Electronic Supplementary Information (ESI) available:

Functionalized periodic mesoporous titanium phosphonate monoliths with large ion exchange capacity

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Experimental Section

Materials. Titanium tetrachloride ($TiCl_4$), pyridine (C_5H_5N) and chlorosulfonic acid ($ClSO_3H$) were obtained from Tianjin Kermel Chemical Co. 1-hydroxy ethylidene-1,1-diphosphonic acid (HEDP) was donated from Henan Qingyuan Chemical Co. Brij 56 ($C_{16}EO_{10}$) were obtained from Nanjing Well Chemical Corp., Ltd. All chemicals were used as received without further purification.

Synthesis of periodic mesoporous titanium phosphonate monoliths. In a typical synthesis procedure, 5.5 g of Brij 56 and 0.005 mol of HEDP were added into a mixed solution of 15 ml of deionised water and 45 ml of ethanol under vigorous stirring, followed by dropwise addition of $TiCl_4$ (P/Ti molar ratio: 4/3) very slowly. The reactor was kept in a cryosel bath to slow down the hydrolysis of $TiCl_4$ and the pH value was adjusted by ammonia and HCl solution to be around ca. 4.0 though the entire process. A homogenous solution was obtained after another 2 hours of stirring. The obtained mixture was sealed in one Teflon-lined autoclave and crystallized statically at 120ºC under autogenous pressure for 48 hours. A transparent viscous liquid was formed after the crystallization, followed by the evaporating of solvent under 50ºC, similar to the evaporation-induced self-assembly (EISA) method, in molds with different shapes, to give the white gel blocks. The gel blocks were dried at 110ºC and transferred carefully to a Soxhlet reactor to remove the surfactant by ethonal for 24 hours, and the final yellowy monolithic products were marked as PMTP-2.

Characterization. Transmission electron microscopy (TEM) was carried out on a Philips Tecnai G20 at 200 kV. Fourier transform infrared (FT-IR) spectra were measured on a Bruker VECTOR 22 spectrometer with KBr pellet technique, and the ranges of spectrograms were 4000 to 400 cm^{-1}. X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-2500 diffractometer with CuKα radiation operated at 40 kV and 100 mA. Thermogravimetry (TG) and differential scanning calorimetry (DSC) were performed using a TA SDT Q600 instrument at a heating rate of 5 °/min using α-Al_2O_3 as the reference. The chemical compositions of Ti, P and S were analyzed by inductively coupled plasma (ICP) emission spectroscopy on a Thermo Jarrell-Ash ICP-9000 (N+M) spectrometer, and C, N and H were analyzed on a Vario-EL elemental analyzer. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Axis Ultra DLD (delay line detector) spectrometer equipped with a monochromatic Al-K_α X-ray source (1486.6 eV). All XPS spectra were recorded using an aperture slot of 300 x 700 microns, survey spectra were recorded with a pass energy of 160 eV, and high resolution spectra with a pass energy of 40 eV. Solid-state ^{31}P and ^{13}C magic angle spinning (MAS) nuclear magnetic resonance (NMR) measurement was performed on a Varian Unity plus-400 spectrometer at spinning rate of 12 and 6 kHz and resonance frequence of 161.9 and 100.5 MHz with recycle time of 5 and 3 s, respectively. N_2 adsorption-desorption isotherms were recorded on a Quantachrome NOVA 2000e sorption analyzer at liquid nitrogen temperature (77 K). The samples were degassed at 150 ºC overnight prior to the measurement. The surface areas were calculated by the multi-point Brunauer-Emmett-Teller (BET) method.

Sulfation of PMTP-2. The PMTP-2 sample was immersed in the mixed solution of anhydrous pyridine and $ClSO_3H$ (v/v = 1:1), which was previously cooled to 0~4 ºC. Then the sulfation reaction was lasted for about 5 hours without cooling until the solution reached the room temperature. The sample was collected through filtration and was Soxhlet-extracted with water again to remove the unreacted $ClSO_3H$, marked as PMTP-2s. The ion exchange capacity was determined from the titration curve. The esterified PMTP-2s (50 mg) was immersed in 10 wt% sodium chloride aqueous solution for 24 hours. The solution was titrated with 0.05 mol/L NaOH to produce the titration curve. Differential titration curve was drawn to determine the ion exchange capacity of PMTP-2s at the inflexion. Unfunctionalized PMTP-2 was also titrated to confirm the contribution from only titanium phosphonate framework. Acid strength of the samples was determined by the Hammett indicator method, using anthraquinone (pK_a = -8.20), *p*-nitrotoluene (pK_a = -11.35), *p*-nitrochlorobenzene (pK_a = -12.70), and 2,4-dinitrotoluene (pK_a = -13.75) as indicators and dichlorosulfoxide or cyclohexane as the solvent (8% indicator).

Catalytic activity. The esterification of oleic acid with methanol, catalyzed by the acid catalysts, was carried out under atmospheric pressure in a 250 ml three-necked flask. The oleic acid, methanol and catalysts were added with the fixed ratio. The mixture was heated to various temperatures under stirring, and the time was started. At given time intervals, about 5 ml of liquor was sampled. The acid value of the product in the oil phase was titrated using phenolphthalein as the indicator, and the conversion of oleic acid was determined by the acid value difference. In this preliminary experiment, 20 ml of methanol, 5 ml of oleic and 1.0 g of catalyst were added, and the reaction was carried out at 75 ºC. Sulfonated mesoporous TiO_2 was also tested as comparison, which was of the similar surface area and S content and also prepared using $ClSO_3H$.

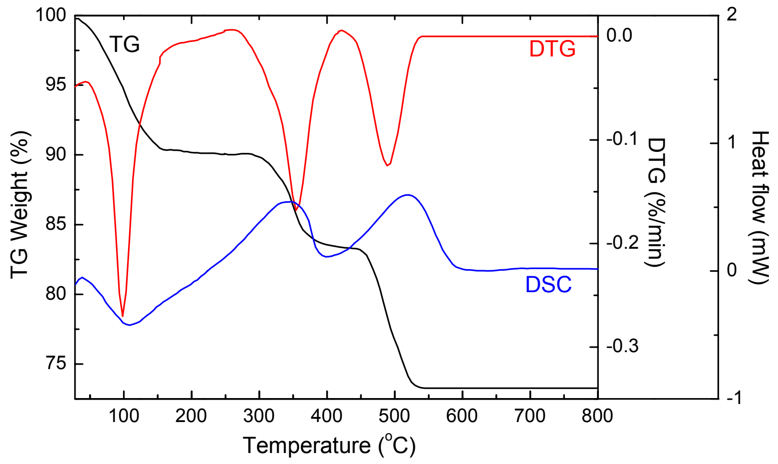

Fig. S1 TG-DSC profiles of the as-synthesized PMTP-2 solid before surfactant removal.

The thermal stability of the synthesized hybrids was determined by the thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Fig. S1). The TGA curves demonstrate initial weight loss of 9.6% from room-temperature to 160ºC, accompanying with an endothermal peak around 98ºC in the DSC curve, which may be assigned to the desorption of the adsorbed and intercalated water. The weight loss of 8.3% from 260 to 410ºC, accompanied with an exothermic peak at around 355ºC, can be attributed to the decomposition of the surfactant and the combustion of carbon species. The third weight loss of 9.9% from 460 to 540ºC, accompanied with an exothermic peak at around 522ºC, can be related to the decomposition of the organic groups in the framework, leaving purely inorganic titanium phosphate network. The TG-DSC analysis confirms that the PMTP-2 materials are thermally stable up to 450ºC. The ICP emission spectroscopy was employed to analyse chemical compositions of the resultant solids (18.43% Ti, 15.82% P in mass), revealing the P/Ti molar ratios approximate to 4:3 in the sample. Combined with the conventional elemental analysis of C and H (6.13% C, 3.23% H in mass), the PMTP-2 sample could be formulated as follows: $Ti_3(O_3PC(CH_3)(OH)PO_3)_{1.99}\cdot xH_2O$ and alternative formulation can be expressed as $Ti_3(HEDP)_2\cdot xH_2O$.

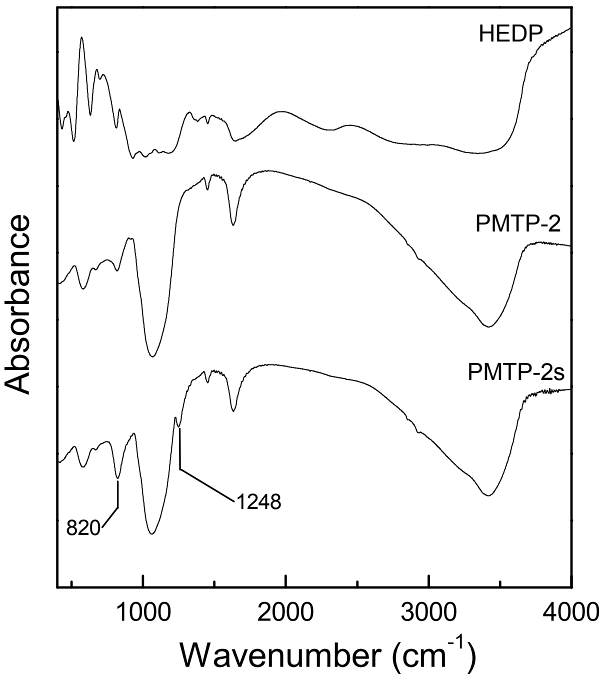

Fig. S2 The FT-IR spectra of the phosphonic acid HEDP, PMTP-2 and sulfated PMTP-2s.

The skeletal structure and surface chemistry of the samples were investigated by the infrared spectroscopy and NMR measurement. The IR spectrum of the PMTP-2, PMTP-2s and HEDP were shown in Fig. S2. The strong broad band at 3400 cm^{-1} and the sharp band at 1630 cm^{-1} correspond to the surface-adsorbed water and hydroxyl groups. The strong band at 1052 cm^{-1} is due to phosphonate P–O···Ti stretching vibrations. The band at 1460 is assigned as the P-C stretching vibration [T. Y. Ma, et al, *J. Phys. Chem. C,* 2008, **112**, 3090.]. The band at 927 cm^{-1} in the spectrum of HEDP, assigned to P–OH stretching vibrations, was not observed in PMTP-2, which implies the extensive condensation and coordination of the phosphoryl oxygen with the titanium atom, leading to mainly bidentate phosphonate units [T. Y. Ma, et al, *J. Phys. Chem. C,* 2008, **112**, 3090.].

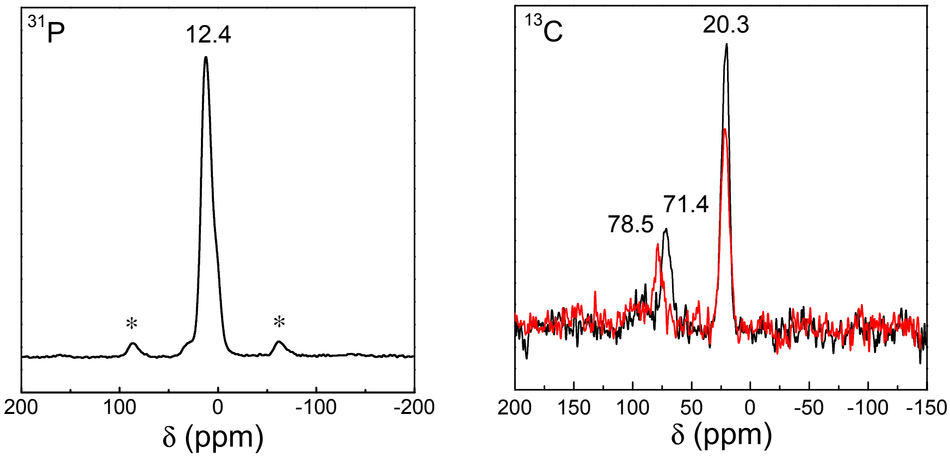

Fig. S3 ^{31}P and ^{13}C MAS NMR spectra of synthesized PMTP-2 material (^{13}C MAS NMR spectrum of PMTP-2s was also shown by red line).

The ^{31}P and ^{13}C MAS NMR spectra of the PMTP-2 sample are shown in Fig. S3. The ^{31}P MAS NMR spectrum of PMTP-2 shows one broad signal around 12.0 ppm, which is characteristic of phosphonates [T. Kimura, *Chem. Mater.,* 2005, **17**, 5521.]. And the broadening of the resonance signal is due to the disordered or low-crystalline nature of solids. These are quite similar to chemical shifts found for diphosphonate groups (≡P-CH_2-P≡) in mesoprous aluminum phosphonates [T. Kimura, *Chem. Mater.,* 2005, **17**, 5521.]. No sharp ^{31}P NMR resonance signal at -4 ppm was observed, indicating that a layered titanium phosphonate phase was not presented in the synthesized mesoporous titanium phosphonates [T. Y. Ma, et al, *J. Phys. Chem. C,* 2008, **112**, 3090.], which is further supported by the TEM observation and IR spectroscopy. ^{13}C MAS NMR spectrum of the sample exhibits the resonances at 20.3 and 71.4 ppm (Fig. S3), which correspond to the C atoms of the terminal CH_3 group and the quaternary carbon atom connected with the P=O group of the phosphonate, respectively. These suggest that no phase separation took place during the preparation of the hybrid samples, and HEDP coupling groups were dispersed homogeneously within the hybrid network.

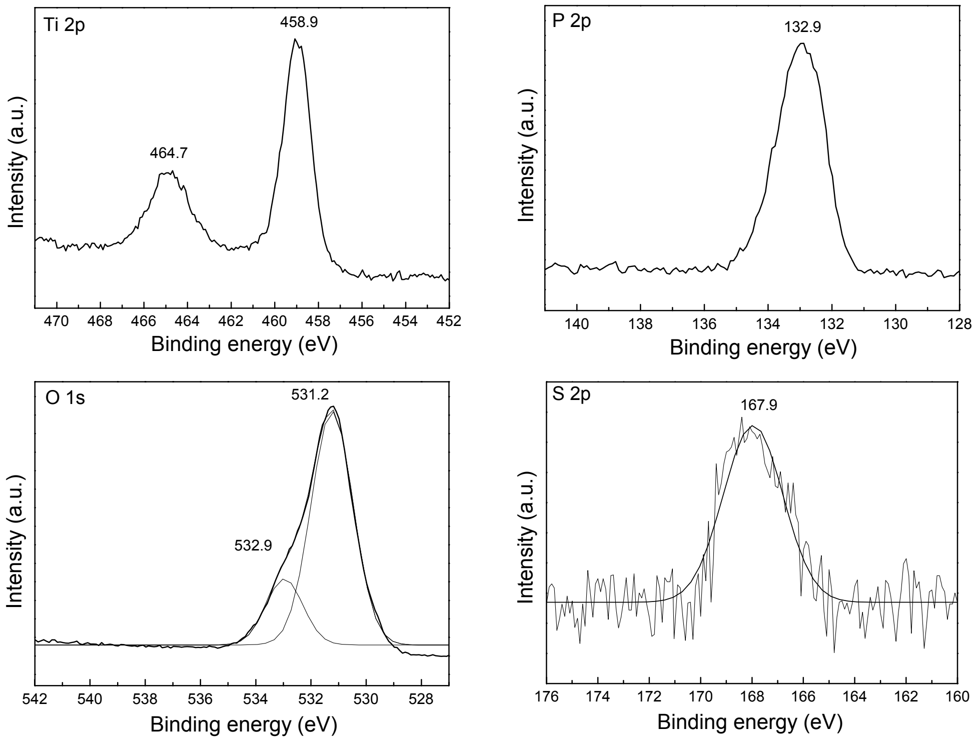

Fig. S4 High-resolution XPS spectra of the Ti 2p, P 2p, O 1s and S 2p regions of PMTP-2s sample.

High-resolution XPS spectra were also taken on the surface of PMTP-2s sample for the investigation of chemical state and surface stoichiometry (Fig. S4). The surface atomic composition of the materials was calculated to be 9.93% Ti, 13.45% P, 14.15% C, 59.93% O and 2.54% S for PMTP-2s. The surface Ti/P ratio was calculated to be 1.35, approximate to 4:3, suggesting compositional homogeneity throughout the hybrid material. The Ti 2p line of PMTP-2s sample is composed of two single peaks situated at 458.9 eV for Ti 2p$_{3/2}$ and 464.7 eV for Ti 2p$_{1/2}$. Compared with the binding energy of pure TiO$_2$ (459 eV for Ti2p$_{3/2}$ and 464.8 eV for Ti2p$_{1/2}$), the binding energy of main Ti 2p decreases in the titanium phosphonate hybrid, which is the result from the organophosphonate incorporation in the titania network [T. Y. Ma, et al, *J. Phys. Chem. C,* 2008, **112**, 3090.]. The P 2p binding energy of PMTP-2s is observed at 132.9 eV, which is characteristic of P^{5+} in phosphonate groups. No peaks of Ti-P bonds appear at 128.6 eV [T. Y. Ma, et al, *J. Phys. Chem. C,* 2008, **112**, 3090.]. The broad O 1s signals at 531.2 eV with a shoulder around 532.9 eV are ascribed to the oxygen co-contributed from Ti-O, P-O, P=O, S=O and O-S bonds respectively. The S 2p binding energy is observed at 167.9 eV corresponding to SO_3^- [R. Molina, et al, *Appl. Surf. Sci.*, 2005, **252**, 1417.], which also indicated the successful sulfation of PMTP-2.

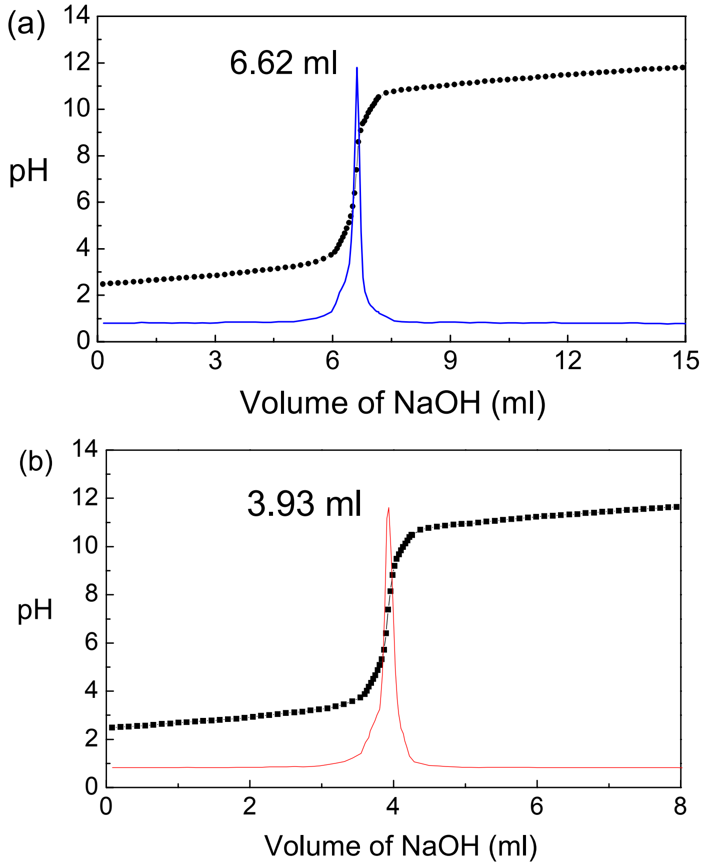

Fig. S5 (a) Titration curve and differential titration curve (blue line) of sulfated PMTP-2s material; and (b) titration curve and differential titration curve (red line) of unfunctionalized PMTP-2 material.

The ion exchange capacity or acid content of the sulfated PMTP-2s and unfunctionalized PMTP-2 was determined from the titration curve by 0.05 mol/L NaOH (Experimental section) and elemental analysis. The consumed NaOH amounted to 6.62 and 3.93 mmol/g for PMTP-2s and PMTP-2, respectively (Fig. S5), which are the total contribution of sulfonic groups and titanium phosphonate framework and single contribution of titanium phosphonate framework. Only one peak was observed in Fig. S5a, probablely because the PMTP-2s was immersed in 10 wt% sodium chloride aqueous solution for such a long period (24 hours) that the two kinds of protons were totally exchanged into the solution. ICP and conventional elemental analysis gave the following results: 13.89% of Ti and 11.92% of P in mass, remaining the P/Ti molar ratios approximate to 4:3, and

4.62% of C, 4.31% of H in mass. 8.63 wt.% of S content was also confirmed by ICP analysis, suggesting around 2.69 mmol/g of H^+ was attributed to sulfonic groups, and 3.93 mmol/g of H^+ was attributed to the titanium phosphonate framework, which was due to defective P-OH groups [*J. Am. Chem. Soc.* **2001,** *123,* 691.], consistent to the titration results. Thus the sulfation process leads to an obvious increasing of the ion exchange capacity compared to the unfunctionalized sample (PMTP-2) and the reported titanium phosphate materials [*J. Am. Chem. Soc.* **2001,** *123,* 691.]. Moreover, as we could see in Table S1 (ESI), even if the ion exchange capacity of PMTP-2 (from defective P-OH groups in phosphonate framework) was around 3.93 mmol/g, the acid strength was still very low, indicating that defective P-OH groups act as weaker Brønsted acid sites than the -SO_3H groups, which were considered to mainly contribute to the acid catalysis performance. In conclusion, the sulfation of PMTP-2 could lead to the obvious increasing of the ion exchange capacity and catalytic activity of the material.

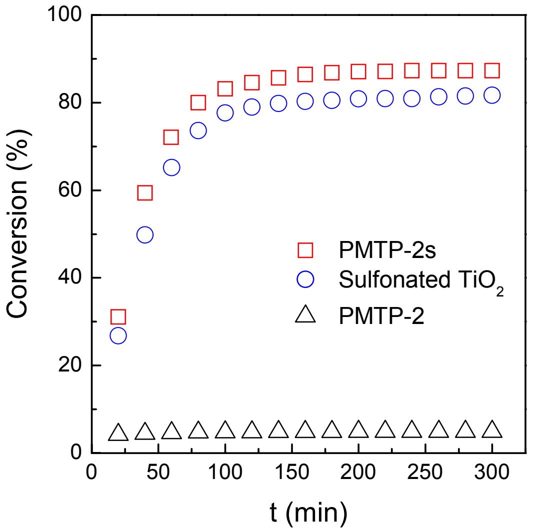

Fig. S6. The conversion profiles of oleic acid in the esterification reaction of oleic acid with methanol, catalyzed by the prepared acid catalysts.

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Table S1. Hammett acidities of the PMTP-2s sample.

	PMTP-2	PMTP-2s					
Hammett indicators		Room[a]	50ºC[b]	60ºC	70ºC	80ºC	85ºC
anthraquinone ($pK_a = -8.20$)	—	+	+	+	+	+	—
p-nitrotoluene ($pK_a = -11.35$)	—	+	+	+	+	+	—
p-nitrochlorobenzene ($pK_a = -12.70$)	—	—	—	—	—	—	—
2,4-dinitrotoluene ($pK_a = -13.75$)	—	—	—	—	—	—	—

[a] as-prepared PMTP-2s sample; [b] PMTP-2s sample treated at 50ºC in water for 2 hours in advance.

The acid strength of the materials is examined by the Hammett indicator method, and the results are listed in Table S1, in which the mark (+) indicates that the color of the base form is changed to that of the conjugated acid form, while the mark (—) means the color is not changed. Acids stronger than $H_0 = -11.93$, which corresponds to the acid strength of 100% H_2SO_4, are superacids [L. Forni, *Catal. Rev.,* 1973, **8**, 65.]. The PMTP-2s sample was estimated to have $H_0 < -11.35$, indicating it was a kind of strong solid acid. Moreover, the strong acidity could be preserved even after treated at 80ºC, suggested that the hydrosulfated groups could be kept at pore walls even in hot waters.

Moreover, as we could see in this table, even if the ion exchange capacity of PMTP-2 (from defective P-OH groups in phosphonate framework) was around 3.93 mmol/g, the acid strength was still very low, indicating that defective P-OH groups act as weaker Brønsted acid sites than the $-SO_3H$ groups, which were considered to mainly contribute to the acid catalysis performance.