Supporting Information

Boric acid affinity molecularly imprinted magnetic nanoparticles for selective recognition and isolation of glycoproteins

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Synthesis of Fe₃O₄ nanoparticles
A mixture of anhydrous sodium acetate (7.2 g), polyethylene glycol (2.0 g), FeCl₃·6H₂O (2.7 g) as a ferric source, and ethylene glycol (80.0 mL), was stirred at 50°C for 15 min until a clear solution was produced. Then, the solution was sealed in a Teflon-lined autoclave and heated at 200°C for 8h. The magnetic nanoparticles were then washed several times with deionized water and ethanol to remove the unreacted raw materials and were then dried at 50°C for 12h.

Synthesis of Fe₃O₄@SiO₂-NH₂ nanoparticles
100.0 mg of Fe₃O₄ nanoparticles were ultrasonically dispersed into 100.0 mL of anhydrous toluene, and 20.0 mL APTES was added dropwise to the suspension. Under the protection of nitrogen, the suspension was stirred by a mechanical stirrer (400 rpm) with a PTFE stirring rod for 48h at room temperature. The modified nanoparticles were then collected by magnetic force and rinsed several times with deionized water and ethanol. The nanoparticles were then dried at 50°C for 12h.

Synthesis of Fe₃O₄@SiO₂-FFPBA nanoparticles
50.0 mg of Fe₃O₄@SiO₂-NH₂ nanoparticles were added to 40.0 mL of anhydrous methanol containing 100.0 mg of 2,3-Difluoro-4-formylphenylboronic acid and 5.0 mg sodium cyanoborohydride. Then, the mixture was stirred by a mechanical stirrer (400 rpm) for 12h with N₂ gas at room temperature. The resulting Fe₃O₄@SiO₂-FFPBA nanoparticles were collected by magnetic separation and washed three times with deionized water. Finally, the nanoparticles were dried at 50°C overnight.

Synthesis of glycoprotein-imprinted Fe₃O₄@SiO₂-FFPBA nanoparticles (MNPs@MIP-glycoprotein)
MNPs@MIP, with OVA as the template glycoprotein, were prepared by the polymerization of TEOS on the surface of Fe₃O₄@SiO₂-FFPBA nanoparticles. In the case of MNPs@MIP-OVA, we first immobilized OVA on to the surface of Fe₃O₄@SiO₂-FFPBA nanoparticles; 2.0 mg of OVA was dissolved in 2.0 mL of 50 mM ammonium hydrogen carbonate buffer solution (pH 8.5, containing 500 mM NaCl) and mixed with 30.0 mg Fe₃O₄@SiO₂-FFPBA in a 250 mL three-necked flask under ultrasonication. The mixture was then shaken at room temperature (1200 rpm) for 2h. The resultant Fe₃O₄@SiO₂-FFPBA-OVA were collected using a magnet and washed three times with 2.0 mL of 50 mM ammonium hydrogen carbonate buffer solution (pH 8.5).

In order to form an imprinted layer, the collected Fe₃O₄@SiO₂-FFPBA-OVA were dispersed in a solution of NH₃·H₂O (0.4 mL), water (35.0 mL), and absolute ethanol (58.0 mL), by ultrasonad for 15 min. Then, 2.0 mL of TEOS was added dropwise and the mixture was mechanically stirred (400 rpm) at room temperature for 30 min. Under an external magnetic field, the obtained
MNPs@MIP-OVA were separated from the solution, washed with deionized water and ethanol, and dried overnight at 40°C in a vacuum.

To remove the glycoprotein templates, the collected MNPs@MIP-OVA were dispersed into 100 mM HAc solution and shaken for 20 min (three times, 2.0 mL for each). Then, the imprinted nanoparticles were magnetically collected, rinsed three times with ethanol, and then dried in a vacuum oven at 40 °C overnight.

As a control sample, the corresponding non-imprinted material (MNPs@NIP) was also prepared under the same conditions in the absence of template glycoprotein.

**Fig. S1** Scanning transmission electron microscope elemental mapping images of the phenylboronic acid modified magnetic nanoparticles.

**Fig. S2** X-ray photoelectron spectroscopy analysis of the magnetic nanoparticles that had been modified with phenylboronic acid.
Fig. S3 Thermogravimetric analysis curves of magnetic nanoparticles modified with different materials.

Fig. S4 Magnetization curves of magnetic nanomaterials that had been molecularly imprinted with phenylboronic acid at room temperature.
Fig. S5 The thickness of the SiO$_2$-imprinted layer after a 60 min reaction in ammonia at various volumes (a-f): 0.2, 0.4, 0.6, 0.8, 1.0, and 1.2 mL.

Fig. S6 Thickness of the SiO$_2$-imprinted layer after reaction with 0.6 mL of ammonia at various reaction times (a-f): 10, 20, 30, 40, 50 and 60 min.
Fig. S7 The effect of reaction time (a) and volume of ammonia (b) on the adsorption capacity of MNPs@MIP to their individual imprinted molecules.

Fig. S8 Reusability of MNPs@MIP-OVA and MNPs@MIP-HRP.