

Supporting Information

Conferring natural-derived porous microspheres with surface multifunctionality through facile coordination-enabled self-assembly process

Pingping Han ^{a,c,†}, Jiafu Shi ^{b,c,†}, Teng Nie ^a, Shaohua Zhang ^{a,c}, Xueyan Wang ^{a,c}, Pengfei, Yang ^a, Hong Wu ^{a,c,d*}, Zhongyi Jiang ^{a,c}

^aKey Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

^bSchool of Environment Science and Engineering, Tianjin University, Tianjin 300072, China

^cCollaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China

^dTianjin Key Laboratory of Membrane Science and Desalination Technology, Tianjin University, Tianjin 300072, China

[†]Pingping Han and Jiafu Shi contributed equally and shared the first authorship.

* Corresponding author: Hong Wu, wuhong@tju.edu.cn

Experimental

pH stability of the TA-Ti^{IV} coating

The pH stability of the TA-Ti^{IV} coating was tested by immersing the TA-Ti^{IV} coated chitin microspheres in buffer solutions with different pH values (CH₃COONa-CH₃COOH pH 4.0; Tris-HCl pH 7.0, 10.0; NaOH pH 13.0) for 2 h. Then, the supernatant was monitored by UV-vis spectrophotometer to clarify the disassembly of TA-Ti^{IV} coating.

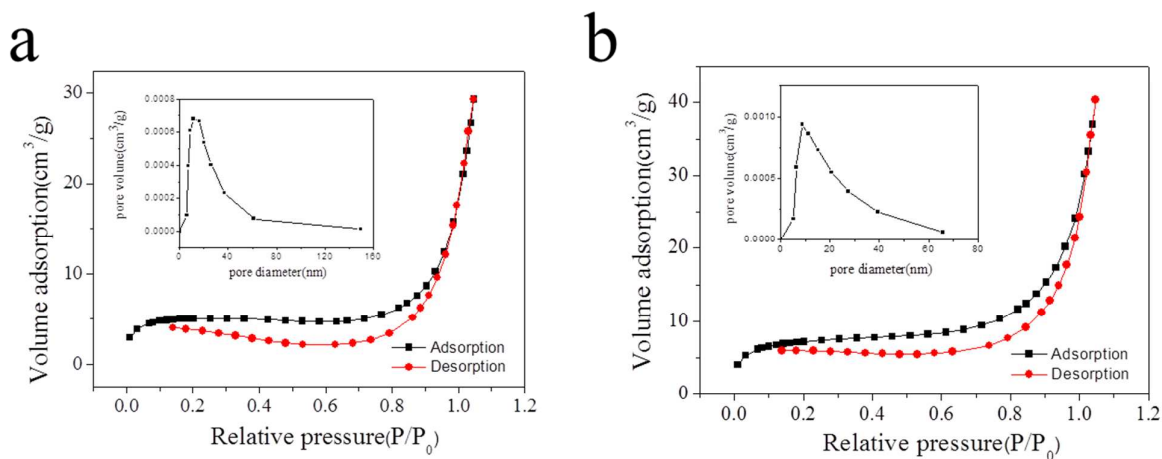


Fig. S1. Nitrogen adsorption-desorption isotherm and Pore size distribution curve by the BJH method of (a) chitin microspheres and (b) multifunctional chitin microspheres.

The BET specific surface area for chitin microspheres and multifunctional chitin microspheres were 17.30 m²/g, and 25.18 m²/g, respectively. The specific surface area was improved.

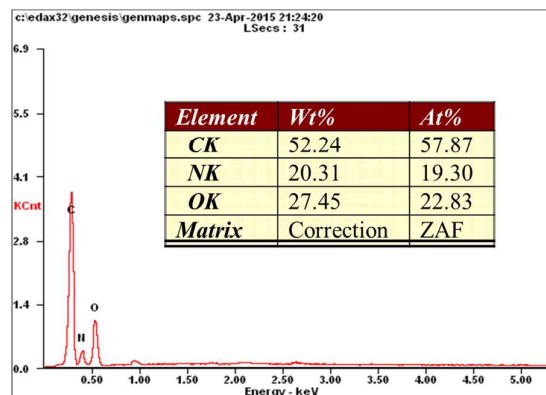


Fig.S2. EDS analysis of the pristine chitin microspheres

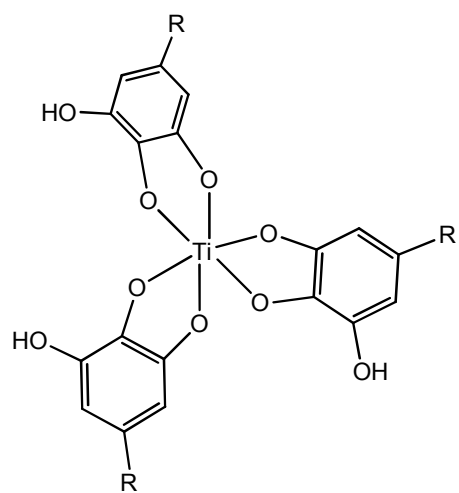


Fig. S3. Probable structure of TA-Ti^{IV} coordination complex.

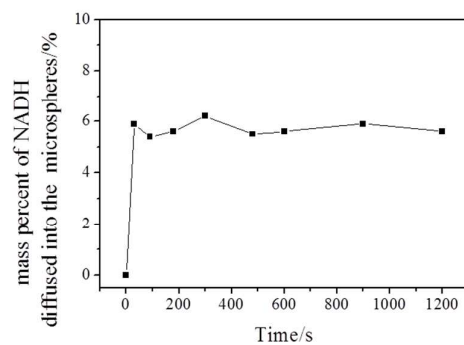


Fig. S4. Evolution of the mass percent of NADH in the solution diffused into the multifunctional

In Figure S4, the mass transfer refers to mass percent of NADH in the solution diffused into the multifunctional porous microspheres.

Table S1 Thermal denaturation kinetic parameters of free and immobilized YADH

Temperature (°C)	$K_d(h^{-1})$		$t_{1/2}$	
	Free YADH	Immobilized YADH	Free YADH	Immobilized YADH
30	0.0122±0.0005	0.0035±0.0002	56.772±2.441	197.550±9.878
40	0.1182±0.0006	0.0070±0.0004	5.865±0.305	98.425±4.429
50	0.1747±0.0113	0.2098±0.0005	3.967±0.178	3.304±0.231
60	0.7923±0.0317	0.5058±0.0101	0.875±0.035	1.370±0.059
70	infinity	0.6626±0.0358	0±0.005	1.046±0.052

Table S2 The change in enthalpy (ΔH°) for the thermal denaturation of free and immobilized YADH

Temperature (°C)	$\Delta H^\circ (kJ mol^{-1})$	
	Free YADH	Immobilized YADH
30	57.52±1.72	61.72±2.13
40	57.44±1.55	61.63±2.05
50	57.36±1.65	61.55±1.89
60	57.27±1.43	61.47±2.11
70	57.19±1.45	61.38±1.91

The half-life ($t_{1/2}$) and thermal denaturation constants (k_d) for free and immobilized enzymes were calculated and listed in Table S1. As the incubation temperature was elevated, the k_d values for both free enzymes and immobilized enzymes increased and the $t_{1/2}$ decreased. The result indicated that the denaturation of enzyme became quicker with the elevated incubation temperature. Compared to free enzyme, the immobilized enzyme showed a lower k_d values and a higher $t_{1/2}$ under the same incubation temperature, indicating a better stability against heat treatment. As the incubation temperature increased, the ΔH° values for free and immobilized enzymes (Table S2) decreased,

demonstrating less energy was required to inactivate enzyme at higher incubation temperature. However, at the same incubation temperature, the ΔH° values for immobilized enzymes were higher than free enzymes, demonstrating that more energy was needed to denature immobilized enzyme.

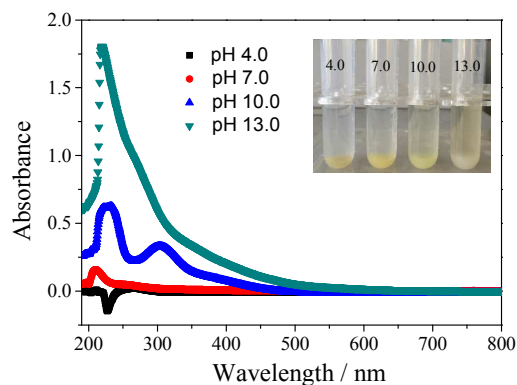


Fig. S5. UV-vis spectra of the supernatant of the TA-Ti^{IV} coating under various pH values. The inset was the optical images of the functional chitin microspheres in aqueous solution at different pH values.

After incubating the functional chitin microspheres into the buffer solution with different pH values (from pH 4.0 to pH 13.0), the supernatant turned to pale yellow from colorless, indicating that the TA-Ti^{IV} coating would disassemble from the chitin microspheres under extreme alkaline condition. The spectrum of the samples incubated at pH 4.0, 7.0 and 10.0 showed no or weak absorbance, suggesting that the TA-Ti^{IV} coating could not disassemble from the chitin microspheres. The spectrum of pH 13.0 showed big absorbance at 220 nm, indicating that the TA-Ti^{IV} coating completely disassembled from the chitin microspheres.