Supporting Information

EXPERIMENTAL SECTION

1. Materials

phosphate buffer (PBS, pH 7.4, 0.02 mol/L), Acrylamide (AAm) and N,N-methylene- bisacrylamide (MBA) of electrophoresis grade, Horseradish peroxidase (HRP), Bovine hemoglobin (BHb), p-aminothiophenol (PATP), was purchased from Sangon (Shanghai, China). Lysozyme (Lys), Cytochrome c (Cyt c), and bovine serum albumin (BSA) were purchased from Sigma. $FeCl_3 \cdot 6H_2O$，$FeCl_2 \cdot 4H_2O$，25%–28% $NH_3 \cdot H_2O$，sodium citrate，gold chloride tetrahydrate，aniline, ammonium persulfate (APS), Acryloyl chloride (AOCl), dimethyl sulfoxide (DMSO), Triethylamine (TEA), methacrylic acid (MAA), and N,N,N,N- tetra-methylethylenediamine (TEMED) of analytical grade were obtained from Xinyuhua (Fuzhou, China). Milli-Q purified water was used for all experiments described here.

2. Preparation of Fe_3O_4@Au/PA (poly-aniline) composite NFs

First of all，the sodium citrate dispersed Fe_3O_4 NPs was synthesized as described previously[1]. Briefly, $FeCl_3 \cdot 6H_2O$ (10 mmol) and $FeCl_2 \cdot 4H_2O$ (5 mmol) were dissolved in deionized water (5 mL) in the three necked flask with a magnetic stirrer under the protection of nitrogen. A mixture of 25%–28% $NH_3 \cdot H_2O$ aqueous solution (5.39 g) and sodium citrate (2.94 g) dissolved in water (10 mL) was added dropwise to the above solution at the temperature of 40 ºC, followed by reaction for 2 h at 60 ºC. The reaction mixture was cooled down in constant volume of 40 mL.

Sodium citrate (0.069 g) was then added into above mixture under vigorous stirring. A total of 32 mg gold chloride tetrahydrate was added rapidly at the boiling stage, and the reaction solution turned to wine red from black in color within a minute. The reaction was continued under reflux for 30 min before being allowed to cool down to

room temperature. The resulting colloidal solution was dissolved with 1 M HCl to remove unwrapped Fe_3O_4 MNPs, then isolated in a magnetic field to remove independent Au NPs and washed several times with water by magnetic separation. The resulting Fe_3O_4@Au colloidal solution in 40 mL deionized water was added with 1 mL 20 mg/mL PATP in 1 M HCl under a magnetic stirrer for 30 min, producing PTAP capped Fe_3O_4@Au NPs solution.

Fe_3O_4@Au/PA composite NFs were synthesized in situ via oxidative polymerization by adding aniline (0.5 g) into the above colloidal solution (40 mL) with mechanical stirring at 0–5 ºC for 30 min. As an oxidant, APS (0.5 g) was added directly stirring at 0–5 ºC for 15 min, then at room temperature (RT) for 10 h. The precipitate was washed several times with water and methanol by centrifugation at 5000 rpm for 5 min. The obtained product was dried under vacuum at 60 ºC for 24 h.

Synthesis of functionalized Fe_3O_4@Au/PA (FUN-NFs). Fe_3O_4@Au/PA (100 mg) was suspended with stirring in a mixture of triethylamine (4 mmol) and dimethyl sulfoxide (DMSO, 10 mL) in an ice-bath. Acryloyl chloride (4 mmol) was added dropwise over 45 min. After removal from the ice bath, the mixture was then stirred at RT for 4 h[2]. The resulting product was filtered, washed with benzene and anhydrous ethanol, dried in a vacuum oven at 60 ºC for 8 h.

3. Preparation of surface Lys-imprinted polymers

Uniform core-shell structured Lys-imprinted polymers were prepared according to the non-covalent approach, using AAm and MAA as functional monomer, MBA as cross-linker. Briefly, pre-polymer solutions were prepared by dissolving MBA (5 mg), AAm (15 mg) and MAA (7 mg) in PBS (5 mL). To this solution, 15 mg of Lys was dissolved and then mixed with the suspension of FUN-NFs (30 mg) dispersed in 5 mL of PBS. After 1 h shaking for preassembly, the mixture was purged with nitrogen

stream for 10 min. Then, a one-step polymerization was carried out by injecting 100 μL of APS solution (10%, w/w) and 5 μL of TEMED to the mixture continued starring at RT for 4 h. The resultant polymer materials were separated and washed with 1.0% (w/v) SDS to remove both the template molecules and residual monomers and then rewashed with water to remove remaining SDS. Finally, the materials were dried to constant weight under vacuum at 40 ºC for 24 h (namely MIPs). For comparison, the control non-imprinted NFs (NIPs) were prepared in the same manner but omitting the template in the reaction system.

4. Adsorption experiment

The adsorption experiments were carried out as follows: 3 mg of MIPs or NIPs were incubated with 1.0 mL Lys solution of various concentrations in PBS under optimized conditions. After centrifugation at 3,000 rpm for 5 min, the final protein concentration of the supernatant was determined by a UV/Vis spectrophotometer at 280 nm. The amount of Lys adsorbed onto the MIPs was calculated by subtracting the amount of unbound compounds from the amount of compounds added to the mixture.

5. Electrochemical characterization

The glassy carbon electrode (GCE) was polished with 0.05 mm alumina slurry followed by rinsing with water, then sonicated in 1:1 nitric acid, ethanol and water (1:1). The material in water (3 mg mL^{-1}) and a solution of chitosan (1 mg mL^{-1}) were mixed with equal volume, 5 μL mixture was then dropped onto the surface of the GCE. After drying in RT for 1 h, the modified electrode was rinsed with water and dried for electrochemical measurement.

6. Characterization

The morphologies and structures of the NFs were examined by TEM (Tecnai G2 F20 S-TWIN 200 KV). Fourier transform infrared (FT-IR) spectra of multifunc-

tionalized NFs were recorded using the Nicolet 360 FT-IR spectrophotometer (Nicolet, USA). Thermo-gravimetric analysis (TGA) was performed for power samples (~3 mg) with a heating rate of 10 ºC min^{-1} up to 800 ºC using a STA 449C (Netzsch, Germany) thermogravimetric analyzer under nitrogen atmosphere. The data of adsorption were obtained by using a Lambda 800 UV-vis spectrophotometer (Perkin Elmer, USA). The electrochemical measurements were performed with a CHI 660D electrochemical workstation (Shanghai, China). A conventional three-electrode system was used comprising a self Assembled GCE as working electrode, a platinum wire as auxiliary electrode, an Ag/AgCl electrode as reference electrode. All experiments were performed under a dry nitrogen atmosphere at room temperature.

7. Binding experiments

The binding experiments were performed at different initial concentration of Lys, ranging from 0.1 to 1.0 mg mL□1 for 2 h, to compare the binding capacity of MIPs against control NIPs. The amount of BHb adsorbed by the MIPs or NIPs (Q, mg/g) was calculated using the following formula:

$$Q = (C_i - C_f)V/m$$

where Q (mg g^{-1}) is the mass of protein adsorbed by unit mass of dry materials, C_i (mg mL^{-1}) and C_f (mg mL^{-1}) are the concentrations of the initial and final solutions, respectively, V (mL) is the total volume of the adsorption mixture, and m is the mass of the particles used. All the tests were conducted in triplicates.

References

1. Yu, Q., Shi, M., Cheng, Y., Wang, M., Chen, H., *Nanotech.* 2008, 19, 265702-265707.
2. Liang,Y., Gu, L., Liu, X., Yang, Q., Kajiura, H., Li, Y., Zhou, T., Shi, G., *Chem. Eur. J.* 2011, 17, 5989 – 5997.

Table S1 Freundlich Isotherm Parameters for Adsorption of Lys

	Q_f	1/n	K_0	R^2
MIPs	0.73	0.83	0.69	0.9935
NIPs	0.40	0.92	0.37	0.9898

Table S2 Adsorption kinetic parameters for Lys adsorption on MIPs

	Q_e, exp	k	Q_e, cal	R^2
Pseudo-first-order	76.8	0.039	78.04	0.9974
Pseudo-second-order		0.001	83.33	0.9942

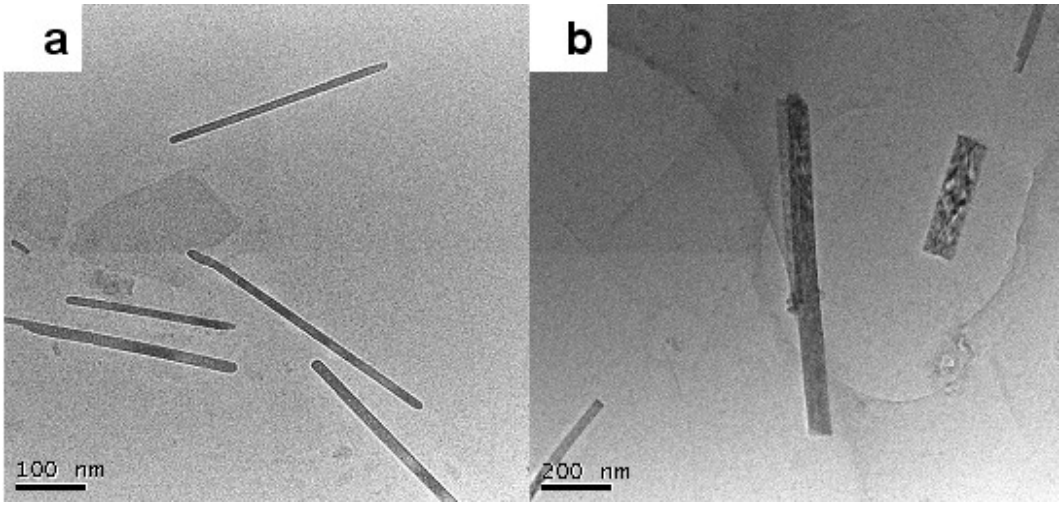

Figure S1. TEM images of the synthesized (a) Fe_3O_4@Au@ PA NFs, (b) MIPs

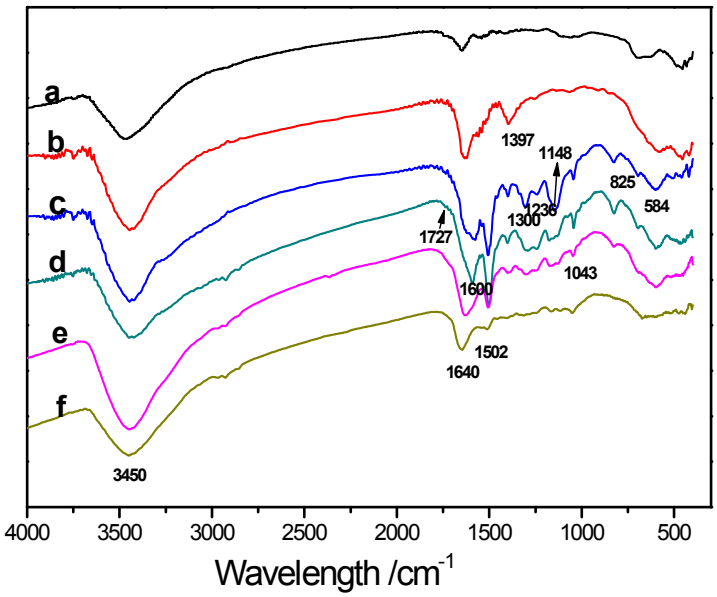

Figure S2. FTIR spectra of Fe_3O_4 NPs (a), Fe_3O_4@Au NPs (b), Fe_3O_4@Au@ PA NFs (c), FUN-NFs (d), NIPs (e), MIPs (f)

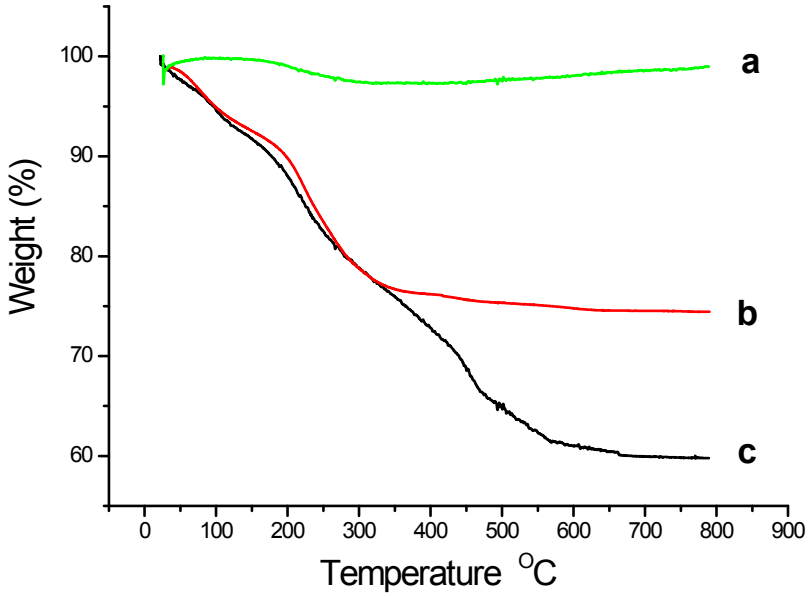

Figure S3. TGA curves of Fe_3O_4@Au NPs (a), FUN-NFs (b), MIPs (c)

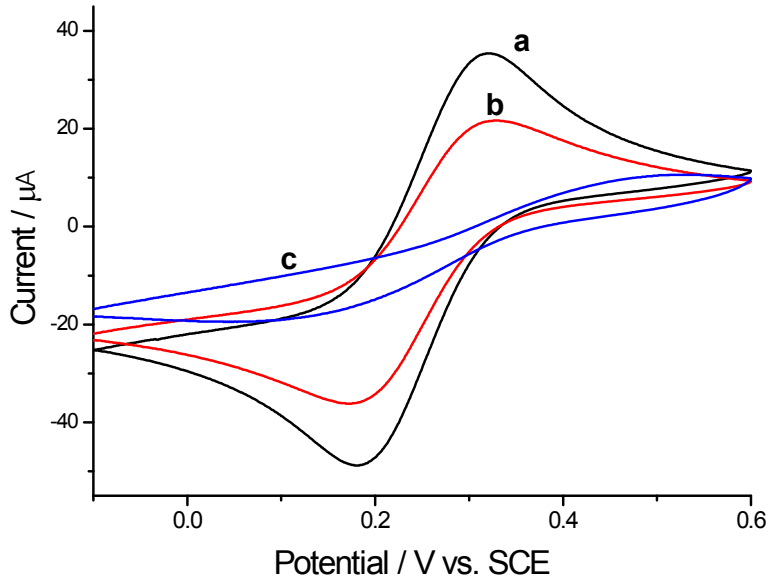

Figure S4. CV for 5mM $K_3[Fe(CN)_6]$ and 0.1M KCl at a NIPs electrode(a), a MIPs electrode (b), a MIPs rebinding 0.5 mg/mL Lys electrode(c). Scan rate: 100mV/s.

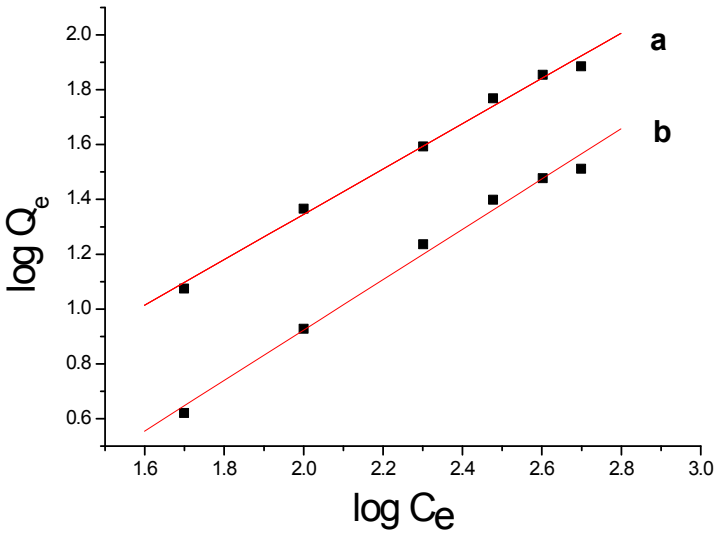

Figure S5. The linear relationship of Freundlich model

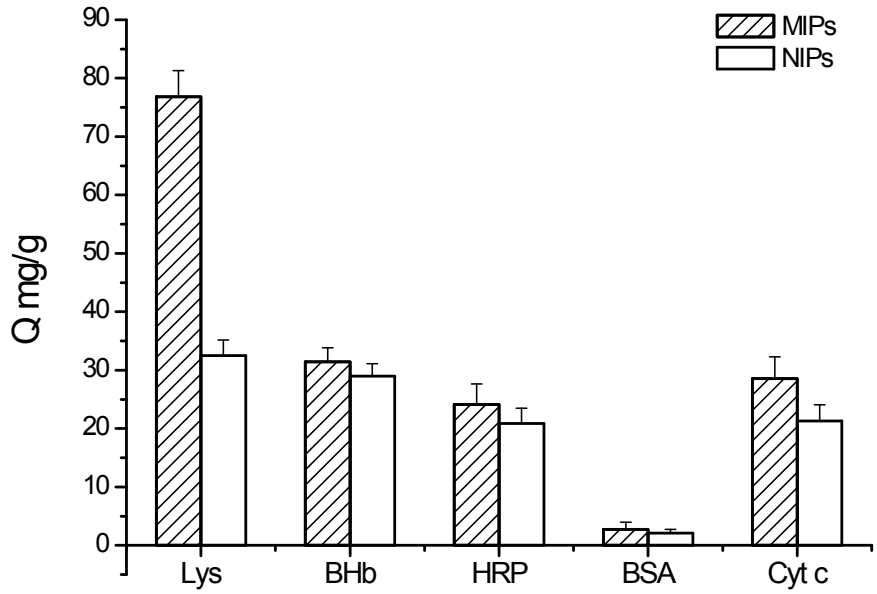

Figure S6. Rebinding amounts of different proteins on the MIPs and NIPs. Adsorption conditions: V =1.0 mL, m =3.0 mg, C_i=0.5 mg/mL, Time 90 min, temperature RT.

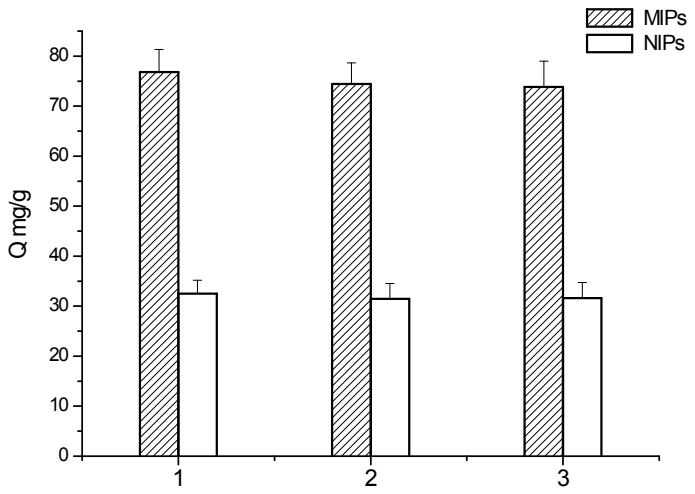

Figure S7. Influence of the regeneration cycles on Lys adsorption to the MIPs and NIPs. Regeneration was performed by washing with 1.0% (w/v) SDS and further with water. Adsorption conditions: V =1.0mL, m =3.0mg, C_i= 0.5 mg/mL, Time 90 min, temperature RT.