Supporting Information

Magnetic PEDOT Hollow Spheres with Single Holes

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All chemical reagents were purchased from Sigma-Aldrich, and used without further purification. Hydroxy-functionalized EDOT (EDOT-OH) was synthesized according to the literature procedure.¹ Polystyrene (PS) beads (Polybead®, 500 nm diameter) were purchased from Polysciences Inc., and used without further purification.

Synthesis of Poly(EDOT-OH) Coated PS Beads: EDOT-OH monomers were dissolved in water by sonication in a water bath sonicator (Elma Transsonic 660/H, 35 kHz) for 30 min to prepare monomer solutions of 30 mM. Monomer solutions were then added to aqueous solutions of PS beads. After the mixed solutions were stirred for 30 min, a solution containing 30 mM of ammonium persulfate (APS) and 10 mM of HCl was introduced. The chemical polymerization proceeded for 16 h at room temperature before it was quenched by ethanol.

Synthesis of Fe₃O₄ Nanoparticles: Magnetite nanoparticles were synthesized by thermal decomposition of iron-oleate complex following published procedures.² Iron-oleate complex was prepared by adding FeCl₃·6H₂O (2.7 g, 10 mmol) and sodium oleate (9.125 g, 30 mmol) into a mixture of ethanol (20 ml), deionized water (15 ml), and hexane (35 ml). After refluxing at 70 °C for 4 h, the upper reddish brown hexane solution containing iron-oleate complex was separated, and washed three times with deionized water (10 ml). Hexane was then evaporated in a rotary evaporator, yielding a dark reddish brown, oily iron-oleate complex (~ 9 g). The complex was then dissolved in 25 g of 1-octadecene together with oleic acid (1.41 g, 5 mmol). The mixture was heated to 320 °C at a ramp of 3–5 °C min⁻¹ for 30 min under argon. The resulting black nanocrystal solution was cooled to room temperature, and 2-propanol (50 ml) was added to precipitate the magnetic nanoparticles. After centrifugation, the nanoparticles were washed with hexane and ethanol three times, and then redispersed in toluene for further use.

Synthesis of Fe_3O_4 Nanoparticles Immobilized on Poly(EDOT-OH) Capsules: Poly(EDOT-OH) coated PS beads were dispersed in 4 ml of ethanol to prepare a 2.5% solution. 1 ml of Fe_3O_4 nanoparticles in toluene solution (10 mg/ml) was added, and the mixture was stirred at room temperature for 1 h to immobilize the Fe_3O_4 nanoparticles on the poly(EDOT-OH) capsules.

Instrumentation: Field emission SEM (FESEM) was conducted with JEOL JSM-7400 at a vacuum of 10^{-8} torr and an accelerating voltage of 10 kV. TEM was performed on a Tecnai F20 electron microscope with an acceleration voltage of 200 kV. UV-visible spectrum was collected using an Agilent 8453 UV-visible spectrometer at room temperature. All solutions were filtered by a polytetrafluoroethylene (PTFE) syringe filter with 0.45-µm pores before measurement.

SDS-PAGE Analysis: The lysozymes trapped in poly(EDOT-OH) capsules were separated by SDS-PAGE according to the method of Laemmli.³ Both poly(EDOT-OH) capsules and poly(EDOT-OH) coated solid PS beads were dispersed in Laemmli buffer (Bio-Rad), and heated to 95 °C for 5 min. 15% gels were prepared for SDS-PAGE analysis. After the completion of SDS-PAGE, gels were stained with commassie blue solution before imaging.

Fig. S1 shows the TEM image of Fe_3O_4 nanoparticles immobilized poly(EDOT-OH) coated solid PS beads. Fe_3O_4 nanoparticles were dispersed in hexane, and then mixed with poly(EDOT-OH) coated solid PS beads in ethanol. Since hexane and ethanol were immiscible, the mixed solutions were first stirred vigorously for 30 min, and then sonicated for 30 min to immobilize Fe_3O_4 nanoparticles on the beads. Compared to the immobilization of Fe_3O_4 nanoparticles on poly(EDOT-OH) coated beads was lower. This was mainly due to the incompatibility of hexane and ethanol, which reduced the Fe_3O_4 loading and dispersion. Fe_3O_4 nanoparticles could only be immobilized on the surface of solid PS beads. In contrast, Fe_3O_4 nanoparticles could be immobilized on the outer surface and the interior of the poly(EDOT-OH) capsules.

Cell Viability Studies: The particle samples were sterilized for 30 min in 70% ethanol. The beads were then washed with PBS buffer twice and full cell culture medium once. The blank culture plate well was used as the control. NIH3T3 and HepG2 cells were trypsinized and suspended in Dulbecco's Modified Eagle Medium (DMEM) with 10% fetal bovine serum (FBS) and 1% penicillin/streptomycin. The cells were seeded in a 24-well plate and incubated for 24 h, and for another 48 h at 37 °C after the change of medium. After incubation for 24 h and 72 h, the supernatant was discarded, and replaced with 0.5 ml of serum-free medium for each well. 50 μ l of MTT (5 mg/ml) were added to each well and incubated for 4 h. The medium was discarded by aspiration, and the formazon was discolved in 500 μ l of dimethyl sulfoxide (DMSO). The plates were read for absorbance at 550 nm. The cell viability was calculated by normalizing with the control.



Fig. S1 TEM image of Fe_3O_4 nanoparticles immobilized poly(EDOT-OH) coated solid PS beads.



Fig. S2 Calculation of the removal of lysozyme by beads and capsules based on the reduction in the intensity of the UV-visible absorption peak at 280 nm. The error bars are based on three data points.

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