Supplementary Information

Preparation and Characterization of Thermoresponsive Poly(N-isopropylacrylamide-co-acrylic acid)-grafted Hollow Fe₃O₄/SiO₂ Microspheres with Surface Holes for BSA Release

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Figure S1. The SEM images and size distribution of Fe₃O₄ (a) and Fe₃O₄/SiO₂ (b) microspheres.

Figure S2. The SEM image of wax/Fe₃O₄/SiO₂ Pickering particles.
**Figure S3.** The hydrodynamic diameter of various microspheres at 28 °C (a) Fe$_3$O$_4$, Fe$_3$O$_4$/SiO$_2$, p-Fe$_3$O$_4$/SiO$_2$ microspheres, (b) P(NIPAM-AA)/Fe$_3$O$_4$/SiO$_2$ microspheres (Sample A1, A2, A3, A4).

**Figure S4.** The XRD patterns of p-Fe$_3$O$_4$/SiO$_2$ microspheres.
Figure S5. FTIR analysis of (a) BSA, (b) P(NIPAM-AA)/Fe3O4/SiO2-BSA microspheres, (c) P(NIPAM-AA)/Fe3O4/SiO2 microspheres.

The FTIR spectrum of BSA showed the peak with C=O (1659 cm⁻¹), N-H (1540 cm⁻¹). However, the FTIR spectrum of P(NIPAM-AA)/Fe3O4/SiO2-BSA microspheres showed the peak with C=O (1645 cm⁻¹), N-H (1535 cm⁻¹). And the peak at 1170 cm⁻¹, 930 cm⁻¹ are belonged to the characteristic peak of BSA which are consistent with the peak at 1165 cm⁻¹, 920 cm⁻¹ of P(NIPAM-AA)/Fe3O4/SiO2-BSA microspheres. These results suggested that BSA are absorbed in the P(NIPAM-AA)/Fe3O4/SiO2 microspheres through hydrogen bonding and van der waale forces between carboxyl-carbonyl or amide-carboxyl groups. It is because that the carbonyl groups and amino groups of P(NIPAM-AA) can form hydrogen bond with the amino groups and carbonyl groups of BSA.

Figure S6. The fitting curve of BSA slow-release curve-Higuchi model.

Higuchi model analysis is often used to study drug release kinetics [1,2]. From Figure S6, it can be seen that the results of the release at 37 °C are analyzed by Higuchi mode. In 0h-8h segment, the correlation coefficient (R²) of P(NIPAM-AA)/Fe3O4/SiO2 microspheres obtained by oxalic acid corrosion 0min, 15min, 30min, 45min was 0.899, 0.975, 0.993, 0.989, respectively; these data suggest that the diffusion control process plays a major role in the release of BSA.
References
