Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Comprehensive Studies on Phosphoric Acid Treatment of Porous Titania toward Titanium Phosphate and Pyrophosphate Monoliths with Pore Hierarchy and Nanostructured Pore Surface

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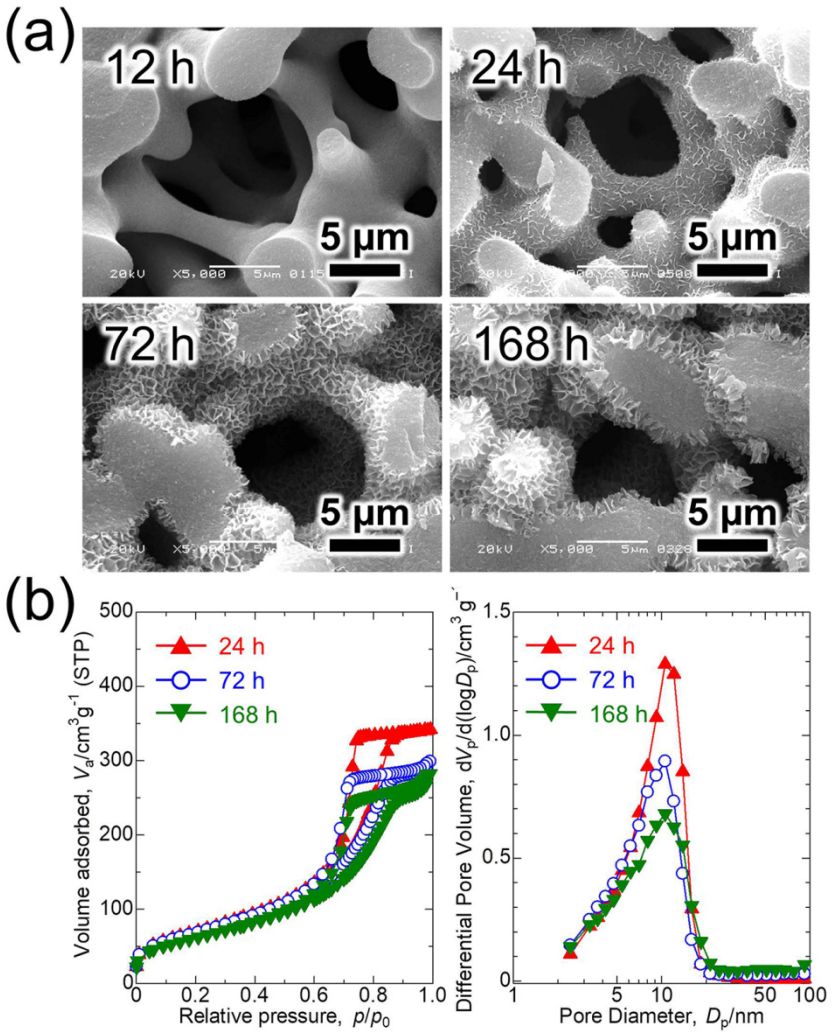

Figure S1 (a) SEM images and (b) N_2 adsorption-desorption isotherms as well as the corresponding mesopore size distributions of the macropore surfaces for the samples treated in 0.1 M H_3PO_4 aq. at 60 ºC for varied treating time.

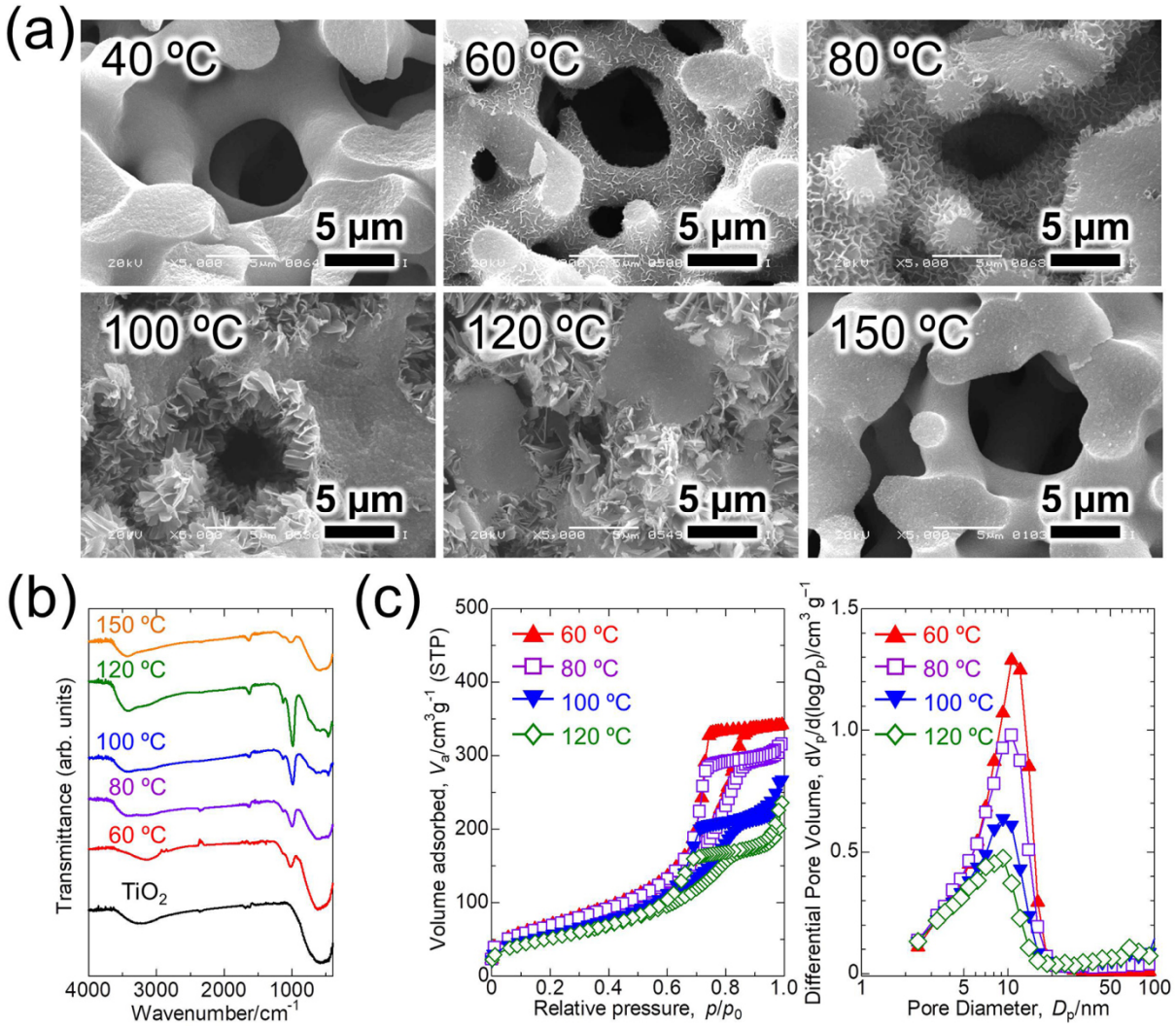

Figure S2 (a) SEM images, (b) FT-IR spectra and (c) N_2 adsorption-desorption isotherms as well as the corresponding mesopore size distributions of the macropore surfaces for the samples treated in 0.1 M H_3PO_4 aq. at different temperatures for 24 h. No wrinkled objects were observed when the temperature was 150 ºC. The treatment at 180 ºC gave the same result.

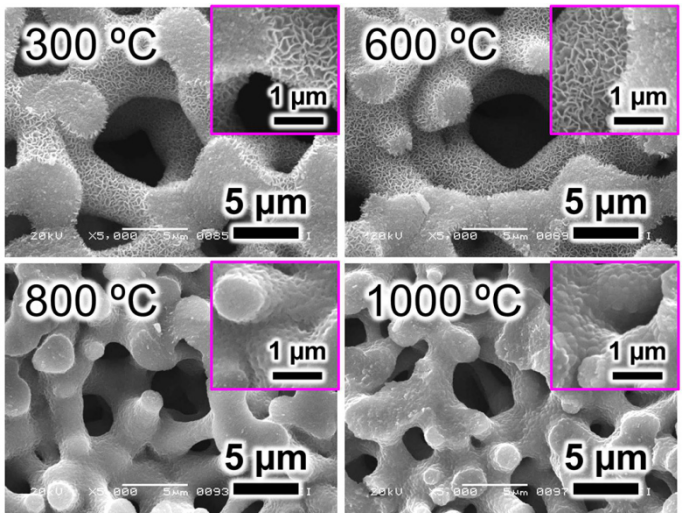

Figure S3 Change in microscopic morphologies of the titania monoliths treated in 1 M H_3PO_4 aq. at 60 ºC for 24 h through the calcination at different temperatures. The winkled texture on the macropore surface was vanished after the calcination above 800 ºC.

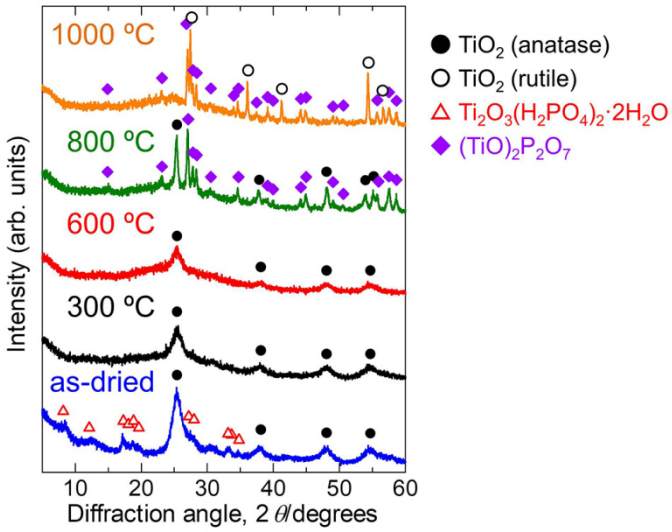

Figure S4 XRD patterns of the titania monoliths treated in 1 M H_3PO_4 aq. at 60 ºC for 24 h before and after the calcination at different temperatures.

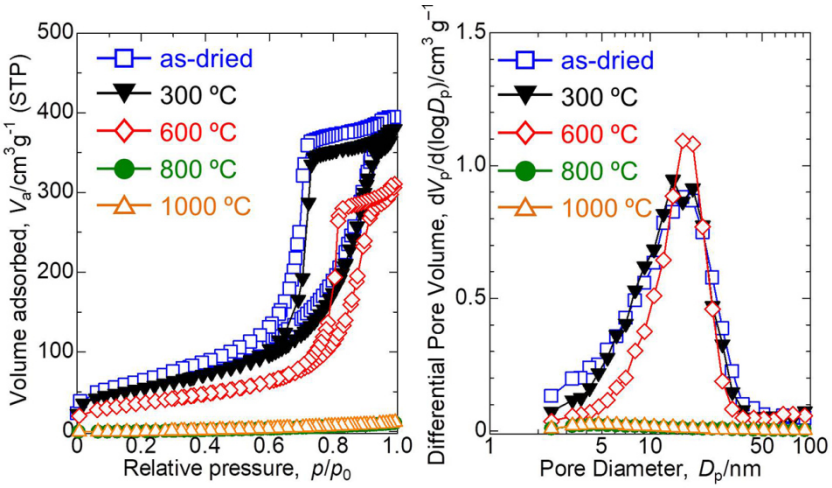

Figure S5 N_2 adsorption-desorption isotherms and the corresponding mesopore size distributions of the titania monoliths treated in 1 M H_3PO_4 aq. at 60 ºC for 24 h before and after the calcination at different temperatures.

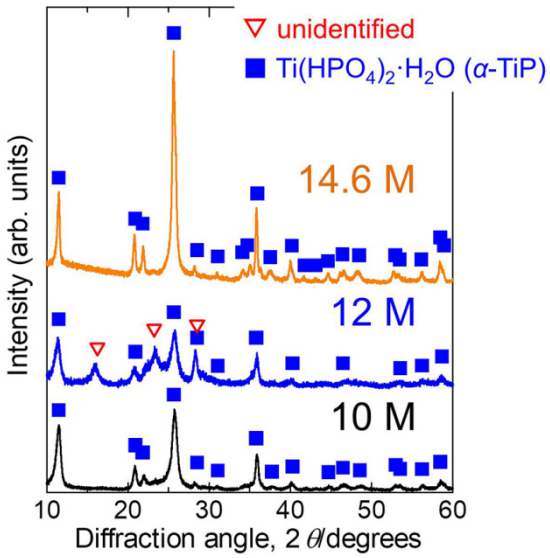

Figure S6 XRD patterns of the samples treated in different concentrations of H_3PO_4 aq. at 80 ºC for 4 h. Before heating, each sample was immersed in the corresponding H_3PO_4 aq. at room temperature for 12 h.

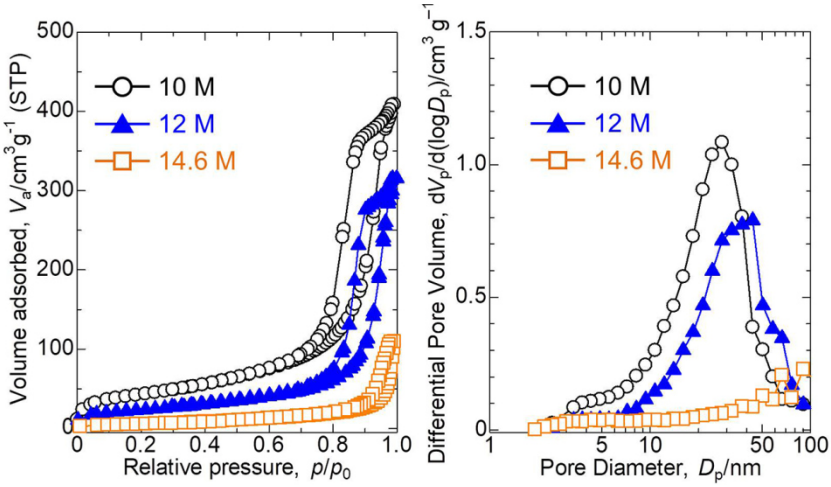

Figure S7 N_2 adsorption-desorption isotherms and mesopore size distributions of the samples treated in different concentrations of H_3PO_4 aq. at 80 ºC for 4 h.

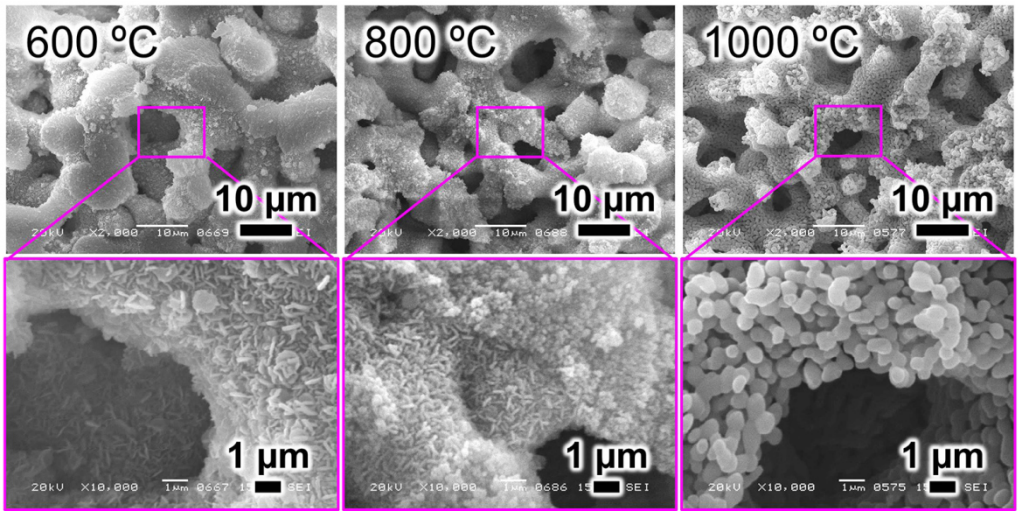

Figure S8 Change in microscopic morphologies of the samples treated in 12 M H_3PO_4 aq. at 80 ºC for 4 h through the calcination at different temperatures.

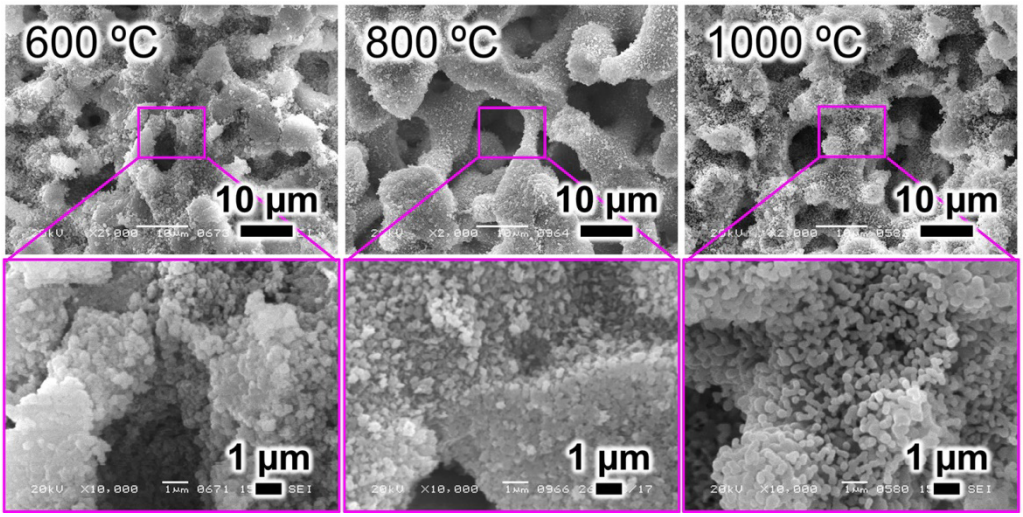

Figure S9 Change in microscopic morphologies of the samples treated in 14.6 M H_3PO_4 aq. at 80 ºC for 4 h through the calcination at different temperatures.

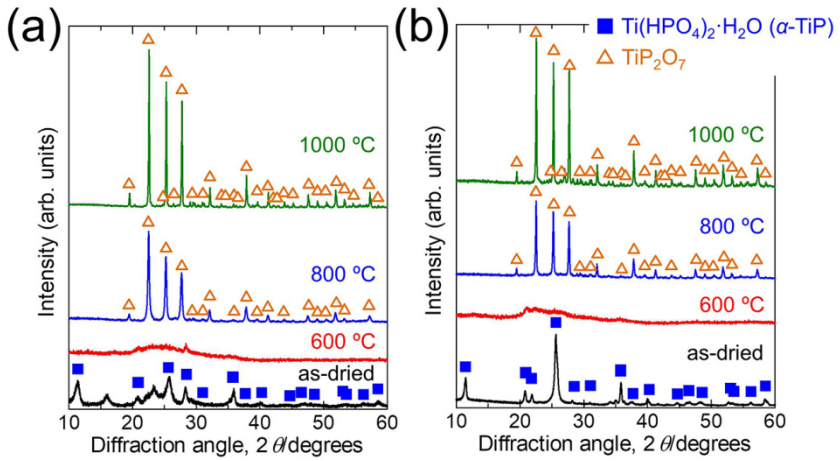

Figure S10 XRD patterns of the calcined samples obtained by calcining the phosphated titania monoliths treated in high concentrations of H_3PO_4 aq. at 80 ºC for 4 h through the calcination at different temperatures: (a) 12 M and (b) 14.6 M.

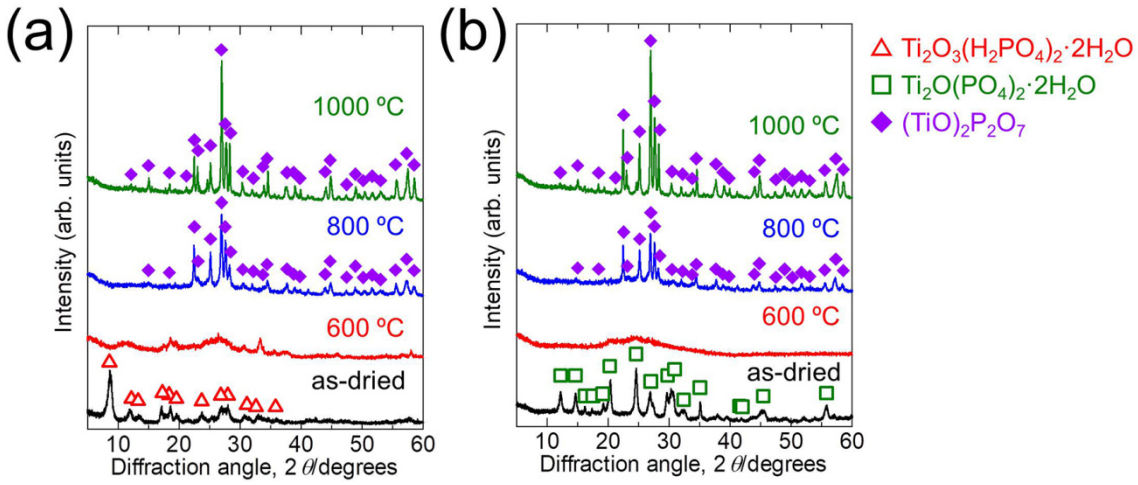

Figure S11 XRD patterns of the calcined samples obtained by calcining the phosphated titania monoliths treated under different hydrothermal conditions at different temperatures: 0.8 M H_3PO_4 aq. at 150 ºC for 24 h and 2 M H_3PO_4 aq. at 180 ºC for 72 h.

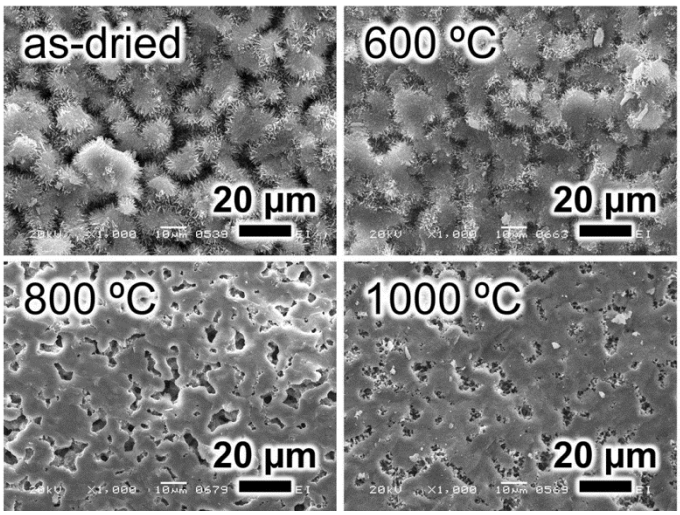

Figure S12 Change in microscopic morphologies of the samples treated in 0.8 M H_3PO_4 aq. at 150 ºC for 24 h through the calcination at different temperatures.

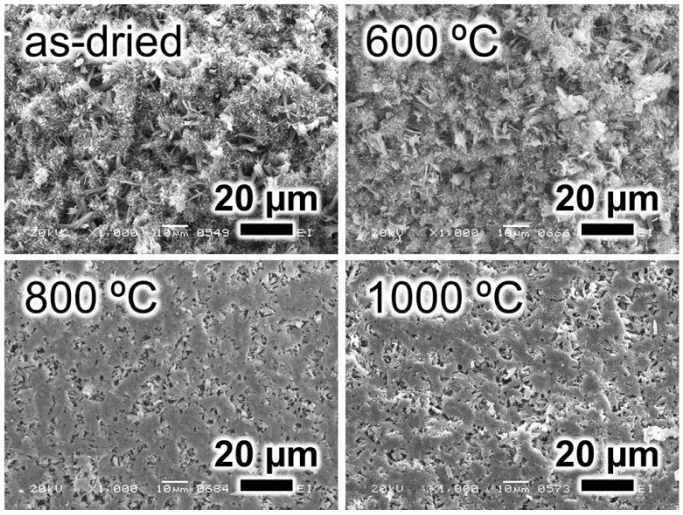

Figure S13 Change in microscopic morphologies of the samples treated in 2 M H_3PO_4 aq. at 180 ºC for 72 h through the calcination at different temperatures.

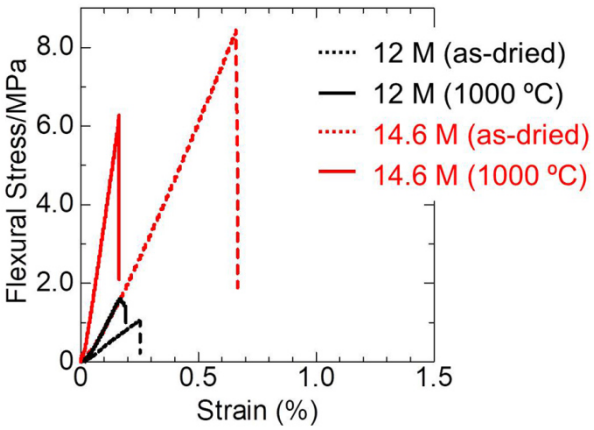

Figure S14 Flexural stress–strain curves for the representative α-TiP and TiP_2O_7 monoliths by a short-beam three-point bending test.

Table S1 Summary of pore characteristics of the samples treated in H_3PO_4 aq. under different conditions measured by N_2 physisorption.

$C_{\text{phosphoric acid}}$ [a] /M	$T_{\text{phosphoric acid}}$ [b] /ºC	$t_{\text{phosphoric acid}}$ [c] /h	S_{BET} [d] /$m^2\ g^{-1}$	$V_{\text{micro-meso}}$ [e] /$cm^3\ g^{-1}$	D_p [f] /nm
–	–	–	245	0.24	4.8
0.1	60	24	254	0.53	11
0.1	60	72	250	0.46	11
0.1	60	168	226	0.43	11
0.1	80	24	249	0.49	11
0.1	100	24	208	0.40	9.2
0.1	120	24	188	0.36	9.2
0.1	150	24	223	0.38	11
0.8	150	24	86	0.37	–
1	60	24	233	0.61	16
2	180	72	31	0.16	–
3	60	24	199	0.53	18
4	60	24	139	0.53	44
10	80	4	153	0.62	28
12	80	4	82	0.47	44
14.6	80	4	22	0.16	–

[a] Concentration of H_3PO_4 aq. [b] Treatment temperature. [c] Reaction time. [d] Specific surface area obtained by the BET method. [e] Micro- and mesopore volume obtained from the nitrogen adsorption isotherms at $p/p_0 = 0.99$. [f] Mean mesopore diameter obtained by the BJH method.