Electronic supplementary information:

Preparation of crystal TiO_2 foam with micron channels and mesopores by freeze-casting method without additives and unidirectional freezing

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1. XRD Pattern of as synthesized TiO_2 NPs before and after Annealing

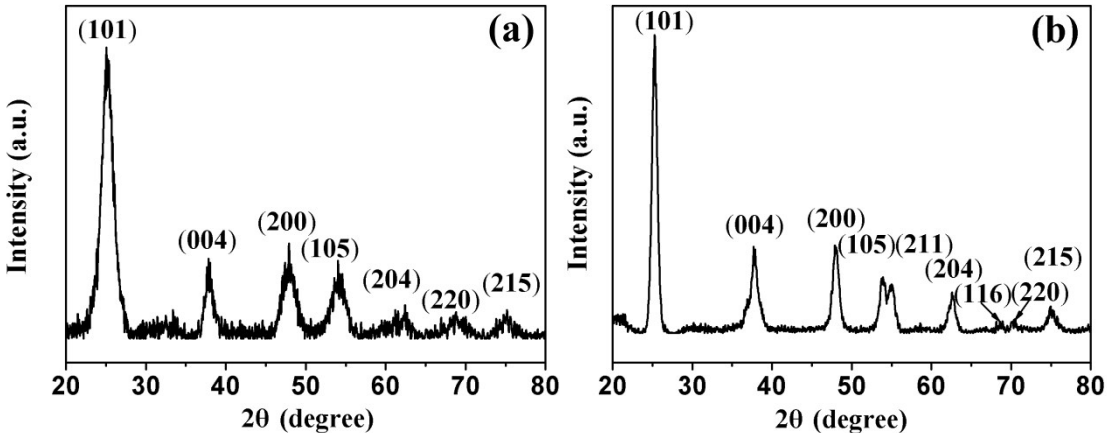

Figure S1. XRD pattern of TiO_2 NPs (a) before and (b) after annealing.

2. XPS spectra of as synthesized TiO_2 nanoparticles

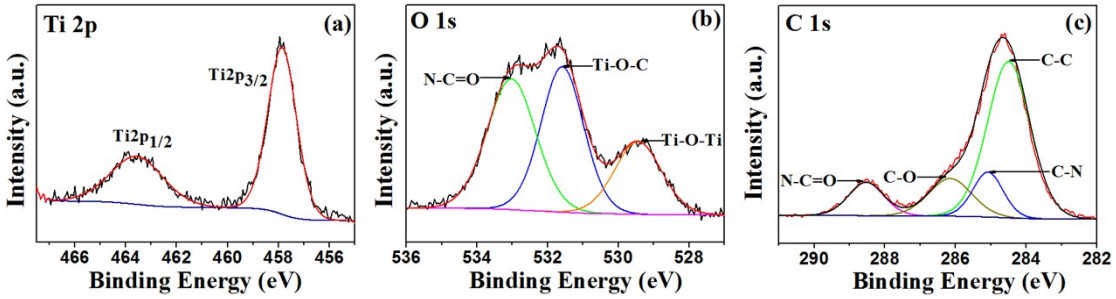

Figure S2. High-resolution XPS spectra of elements of TiO_2 nanoparticles: (a) Ti 2p, (b) O 1s, (c) C 1s.

3. Determination of packing density of ligand on TiO_2 by themogravimetric analysis

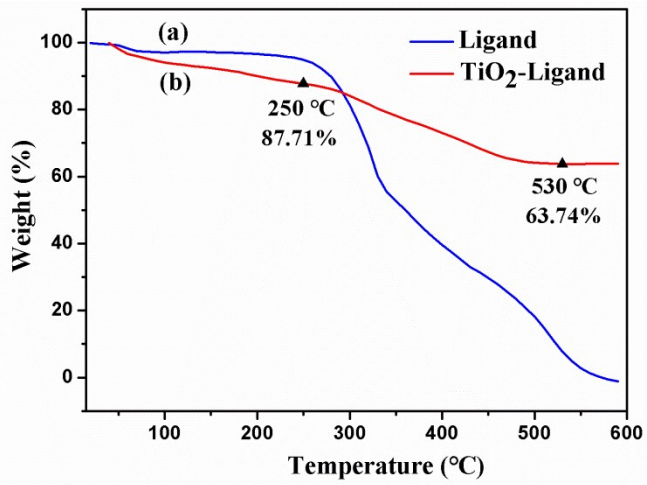

Figure S3. TGA curve of (a) ligand and (b) TiO_2-ligand nanoparticles.

The packing density of the TiO_2 foam has been studied by thermogravimetric analysis (TGA) measurements (Figure S3). It can be seen that the ligand begin to combust at 250 ˚C and burn out at about 600 ˚C. For the TGA curve of nanoparticles with ligands, there are obvious weight loss between 250 ˚C and 530 ˚C, which must be attributed to the combustion of ligand. Therefore, the mass of ligand in the sample (1.133 mg) is 4.728 × (87.71 % - 63.74 %) = 1.133 mg.

In order to calculate the packing density, the shape of the TiO_2-ligand nanoparticles was assumed to be perfectly spherical with a diameter of 4.4 nm (see the TEM images of Figure 1b in main text) and the total surface area of 4.728 mg TiO_2-ligand nanoparticles was evaluated by the following process:

Surface area of a single TiO_2 particle (S_0) = $4\pi r^2$ = 60.79 nm^2

Volume of a single particle (V_0) = $\frac{4}{3}\pi r^3$ = 44.58 nm^3

The bulk density of TiO_2 (ρ) is 3.84 g/cm^3, therefore, the mass of a single TiO_2 particle (M_0) is: $M_0 = V_0\rho = 1.71 \times 10^{-19}$ g

The mass of particles in the sample (3.014 mg) is 4.728 × 63.74% = 3.014 mg

The total number of particles (N) in the sample is:

$$N = \frac{3.014\ mg}{M_0} = 1.76 \times 10^{16}$$

Total surface area of 3.014 mg TiO_2 particles (S) = N S_0 = 1.07×10^{18} nm^2

The total mass of ligand is 1.133 mg and the molar mass of ligand is 840 g/mol, so the numbers of attached ligand molecule are calculated by $\frac{1.133\ mg}{840\ g/mol} N_A =$ 8.12×10^{17} ($N_A \approx 6.02 \times 10^{23}$)

So, the packing density can be calculated by:

$$\frac{the\ numbes\ of\ attached\ ligand\ molecules}{the\ total\ surface\ area\ of\ particles} =$$ 0.76 molecules/nm^2

4. FESEM images and EDX spectra of skeleton of foam before and after annealing

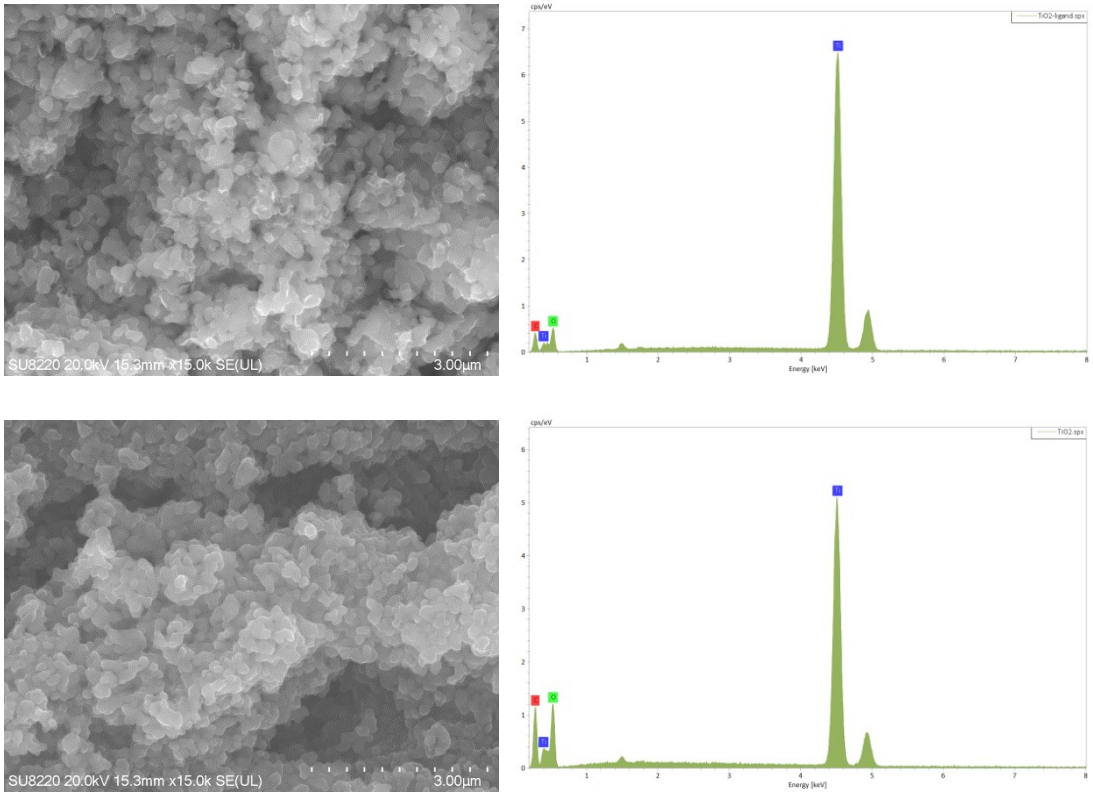

Figure S4. FESEM images and EDX spectra of backbone of TiO_2 foam before (up) and after (down) annealing.

5. SEM images of froze samples dried with supercritical CO_2 and also by solvent evaporation at room temperature

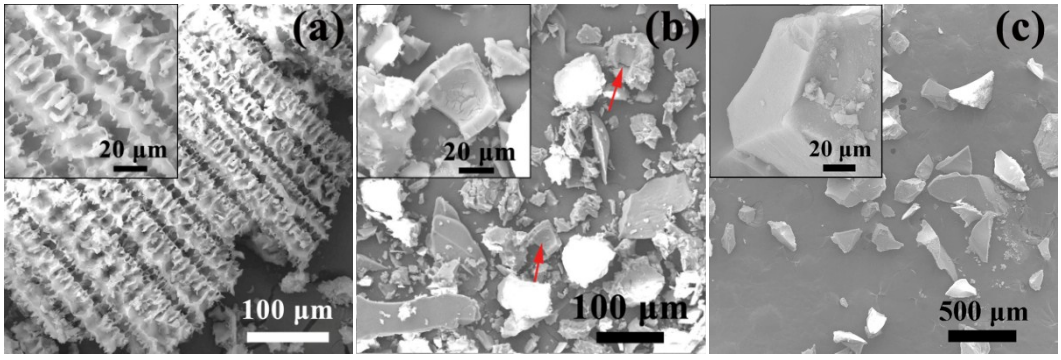

Figure S5. SEM images of froze samples dried by (a) supercritical CO_2 or (b) solvent evaporation at room temperature, (c) SEM image of sample dried by supercritical CO_2 directly without freezing.

Contrastingly, two concentrated suspensions were frozen in liquid nitrogen for 30 min and dried with supercritical CO_2 (sample a) and also by solvent evaporation at room temperature (sample b). On the other hand, another concentrated suspension was

dried with supercritical CO_2 directly without freezing (sample c). From the SEM images of sample frozen in liquid nitrogen and dried with supercritical CO_2, regular micrometer channels with width of 15 μm were observed (Figure S5a). For the sample dried by solvent evaporation at room temperature, although it was collapsed during evaporating benzene at 20 ˚C for 48 h, there were still a few fragments having micrometer pores and thick walls (red arrows in Figure S5b). This could be due to the fact that channels had been formed during liquid nitrogen freezing, but, most of them were collapsed, and only the channels with very thick walls were strong enough to offset the surface tension of benzene evaporation. In contrast to the sample (a), sample (c) did not freeze in liquid nitrogen and it was a serious volume shrinkage even dried by supercritical CO_2 and no micrometer-size channel or pore can be seen (Figure S5c) , indicating that there was no channel at all. From all the above results, it is clearly demonstrated that freezing in liquid nitrogen is an essential step for channels formation.

6. Morphology of samples prepared from naked TiO_2 particles and 2-bromo-n-(3, 4-dihydroxyphenethyl)-2-methylpropanamide-grafted TiO_2 in benzene

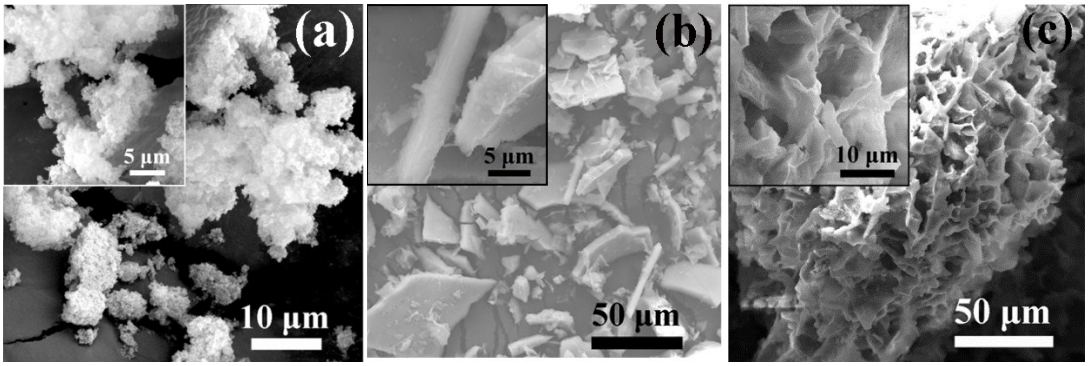

Figure S6. SEM images of samples obtained by centrifuging and freeze drying of suspension of (a) naked TiO_2 particles and (b, c) 2-bromo-N-(3, 4-dihydroxyphenethyl)-2-methylpropanamide-grafted TiO_2 in benzene.

7. Nitrogen physisorption isotherms for TiO_2 foam, the corresponding TiO_2 powders and P25 powders

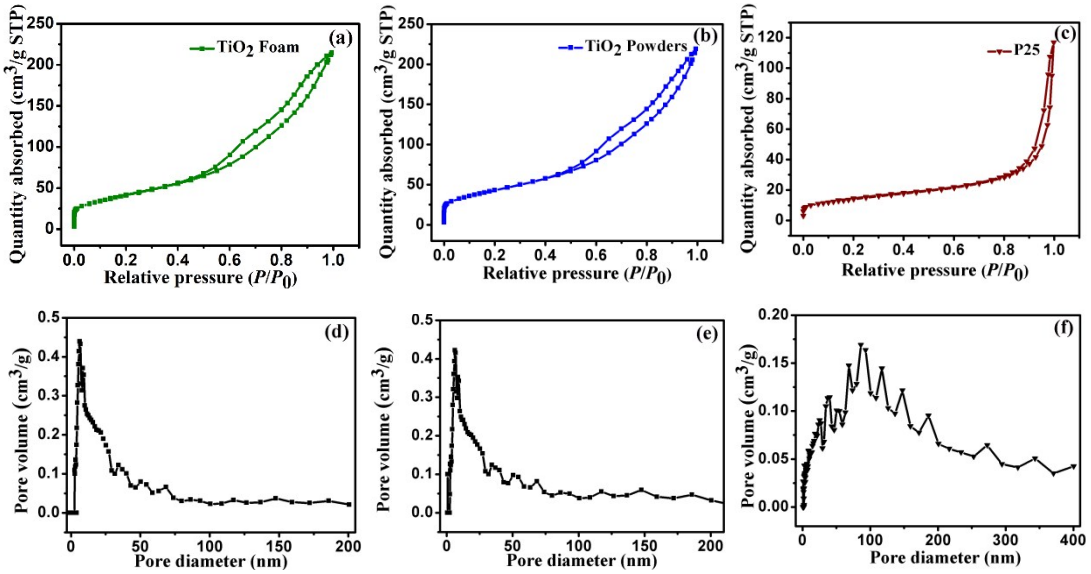

Figure S7. Nitrogen physisorption isotherms and the corresponding pore-size distributions for TiO_2 foam (a) (d), TiO_2 Powders (b) (e), and P25 (c) (f).

The nitrogen adsorption-desorption isotherms of TiO_2 foam (Figure S7a) and TiO_2 powders (Figure S7b) imply that both of them possess a typical mesoporous structure and that pore size distribution mainly lies in 3-30 nm range. The similar BET specific

surface areas of TiO_2 powders (157 m^2/g) and TiO_2 foam (150 m^2/g) further confirm that the micron channels are beneficial for mass transportation. In comparison, as shown in Figure S7c, the BET specific surface area of P25 powders is 50 m^2/g, which only reaches 33% of that of the TiO_2 foam or TiO_2 powders.