite seed layer and (b) film EG-0 covered by twin crystals. (*) Peaks from SSP. (A zoom-in figure of the diffraction peaks is inserted.)

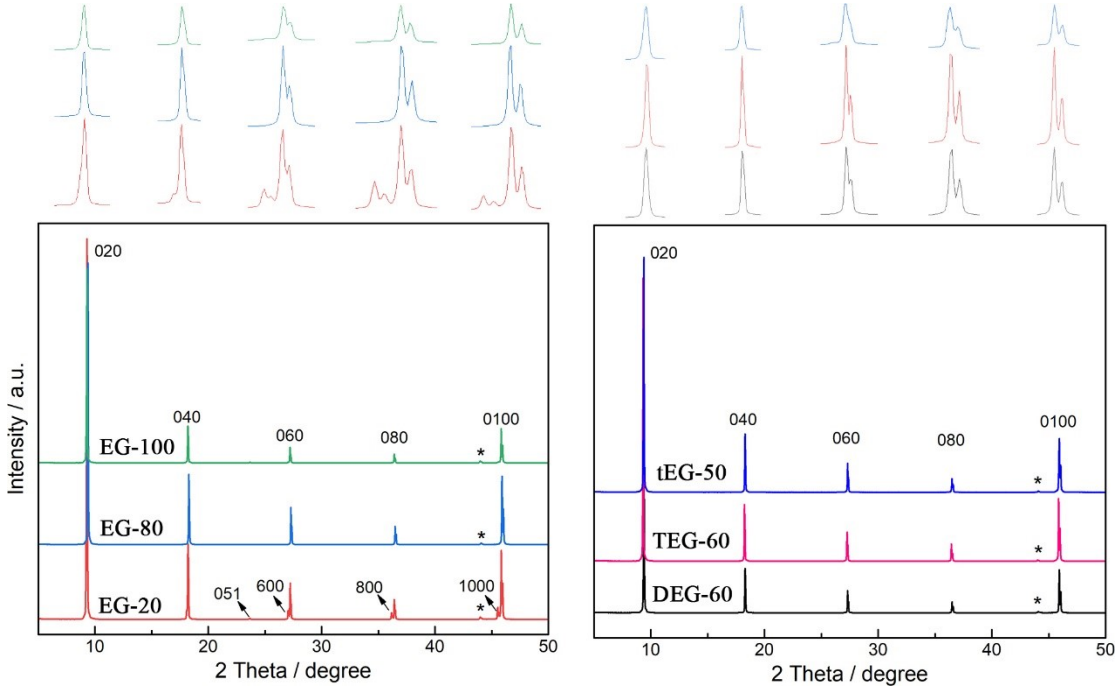

Figure S2. XRD patterns of MFI zeolite films synthesized by solvothermal secondary growth using different diols. (*) Peaks from SSP.

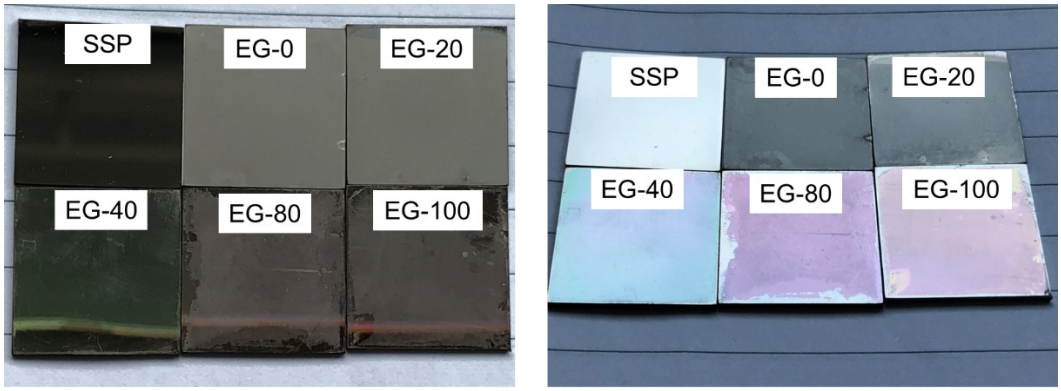

Figure S3. Optical photograph of MFI zeolite films synthesized by using different amount of EG solvent.

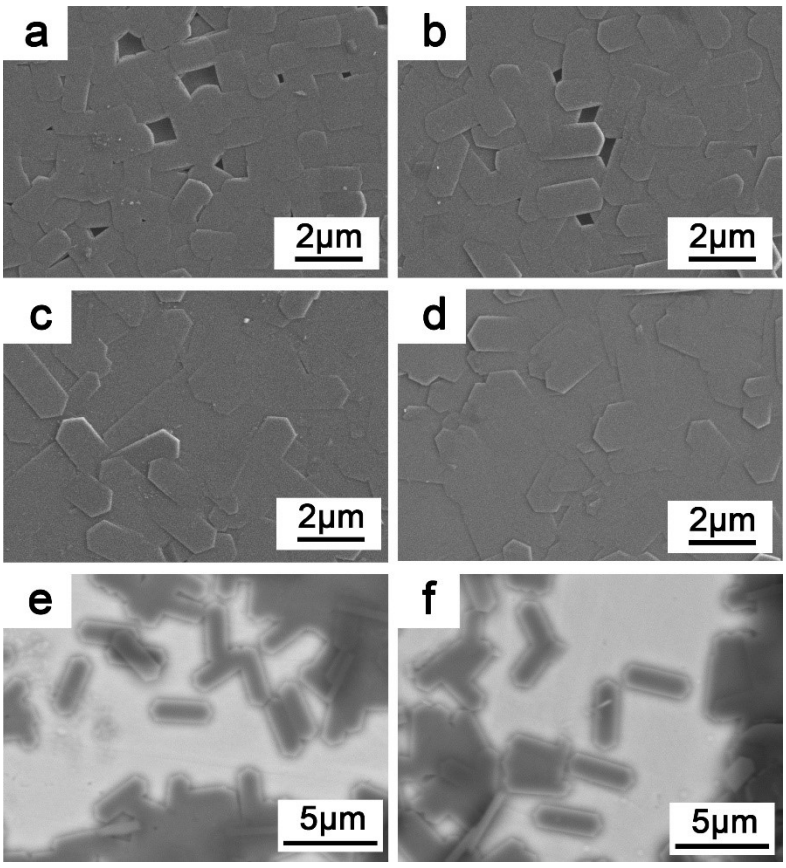

Figure S4. SEM images of MFI zeolite films synthesized at 175 ^{o}C for 2 h (a), 3 h (b), 5 h (c), and 6 h (d) with synthesis solution composition of 1TEOS : 0.2TPAOH : 100H_2O: 80EG. SEM images of MFI zeolite crystals at the edge of the films synthesized for 5 h (e) and 6 h (f).

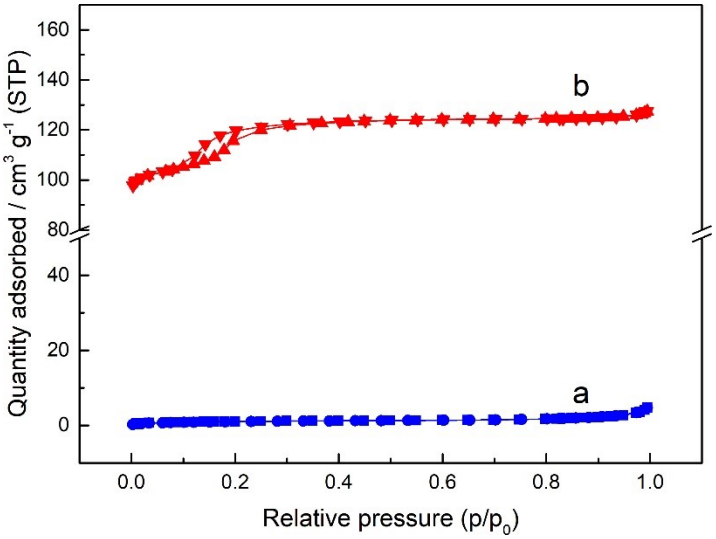

Figure S5. N_2 adsorption/desorption isotherms of the zeolite EG-80-C. (a) before and (b) after calcination.

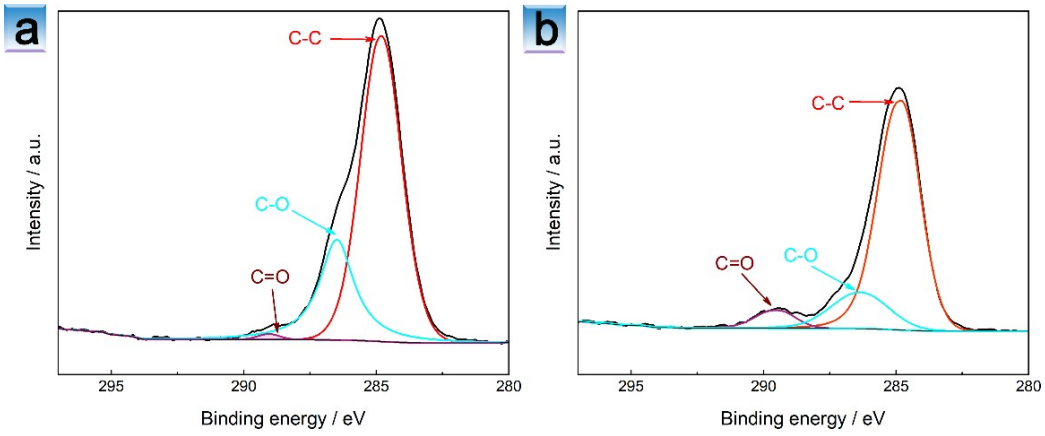

Figure S6. C1s XPS spectra of the zeolite EG-80-C. (a) before and (b) after calcination.

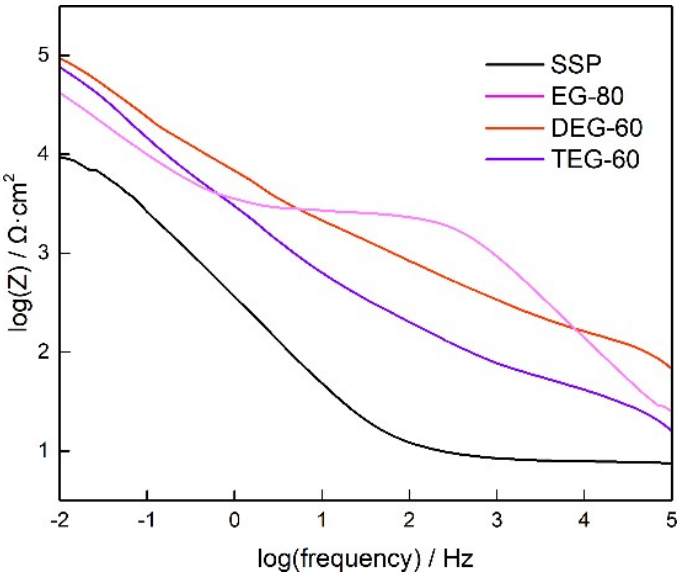

Figure S7. Bode plots from EIS tests on the bare SSP and the zeolite films coated SSPs.

Table S1 The length growth rate of MFI seed crystals on SSP by using different molar amount of diols.[a]

Diols	Molar amount	Growth rate (μm h^{-1})
EG	20	1.17
	40	0.87
	80	**0.53**
	80[b]	**0.54**
	80[c]	**0.53**
	100	0.40
DEG	20	1.10
	40	0.70
	60	**0.50**
	80	0.27
TEG	20	1.07
	40	0.63
	60	**0.44**
	80	0.23
*t*EG	20	1.00
	40	0.50
	50	**0.20**
	60	0.00

[a] The growth rate was calculated according to the formula of (crystal size − seed size)/(synthesis time − 1). The seed size is 1 μm. The samples were synthesized at least twice to reduce the uncertainty. The samples were synthesized at 175 °C for 4 h unless otherwise specified.
[b] Synthesis time: 5 h.
[c] Synthesis time: 6 h.

Table S2 Textural properties of EG-80-C zeolite before and after calcination.

EG-80-C	S_{micro}[a] [$m^2\ g^{-1}$]	S_{BET}[b] [$m^2\ g^{-1}$]	V_{micro}[a] [$cm^3\ g^{-1}$]	V_{meso}[c] [$cm^3\ g^{-1}$]	V_{pore}[d] [$cm^3\ g^{-1}$]
Before calcination	0.587	3.76	0.0002	0.007	0.0072
After calcination	107.3	368.4	0.063	0.134	0.197

[a]t-Plot method. [b]BET method. [c]$V_{meso} = V_{total} - V_{micro}$. [d]Volume adsorbed at $p/p_0 = 0.995$.