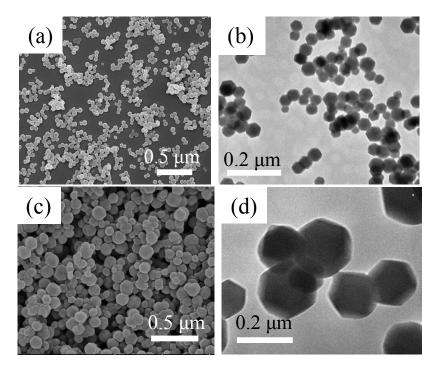
## **Supporting Information**

MOF-templated rough, ultrathin inorganic microcapsules for enzyme immobilization

Xiaoli Wang,<sup>a, b</sup> Jiafu Shi,<sup>a, b</sup> Shaohua Zhang,<sup>a, b</sup> Hong Wu,<sup>a, b</sup> Zhongyi Jiang,\* <sup>a, b</sup> Chen Yang,<sup>a,b</sup> Yuxin Wang,<sup>a</sup> Lei Tang<sup>a</sup> and Anfu Yan<sup>a</sup>

<sup>a</sup> Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, People's Republic of China. \*Z. Jiang. E-mail: zhyjiang@tju.edu.cn. Fax: +86-022-27406646. Tel: +86-022-27406646.

<sup>b</sup> Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, People's Republic of China.



**Figure S1**. SEM and TEM images of the as–synthesized ZIF-8 particles (a, b)  $\sim$ 50 nm, (c, d)  $\sim$ 150 nm.

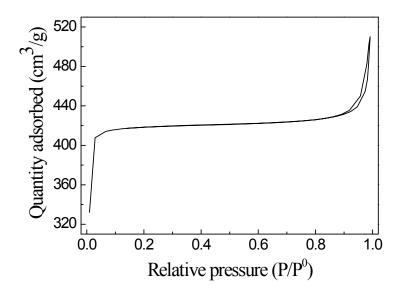
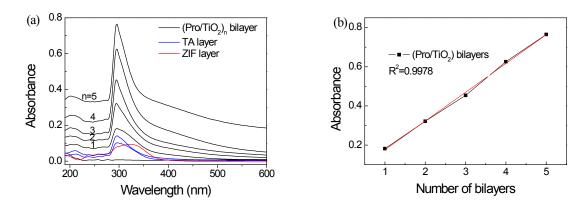
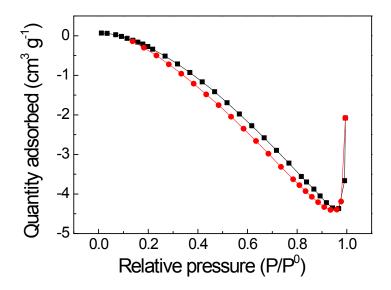


Figure S2. Nitrogen adsorption—desorption isotherms of the as—synthesized ZIF-8 particles.

To further confirm the assembly procedure, TA/ZIF-8/TA(Pro/TiO<sub>2</sub>)<sub>n</sub> multilayer film was performed on quartz plate (size 25 mm ×12 mm ×1 mm). Before assembly, quartz plates were cleaned with RCA cleaning solution (5:1:1 H<sub>2</sub>O:H<sub>2</sub>O<sub>2</sub> (30%):NH<sub>3</sub> (25%)) at 60 °C for 60 min, rinsed with deionized water and dried with nitrogen gas. Then, the plates were endowed with -NH<sub>2</sub> functional groups by immersing in 5 mg mL<sup>-1</sup> of PEI solution for 30 min. The precoated PEI plates were successively assembled with TA/ZIF-8/TA(Pro/TiO<sub>2</sub>)<sub>n</sub> multilayer architecture. The plates were washed with water and dried with a nitrogen stream after each assembly. UV-vis spectra were scanned after each layer deposition. Figure S3a showed the UV-vis spectra of the TA/ZIF-8/TA(Pro/TiO<sub>2</sub>)<sub>n</sub> multilayer film (n=1-5). The absorbance at 296 nm *vs* the number of bilayer was plotted in Figure S3b. The growth of the film exhibited a good linear correlation with correlation coefficients of R<sup>2</sup>=0.9978 for assembly of (Pro/TiO<sub>2</sub>) bilayer, suggesting the successful assembly based on biomineralization principle.



**Figure S3**. (a) UV–vis spectra of TA/ZIF-8/TA(Pro/TiO<sub>2</sub>)<sub>n</sub> multilayer film; (b) Optical absorption at  $\lambda_{max} = 296$  nm for (Pro/TiO<sub>2</sub>)<sub>n</sub> bilayers, n was the bilayer number of (Pro/TiO<sub>2</sub>).



**Figure S4**. Nitrogen adsorption—desorption isotherms of TiO<sub>2</sub> MCs, and the result indicated that the porous structure of TiO<sub>2</sub> MCs can not be determined by the BET analysis.