Supplementary Material (ESI) for Chemical Communications

Bioinspired synthesis of hierarchically macro-mesoporous titania with tunable macroporous morphology using cells-assembly as macrotemplates

Xiaohong Sun,[a] Chunming Zheng,[a] Jingjing Yan,[a] Xinping Wang[b] and Naijia Guan*[a]

[a] *Key Lab of Functional Polymer Materials, Department of Materials Chemistry, College of Chemistry, Nankai University, Tianjin 300071, PR China. Fax: 86 022 23509140; Tel: 86 022 23509140; E-mail: guannj@nankai.edu.cn*
[b] *College of Life Sciences, Nankai University, Tianjin 300071, PR China.*

Electronic Supplementary Information

Experimental Section:

Assembly of Cells and Preparation of Macro-Mesoporous Titania Materials:

Cells assembly with different cell shapes (spherical saccharomyces cerevisiae cells for sample A, baculiform stenotrophomonas acidaminiphila cells for sample B, filamentous grifola frondosa cells for sample C) were first fixed by glutaraldehyde and then vacuum freezing dried prior to use. For the sol-gel titania incorporation, cells assembly were dipped into a sol-gel of titanium tetraethoxide (TET), PEG 1500, ethanol, water and nitric acid with a molar ratio of 1: 0.02: 8.5: 0.8: 0.17 for 10 min. Then, the cells assembly were filtered under reduced pressure to remove redundant solution held in the assembly and held in air at room temperature for 24 h to complete the hydrolysis reaction. Finally, the obtained cells assembly-titania was heated at 500 ℃ in air for 4 h, resulting in the formation of macro-mesoporous titania materials.

Preparation of Mesoporous Titania Materials:

The mesoporous titania materials were synthesized using the similar procedure to the macro-mesoporous titania materials just without using the cells assembly as the macroporous template.

Preparation of Titania Nanoparticles

For the synthesis of titania nanoparticles, β-cyclodextrin (10 mmol) was dissolved in deionized water (180 mL) at a constant temperature of 60 ℃, and tetrabutyl titanate (100 mmol) was added dropwise with vigorous stirring. The pH of the solution was adjusted to 10 by adding sodium hydroxide. After homogenization for about 2 h, the mixture obtained was transferred into a teflon-lined autoclave (250 mL capacity) for crystallization at 150 ℃ for 48 h. The resulting precipitate was separated from the liquid phase by centrifugation and then washed with

N,N-dimethylformamide to remove the organic compounds remaining. The final product was dried at 80 ℃ overnight and appeared as a fine white powder.

Characterization:

SEM images were measured on a Shimadzu SS-550 instrument. X-ray powder diffraction (XRD) patterns of the samples were performed on a Rigaku D/max 2500 diffractometer with a graphite monochromator and Cu Kα radiation (λ = 0.154 nm). TEM measurements were performed on a Philips Tecnai F20 microscope. N2 adsorption and desorption isotherms were measured at 77 K on a Micromeritics TriStar 3000 apparatus. The samples were outgassed at 120 ℃ overnight before measurements were made. The surface area was obtained by the Brunauer-Emmett-Teller (BET) method and the pore size distribution was calculated from the adsorption branch of the isotherm.

The Titania Crystallite Size from the XRD Calculation and the Particle Size from the TEM Results:

The average crystallite sizes of the macro-mesoporous titania smaple B and mesoporous titania were estimated to be both about 10 nm from the XRD result (see Figure S1) using the Debye-Scherrer equation, $D = K\lambda/(\beta\cos\theta)$, where D is the average crystal diameter, β is the corrected peak width (full width at half maximum), K is a constant related the shape of the crystallites (K=0.94), λ is the wavelength of the X-rays employed, and θ is the diffraction angle. The width of the diffraction peak with the highest intensity was selected for the calculation. Figure 2S shows the clearer TEM image of the macro-mesoporous titania smaple B. The average particle size is also found about 10 nm based on the TEM image, which confirmed the obtained crystallite size from XRD calculation indirectly.

The Role of Glutaraldehyde:

Cells assembly with different cell shapes (spherical saccharomyces cerevisiae cells for sample A, baculiform stenotrophomonas acidaminiphila cells for sample B, filamentous grifola frondosa cells for sample C) were first fixed by glutaraldehyde and then vacuum freezing dried prior to use as the macrotemplates. The glutaraldehyde fixing procedure is the general approach to fix bacteria and cells. The aldehyde group on either end of glutaraldehyde forms Shiff bases (-CH=N-) with the amino groups of cell surface proteins during the fixing process. The use of glutaraldehyde will be possible to introduce the aldehyde group to the cells-assembly surface. In order to understand the role of glutaraldehyde in our case, we tried to synthesize the TiO_2 material with cells-assembly as macrotemplate without using glutaraldehyde fixing. Surprisingly we could also get the similar macroporous structures as using the glutaraldehyde fixing procedure (see SEM image in Figure S4). But since no glutaraldehyde fixing procedure, the macroporous structure seemed not reflect the structure of the starting cells very well because during the titanium precursor hydrolysis reaction, the shape of the cells without fixing did not maintain well. To conclude, glutaraldehyde is not necessary factor to obtain the macroporous

structure but an effective method to get the better one.

Measurement of Photocatalytic Activity:

The photocatalytic activity of the macro-mesoporous titania materials was determined by the comparison of the degradation capacities of methylene blue (MB) under UV irradiation at room temperature with mesoporous titania (without using cells assembly as macrotemplate) and nanopartilces anatase titania (with similar particle size of ca. 10 nm). MB aqueous solution (15 mg L^{-1}, 200 mL) and photocatalysts (5 mg) were mixed in a doublewalled 250 mL quartz reactor (equipped with magnetic stirrer and cooled by water) with a 125-W high-pressure Hg lamp (main wavelength around 365 nm) as a UV light source. The titania-MB suspension was firstly under ultrasonic processing for 5 min and allowed to equilibrate under stirring for 30 min in dark prior to each experiment. Each run of reactions was lasted for 75 min. During irradiation, a small part (ca. 5 mL) of the solution was withdrawn periodically, the catalyst was immediately separated by centrifugation, and the supernatant was analyzed to determine the residual MB concentration with an UV-vis spectrophotometer (Shimadzu, UV-240) in 664 nm.

XRD Patterns:

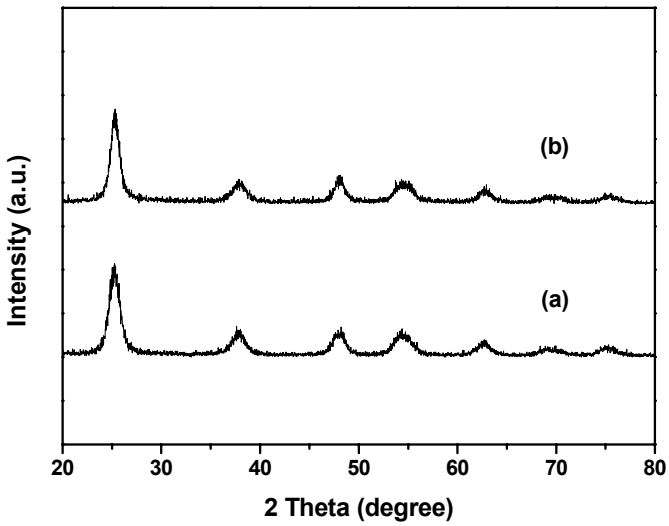


Figure S1. X-ray diffraction (XRD) patterns of the macro-mesoporous titania (a) and mesoporous titania without using the cells-assembly as macrotemplate (b).

TEM Image:

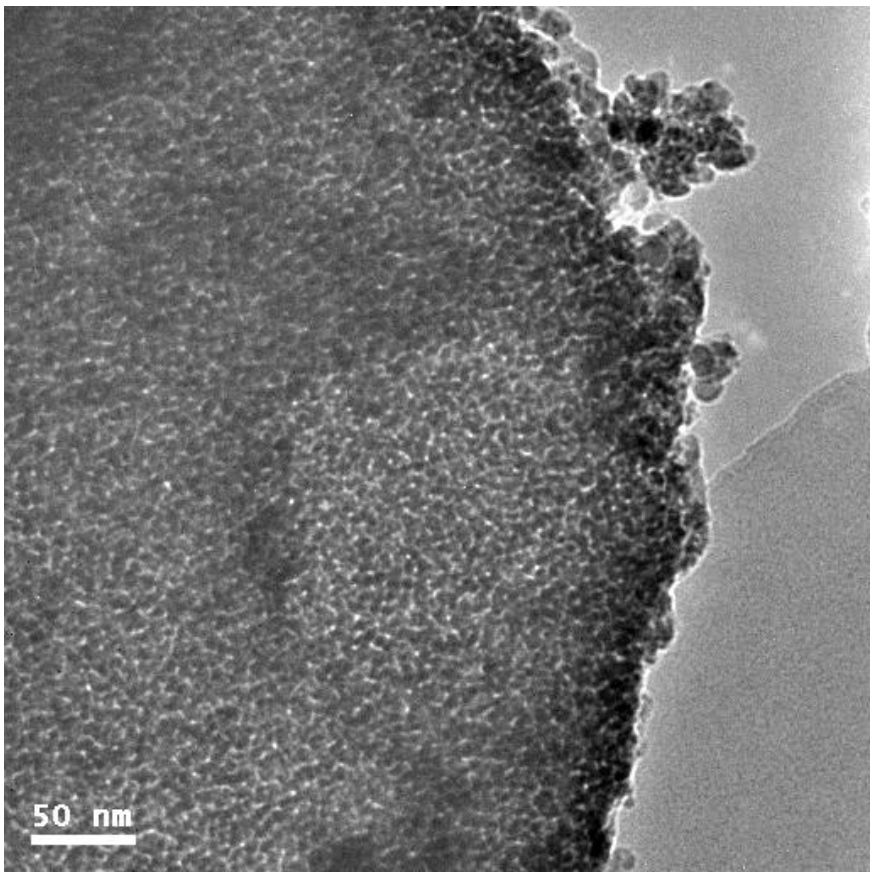
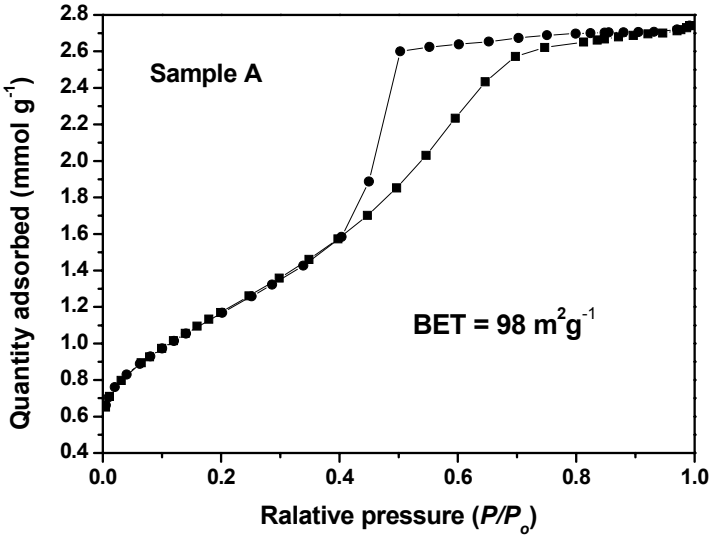


Figure S2. TEM image of the macro-mesoporous titania sample B.

BET Measurement:



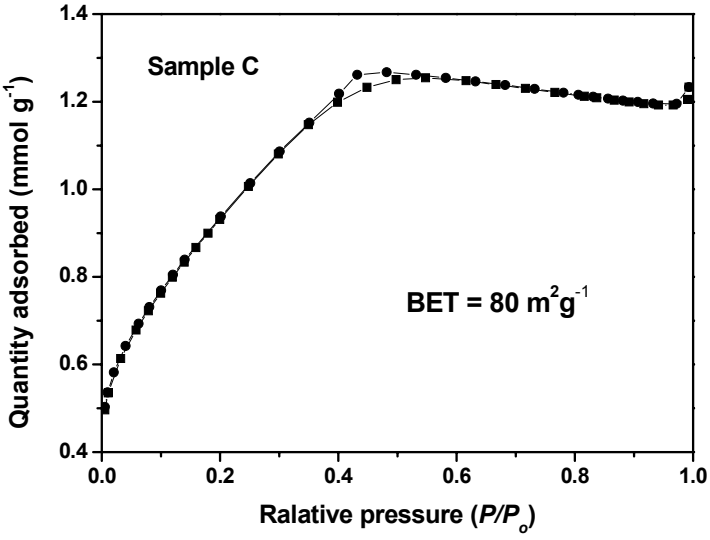


Figure S3. N_2 adsorption-desorption isotherms and the Brunauer-Emmett-Teller (BET) surface area of the macro-mesoporous titania sample A and C.

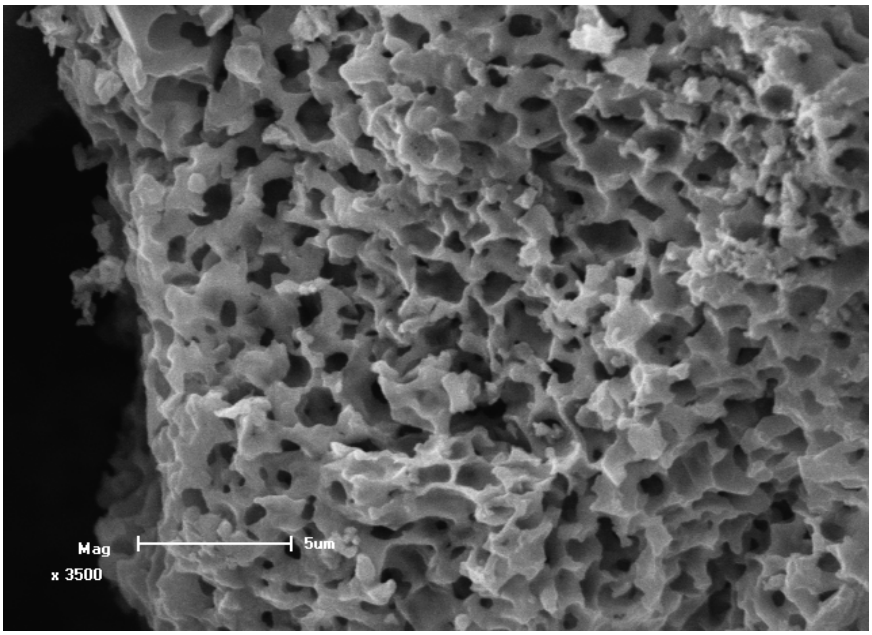


Figure S4. SEM image of the material using spherical *saccharomyces cerevisiae* cells as macrotemplate without glutaraldehyde fixing.