Support Information

SiO_2-Coated Fe_3O_4 Nanoparticle/Polyacrylonitrile Beads for One-Step Lipase Immobilization

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1. Detailed Procedures for Optimizing the Fabrication Conditions of L/FP

Optimization of PAN. Molecular Weight

PAN with different molecular weights (M.w.=10 k, 30 k, 50 k, 80 k, 150 k, and 250 k) were firstly dissolved in DMF at a concentration of 20 wt%. The 1 mL the PAN solution was mixed with 27.5 mg Fe_3O_4 nanoparticles, 0.9 mL DMF, and 0.1 mL PEG 200 substantially. Next, the mixture was extruded from a needle with a diameter of 0.2 mm and dropped into the 2 mg/mL lipase solution (as a coagulation bath). After stirring for 24 h at RT, magnetic PAN composite beads with lipase were washed by PBS buffer (50 mM, pH=7.0). Finally, the L/FP hollow composite beads with different molecular weight of PAN were obtained. The porosity of the L/FPs was measured by the method in **Section 2.5** of the manuscript and the activity measured by the method in **Section 2.6.2** of the manuscript.

Optimization of PAN Concentration

PAN (M.w.= 80 k) was firstly dissolved in DMF at a concentration of 20 wt%. The PAN solution was mixed with 27.5 mg Fe_3O_4 nanoparticles, 0.9 mL DMF, and 0.1 mL PEG 200 substantially with a final concentration of 3.6, 5.5, 7.3, 8.9, 10, 11.1, 14, 16, 18, and 20 wt% respectively. Next, the mixture was extruded from a needle with a diameter of 0.2 mm and dropped into the 2 mg/mL lipase solution (as a coagulation bath). After stirring for 24 h at RT, magnetic PAN composite beads with lipase were washed by PBS buffer (50 mM, pH=7.0). Finally, the L/FP hollow composite beads with different molecular weight of PAN were obtained (the concentration of PAN under 3.6 wt% was hard to solidify as a bead). The porosity of the L/FPs was measured by the method in **Section 2.5** of the manuscript and the activity measured by the method in **Section 2.6.2** of the manuscript.

Optimization of the Concentration of Fe_3O_4 Nanoparticles

PAN (M.w.= 80 k) was firstly dissolved in DMF at a concentration of 20 wt%. The PAN solution with a final concentration of 10 wt% was substantially mixed with Fe_3O_4 nanoparticles at concentration of 0, 2.5, 5, 10, 20, 40, 60, 80, 100, 120, 150, 200, 400, 600, 800, 1000 mmol/L respectively (10% PEG 200 in DMF as solvents). Next, the mixture was extruded from a needle with a diameter of 0.2 mm and dropped into the 2 mg/mL lipase solution (as a coagulation bath).

After stirring for 24 h at RT, magnetic PAN composite beads with lipase were washed by PBS buffer (50 mM, pH=7.0). Finally, the L/FP hollow composite beads with different molecular weight of PAN were obtained (the concentration of PAN under 3.6 wt% was hard to solidify as a bead). The porosity of the L/FPs was measured by the method in **Section 2.5** of the manuscript and the activity measured by the method in **Section 2.6.2** of the manuscript.

Optimization of the Types of Porogens

PAN (M.w.= 80 k) was firstly dissolved in DMF at a concentration of 20 wt%. The 1 mL the PAN solution was mixed with 27.5 mg Fe_3O_4 nanoparticles, 0.9 mL DMF, and 0.1 mL porogens (glycerol, PEG 200/400/600/2000, and PEI 600/1800/10000 respectively) substantially. Next, the mixture was extruded from a needle with a diameter of 0.2 mm and dropped into the 2 mg/mL lipase solution (as a coagulation bath). After stirring for 24 h at RT, magnetic PAN composite beads with lipase were washed by PBS buffer (50 mM, pH=7.0). Finally, the L/FP hollow composite beads with different molecular weight of PAN were obtained. The porosity of the L/FPs was measured by the method in **Section 2.5** of the manuscript and the activity measured by the method in **Section 2.6.2** of the manuscript.

Optimization of the concentration of PEG 200

PAN (M.w.= 80 k) was firstly dissolved in DMF at a concentration of 20 wt%. The 1 mL the PAN solution was mixed with 27.5 mg Fe_3O_4 nanoparticles and 1 mL different solvents (0, 0.5, 1.25, 2.5, 5, 10, and 20% PEG 200 in DMF respectively) substantially. Next, the mixture was extruded from a needle with a diameter of 0.2 mm and dropped into the 2 mg/mL lipase solution (as a coagulation bath). After stirring for 24 h at RT, magnetic PAN composite beads with lipase were washed by PBS buffer (50 mM, pH=7.0). Finally, the L/FP hollow composite beads with different molecular weight of PAN were obtained. The porosity of the L/FPs was measured by the method in **Section 2.5** of the manuscript and the activity measured by the method in **Section 2.6.2** of the manuscript.

Optimization of Lipase Coagulation Bath

PAN (M.w.= 80 k) was firstly dissolved in DMF at a concentration of 20 wt%. The 1 mL the PAN solution was mixed with 27.5 mg Fe_3O_4 nanoparticles, 0.9 mL DMF, and 0.1 mL PEG 200 substantially. Next, the mixture was extruded from a needle with a diameter of 0.2 mm and dropped into the lipase solution at concentration of 0.023, 0.398, 1.315, 3.165, 3.763, and 5.573 g/L respectively (as a coagulation bath). After stirring for 24 h at RT, magnetic PAN composite beads with lipase were washed by PBS buffer (50 mM, pH=7.0). Finally, the L/FP hollow

composite beads with different molecular weight of PAN were obtained (the concentration of PAN under 3.6 wt% was hard to solidify as a bead). The porosity of the L/FPs was measured by the method in **Section 2.5** of the manuscript and the activity measured by the method in **Section 2.6.2** of the manuscript.

Optimization of DMF Concentration in the Coagulation

PAN (M.w.= 80 k) was firstly dissolved in DMF at a concentration of 20 wt%. The 1 mL the PAN solution was mixed with 27.5 mg Fe_3O_4 nanoparticles, 0.9 mL DMF, and 0.1 mL PEG 200 substantially. Next, the mixture was extruded from a needle with a diameter of 0.2 mm and dropped into the 2 g/L lipase solution containing 0, 20, 40, 60, 80, and 100% DMF respectively (as a coagulation bath). After stirring for 24 h at RT, magnetic PAN composite beads with lipase were washed by PBS buffer (50 mM, pH=7.0). Finally, the L/FP hollow composite beads with different molecular weight of PAN were obtained (the concentration of PAN under 3.6 wt% was hard to solidify as a bead). The porosity of the L/FPs was measured by the method in Section 2.5 of the manuscript and the activity measured by the method in Section 2.6.2 of the manuscript.

Optimization of Composite Bead Sizes

PAN (M.w.= 80 k) was firstly dissolved in DMF at a concentration of 20 wt%. The 1 mL the PAN solution was mixed with 27.5 mg Fe_3O_4 nanoparticles, 0.9 mL DMF, and 0.1 mL PEG 200 substantially. Next, the mixture was extruded from a needle with different diameters and dropped into the 2 g/L lipase solution (as a coagulation bath). After stirring for 24 h at RT, magnetic PAN composite beads with lipase were washed by PBS buffer (50 mM, pH=7.0). Finally, the L/FP hollow composite beads with different molecular weight of PAN were obtained (the concentration of PAN under 3.6 wt% was hard to solidify as a bead). The porosity of the L/FPs was measured by the method in **Section 2.5** of the manuscript and the activity measured by the method in **Section 2.6.2** of the manuscript.

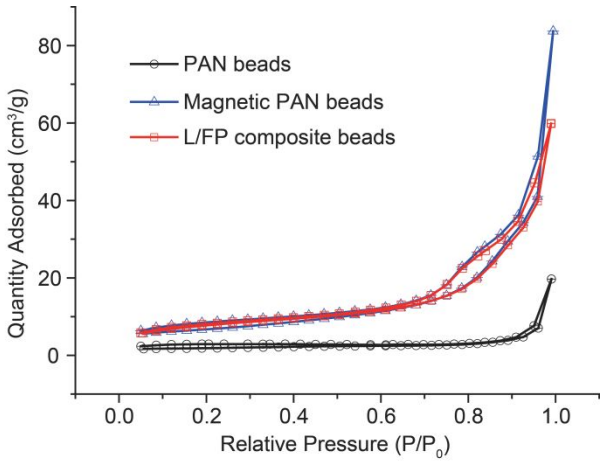

Figure S1. N_2 adsorption and desorption isotherms of the PAN hollow beads (black), magnetic PAN hollow beads (blue), and L/FP hollow composite beads (red).

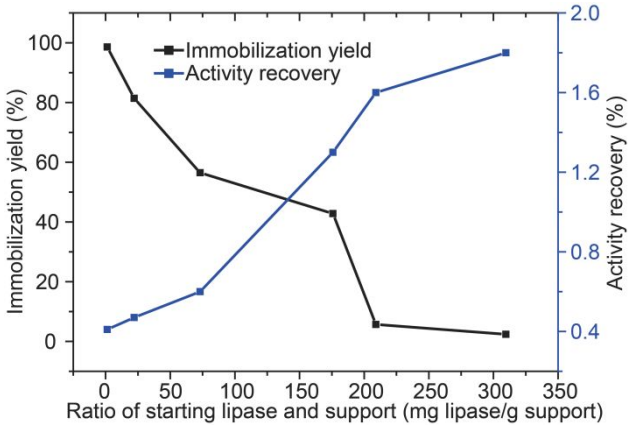

Figure S2. Immobilized yield (black) and activity recovery (blue) of L/FP based on a gradient of the mass ratio of starting lipase and support.