Supporting information

Water-Assisted Crystallization of Mesoporous Anatase TiO_2 Nanospheres

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Experimental

Chemicals

Hydroxypropyl cellulose (HPC), sodium fluoride, sodium chloride, β-casein were purchased from Aldrich Chemical Co. Tetrabutyl orthotitanate (TBOT) was obtained from Fluka. Dimethyl sulfoxide (DMSO) and ethanol (200 proof) were obtained from Fisher Scientific. All solutions were prepared in deionized water (18 MΩ) using a MilliQ^{TM} water purification system (Millipore, Billerica, Ma, USA).

Synthesis of TiO_2 nanoparticles

TiO_2 spheres with an average diameter of ca. 200 nm were synthesized through a sol-gel method. In a typical synthesis, 0.85 mL of tetrabutyl orthotitanate (TBOT) was added to a mixture of 300 μL of sodium chloride (0.04 M), 0.15g hydroxypropyl cellulose (HPC), and 50 mL of 200-proof ethanol under the protection of N_2 atmosphere. After sitting for 3 h, the products were centrifuged and washed with 200-proof ethanol for several times.

Preparation of microporous TiO_2 particles

The titania particles were isolated, washed with water, and then re-dispersed into a mixture of 19 mL of de-ionized water and 1 mL of NaF (1mg/10mL), followed by heating at desired temperature for an appropriate time under magnetic stirring. Samples were vacuum dried for 2 h to remove water residual before being used in the enrichment experiments and other measurements.

Enrichment of phosphorylated protein (β-casein) using the microporous TiO_2

In a typical experiment, 1 mg β-casein was dissolved in 1 mL water and used as stock solution. 20 mg TiO_2 sample and 20 μL of stock solution were added to 1 mL Milli. Q^{TM}water and incubated at 25 ^{o}C for 1.5 h. The suspension was then centrifuged at

11000 rpm for 4 minutes to discard the precipitate and the supernatant was collected for CE analysis.

Characterization

The sample morphology was characterized by using transmission electron microscopy (TEM, Tecnai T12). The crystalline structures were evaluated by X-ray diffraction (XRD) analysis using a Bruker D8 Advance Diffractometer with Cu Kα radiation(λ=1.5406 Å). Nitrogen adsorption isotherms were obtained at 77K using a nitrogen sorption instrument (Micromeritics ASAP 2010). Pore size distributions were calculated by the BJH method using the adsorption branches of the isotherm. The capillary electrophoresis experiments were performed on a P/ACETM MDQ Glycoprotein Capillary Electrophoresis System (Beckman Coulter, Fullerton, CA, USA). A 40-cm fused-silica capillary (75μL id, 365μL od, Polymicro Technologies, Phoenix, AZ, USA) with an effective length of 30 cm was used. For CE separation, the capillary was treated by 0.1 N NaOH for minutes and then water for 1 minute at 30 psi before being filled with the 10 mM borate buffer. The sample was injected hydrodynamically at 0.5 psi for 5s, and the separation was performed at +25kV with UV-absorption detection at 200 nm.

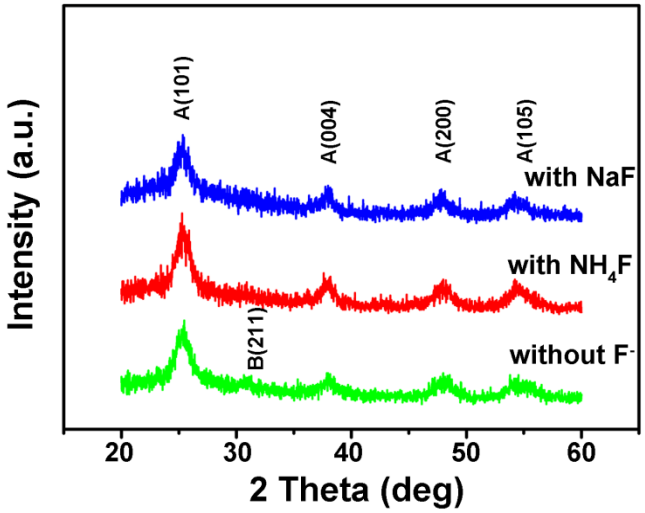

Figure S1. XRD patterns of TiO_2 particles obtained by heating the samples at 75 °C in aqueous solutions with and without F- ions.

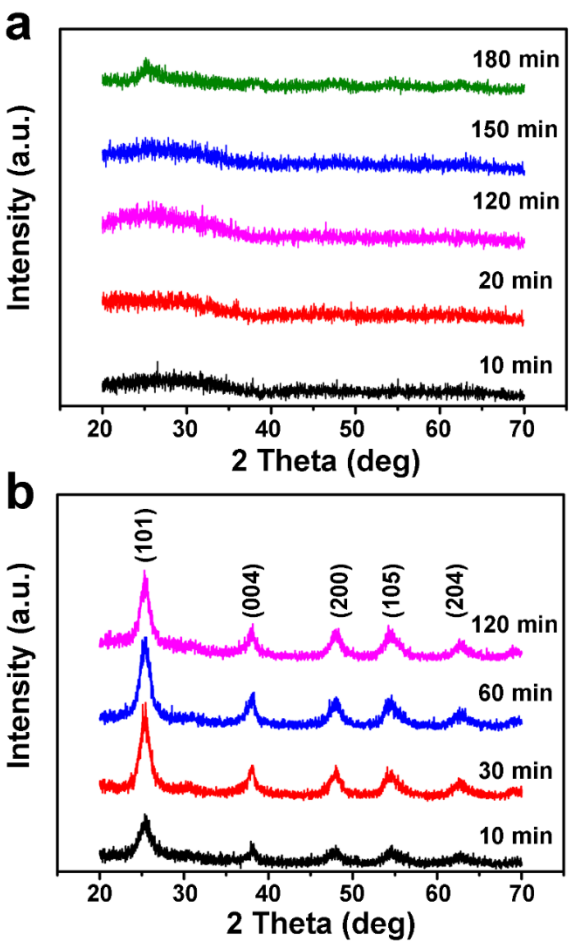

Figure S2. XRD patterns of TiO_2 particles obtained by heating at different temperatures: (a) 50 °C; and (b) 100 °C.

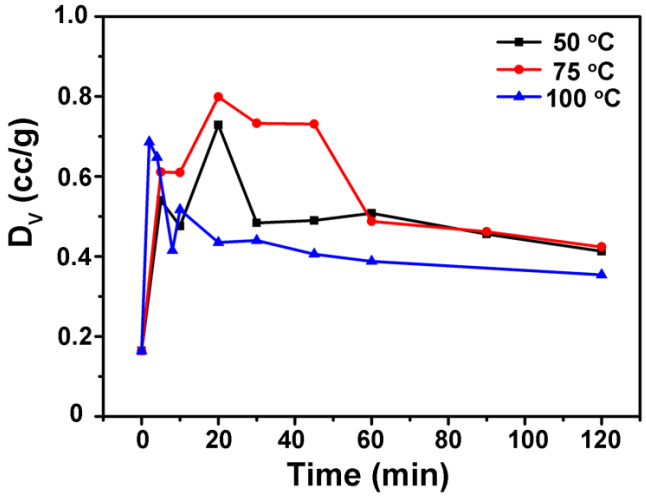

Figure S3. Change of pore volume as a function of heating time for TiO_2 particles treated at three different temperatures.

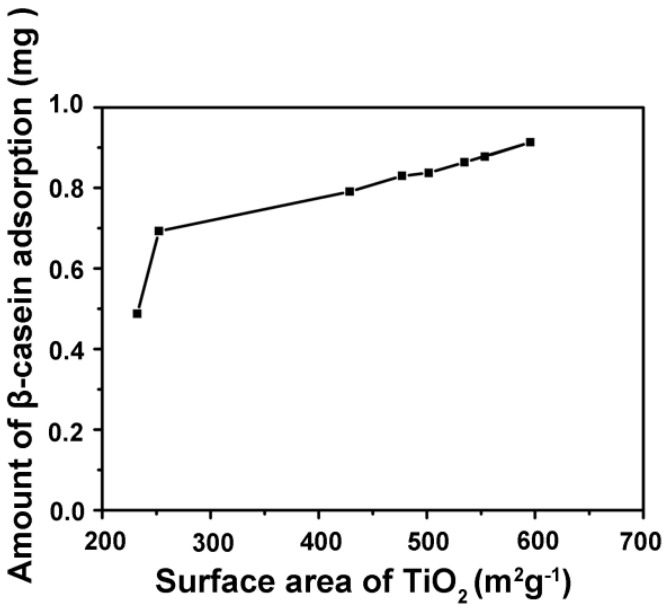

Figure S4. Quantitative correlation between the surface area of the TiO_2 and the adsorbed amount of β-casein for 20 mg of TiO_2 sample prepared by heating in water at 50 °C.