Electronic Supplementary Material (ESI) for Analyst.

Supporting Information

Controlled synthesis of PEGylated surface protein-imprinted nanoparticles

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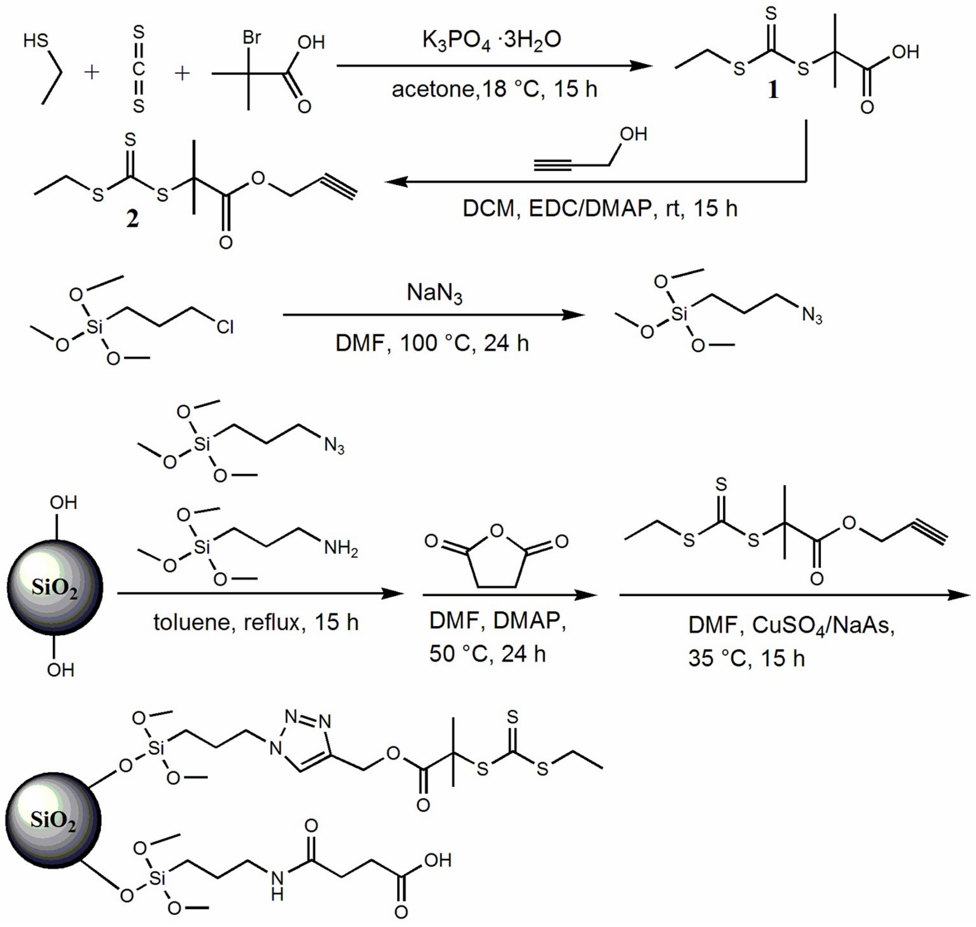

Fig. S1. Detailed procedure for the synthesis of the RAFT CTA grafted SiO_2 nanoparticles.

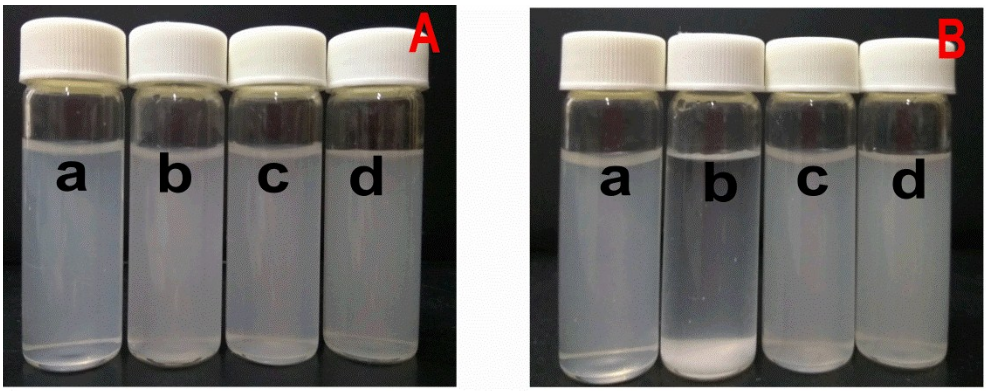

Fig. S2. Pictures showing (A) the initial dispersion and (B) that after 1-hour setting in a phosphate buffer (pH 7.0, 10 mM) of the different nanoparticles: (a) SiO_2, (b) SiO_2-NH_2/N_3, (c) SiO_2-COOH/N_3, and (d) SiO_2-COOH/CTA. All of the particle contents were 1 mg/mL. Initially, all the particles could be dispersed by ultrasound. It is shown that, after 1-hour setting, the SiO_2-COOH/CTA particles and another kind of carboxyl-bearing particles (SiO_2-COOH/N_3) were still stably dispersed like the SiO_2 nanoparticles, in contrast to the SiO_2-NH_2/N_3 particles without carboxyl groups. The observed stability can be attributed to the electrostatic repulsion between the deprotonized carboxyl groups.

Table S1. Adsorption capacities of the differently modified nanoparticles toward Lyz.

	Adsorption capacity[a] (mg/g)
SiO_2	23.4 ± 0.3
SiO_2-NH_2/N_3	4.6 ± 0.2
SiO_2-COOH/N_3	45.2 ± 0.6
SiO_2-COOH/CTA	37.4 ± 0.4

[a] measured by incubating ~5 mg of different nanopaticles in 1.5 mL of phosphate buffer (pH 7.0, 10 mM) containing 0.6 mg of Lyz at 35 ºC for 1 h.

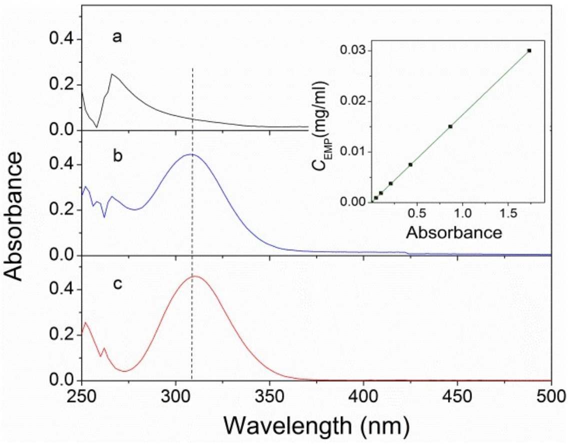

Fig. S3. UV–Vis spectra of (a) SiO_2-COOH/N_3 particles, (b) SiO_2-COOH/CTA particles and (c) free CTA (EMP) measured in DMF. The concentrations of both particles were 1 mg/mL. The inset is the standard absorption curve of free EMP dissolved in DMF at a wavelength of 308 nm.

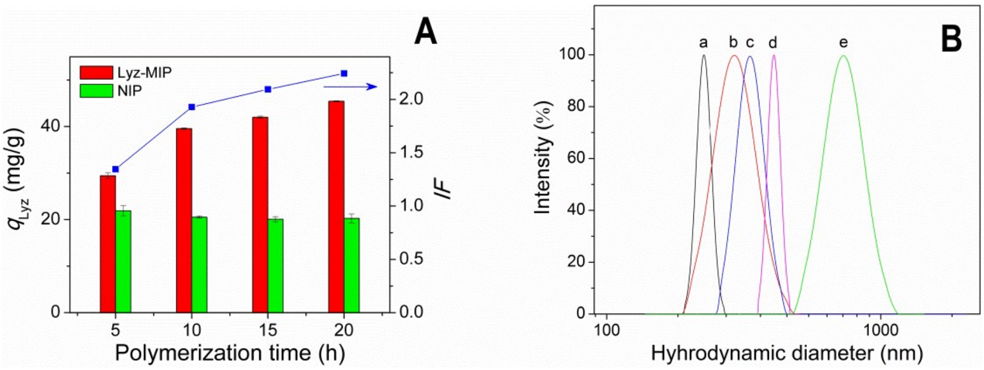

Fig. S4. (A) The effect of the first step of SI-RAFT APP time on the imprinting performance of the core-shell Lyz-MIP particles; (B) The hydrodynamic diameters (measured in pure water at 15 °C) of the core-shell Lyz-MIP particles obtained with increasing polymerization time: (a) 0 h (corresponding to the initial SiO_2-COOH/CTA particles), (b) 5 h, (c) 10 h, (d) 15 h, and (e) 20 h (the average diameters were measured to be 216.0, 333.0, 423.4, 462.6, and 567.7 nm, respectively).

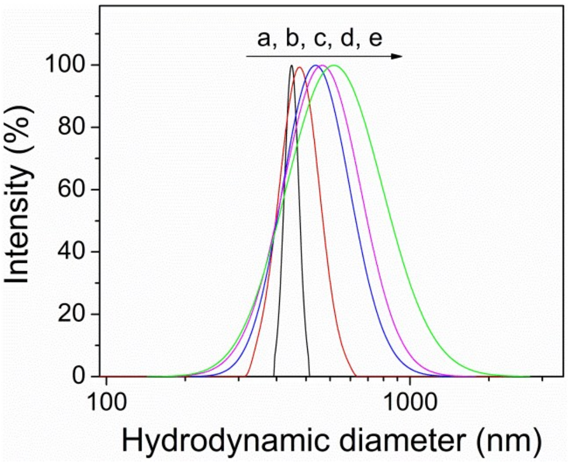

Fig. S5. The hydrodynamic diameters (measured in pure water at 15 °C) of the PEGylated Lyz-MIP particles obtained via the second step of SI-RAFT polymerization with increasing reaction time: (a) 0 h (corresponding to the core-shell structured Lyz-MIP particles), (b) 5 h, (c) 15 h, (d) 24 h, and (e) 36 h.

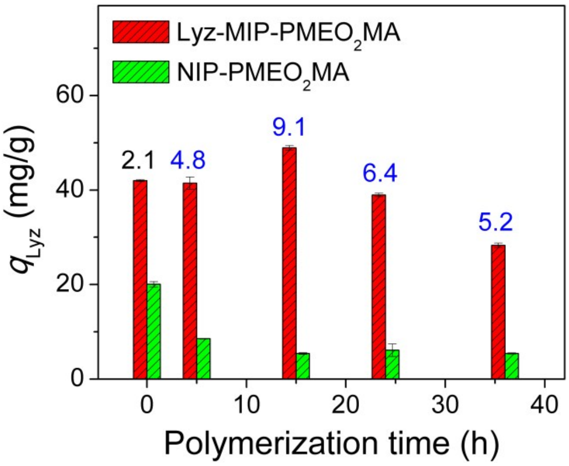

Fig. S6. Lyz binding to the Lyz-MIP-PMEO$_2$MA and NIP-PMEO$_2$MA nanoparticles prepared via the second step of SI-RAFT APP with increasing polymerization time (C_0 = 0.4 mg/mL, 35 °C). The *IF* values are indicated above the MIP bars. Actually, at time zero, the corresponding particles are the core-shell Lyz-MIP and NIP, respectively.

Table S2 Comparison of some Lyz-MIPs synthesized via free radical polymerization in the presence of charged monomers.

Lyz-MIPs	Imprinting factor (*IF*)		Refs
	without NaCl	adding NaCl	
imprinted nanogels	2.3		[1]
surface-imprinted nanoparticles	1.6		[2]
surface-imprinted nanoparticles	1.8		[3]
surface-imprinted nanoparticles	1.6	2.0 (40 mM NaCl)	[4]
imprinted hydrogels	1.2	2.9 (20 mM NaCl)	[5]
surface-imprinted microparticles	3.6		[6]
surface-imprinted nanoparticles [a]	2.4		[7]
surface-imprinted nanoparticles	2.3	6.0 (100 mM NaCl)	[8]
imprinted hydrogels [b]	~2.0	8.6 (50 mM NaCl)	[9]
PMEO$_2$MA-grafted surface-imprinted nanoparticles	9.1		this work

[a] synthesized by copolymerization of MEO$_2$MA with MAA and a Cu^{2+} chelating monomer based on solution polymerization mechanism, and therefore metal coordination was present besides electrostatic interactions. [b] synthesized using PEG-based cross-linker with ionic monomers.

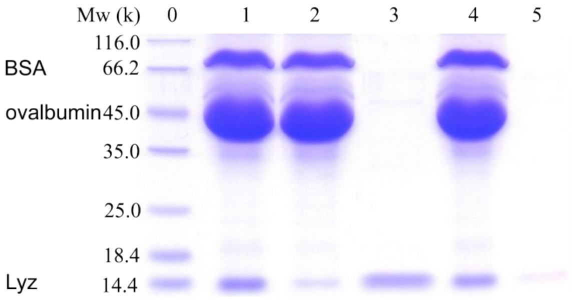

Fig. S7. SDS-PAGE analysis for studying the selectivity of the PEGylated Lyz-MIP and NIP nanoparticles toward Lyz from fresh chicken egg-white. Lane 0, protein marker for molecular weights; lane 1, 20-fold diluted egg-white solution; lane 2, the egg-white solution after adsorption with the Lyz-MIP particles; lane 3, elute from the protein-binding Lyz-MIP particles; lane 4, the egg-white solution after adsorption with the NIP particles; lane 5, elute from the protein-binding NIP particles. Clearly, the MIP particles selectively adsorpted major amounts of Lyz in the egg-white solution (see lane 1, 2 and 3). In contrast, the NIP particles showed quite little binding of Lyz (see lane 1, 4 and 5).

References

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