

Supporting Information

Layer-by-Layer Self-assembly Films for Building Magnetic Driven Walking Devices

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Experimental

Materials: Methoxy PEG(PEG, $M_w = 2000$) was purchased from Aldrich Chemical Co, and dried over P_2O_5 under vacuum at 40 °C for 48 h before use. The branched structure of polyethylenimine (PEI, 30% aqueous solution, $M_w=10000$) was procured from Polysciences Inc. α -CD was purchased from Aladdin Chemistry Co., Ltd. Morpholinoethane sulfonic acid (MES), N-hydroxysuccinimide (NHS), sodium chloride (NaCl), sodium hydroxide, sodium bromide (NaBr), sodium hypochlorite (NaClO), 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDCI), hydrochloride, anhydrous sodium sulfate (Na_2SO_4) and all the other chemicals and solvents were analytical grade and used without further purification.

Synthesis of PEG-COOH: PEG-COOH was synthesized according to the method of Bekkum et al.¹ Briefly, 2.5 mmol PEG and 25 mmol NaBr were dissolved in 100 ml water, then 30 mL of NaClO was added, followed by stirring for 10 min at ice bath in a 250 mL flask. The pH of system was adjusted to 5.5 with dilution of HCl. Then 10 mL of TEMPO (1 mg/mL) was added, and the pH of mixture was adjusted to 3.0 by dilution of HCl. Afterward, the reaction mixture was stirred at 0 °C for 3 h. Finally the polymer was extracted three times with chloroform. The extraction was dried over anhydrous Na_2SO_4 . The precipitates ($Na_2SO_4 \cdot xH_2O$) were removed by filtration. The filtrate was distilled under reduced pressure to concentrate, and the oily residue was dried under vacuum at room

temperature to obtain PEG-COOH. Figure S1 showed a typical ^1H NMR spectrum of PEG-COOH.

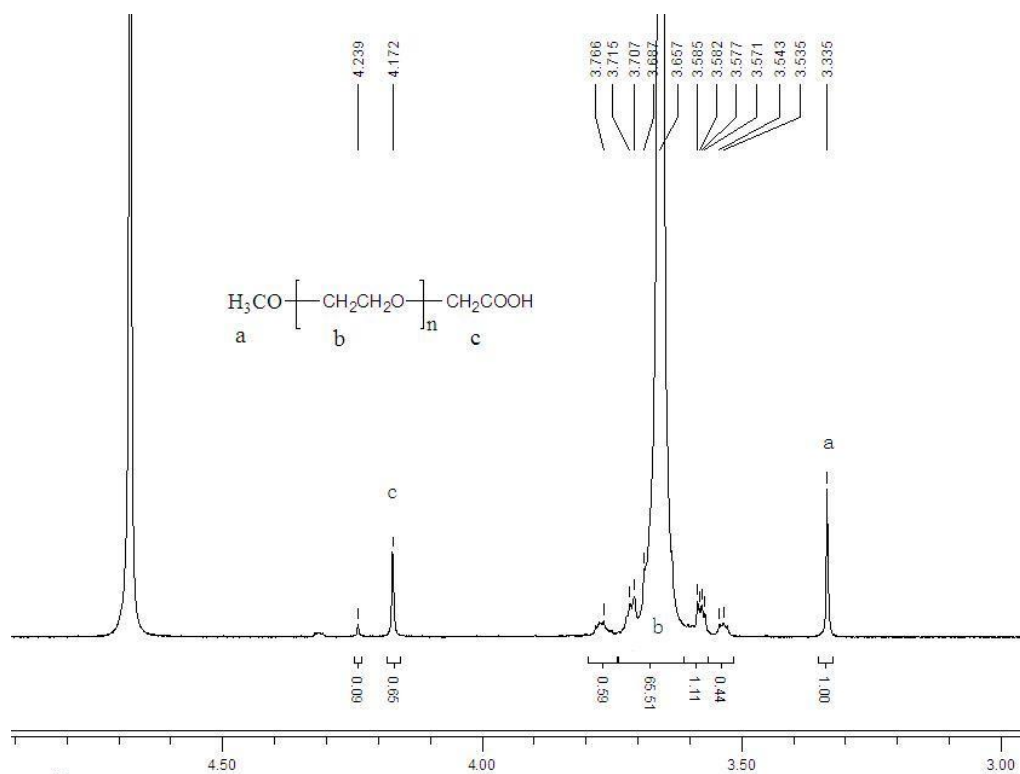


Figure S1 ^1H NMR spectrum of PEG-COOH ($M_n=2,000$) in D_2O .

Synthesis of PEI-PEG: PEI-PEG was prepared according to the procedure of literature.² 0.1 mmol PEI was added in a 20 mL buffer solution of 0.1 M MES and 0.5 M NaCl (the pH of the buffer solution was 5.5). And then 0.05 mmol NHS and 0.1 mmol EDCI (molar ratio of EDCI: NHS: $\text{COO}^- = 2:1:2$) were added to 20 ml PEG-COOH (0.1mmol) solution, followed by stirring for 20 min at ice bath to activate the carboxylic acid groups. Then the PEG-COOH solution was added dropwise to the 20 mL PEI solution. The reaction mixture was stirred for 24 h at ice bath in a 100 ml flask. The crude block copolymer was dialyzed by a Spectra Pore membrane with a molecular weight cutoff of 3500 mol^{-1} for 48 h to remove the redundant PEG-COOH and other small molecules such as NHS, MES, and so on. Then the dialysate was distilled under reduced pressure to

concentrate. The buff solid product was obtained after dried under vacuum at room temperature. Figure S2 showed a typical ^1H NMR spectrum of PEI-PEG.

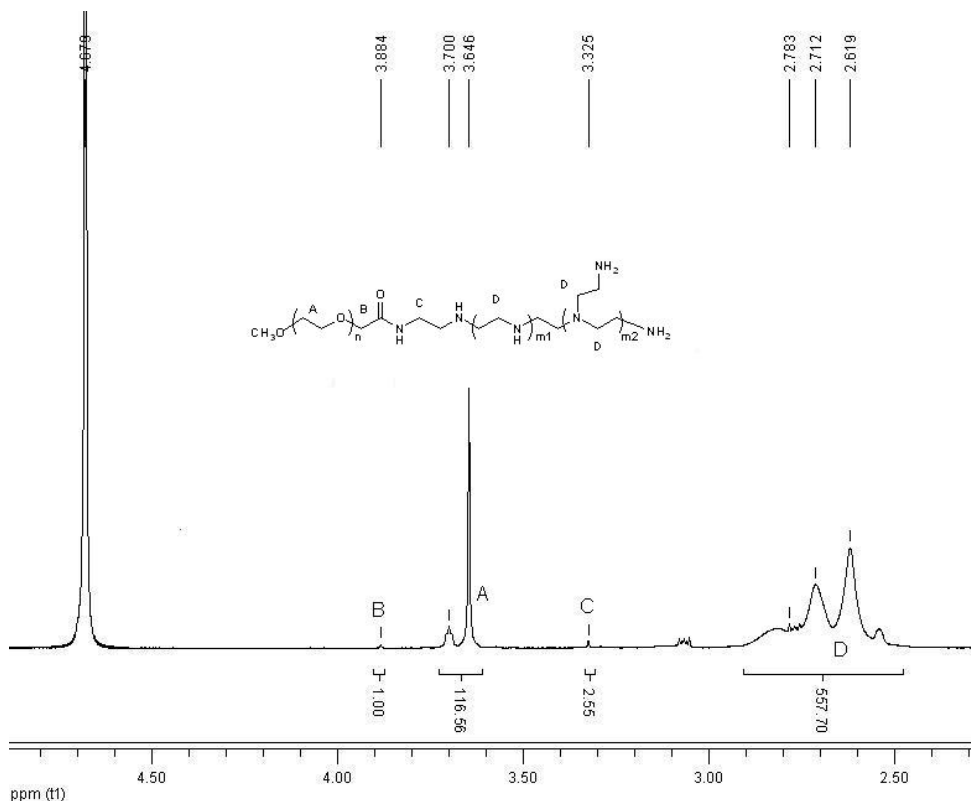


Figure S2 ^1H NMR spectrum of PEI-PEG in D_2O .

Preparation of magnetofluid (Fe_3O_4): 0.47 g FeSO_4 , 0.89 g FeCl_3 and 20 mL H_2O were added into a 100 mL flask. The mixture was stirred at 600 rpm under N_2 until dissolved. Then 5 mL $\text{NH}_3 \cdot \text{H}_2\text{O}$ was quickly dropped into the solution and the mixture was stirred sequentially for 30 min.³ Finally the magnetofluid was obtained.

Preparation of self-assembly PEI-PEG/ α -CD/ Fe_3O_4 spheres: α -CD aqueous solution (6 % w/v, 12 mL) and 1 mL magnetofluid were added dropwise to PEI-PEG aqueous solution (2 % w/v, 4 mL) under stirring at room temperature. After the mixture was stirred for 24 h, the aggregates were collected by centrifugation at 12,000 rpm and lyophilized.

Layer-by-Layer (LBL) Self-assembly Films: The LBL films was prepared by a cyclic repetition of the following operations: (1) dipping of the cellulose nitrate substrate in

1% aqueous solution of PEG-PEI/ α -CD/ Fe_3O_4 for 5 min; (2) rinsing with deionized water for 1 min; (3) dipping in sodium alginate (Alg) solution for 5 min; and (4) rinsing with water. After depositing 100 cycles, the LBL films were immersed in acetone for 48 h to dissolve the cellulose nitrate substrate,⁴ leaving a brown colored film freely suspended in the solution. The obtained thin film was washed by new portion acetone solution for several times to remove the remaining cellulose nitrate molecules completely.

In order to verify the host-guest interaction between PEI-PEG and α -CD, X-ray diffraction (XRD) pattern measurements were performed. Figure S3 showed the XRD patterns of α -CD, PEI-PEG, PEI-PEG/ α -CD. It can be seen that PEI-PEG/ α -CD showed typical polymer- α -CD inclusion channel crystalline peak ($2\theta=19.9^\circ$), while the α -CD crystalline peak ($2\theta=21.5^\circ$) and PEI-PEG crystalline peaks ($2\theta=19.2^\circ$ and 23.3°) were absent,⁵ indicating that the the α -CDs threaded on the PEI-PEG copolymer.

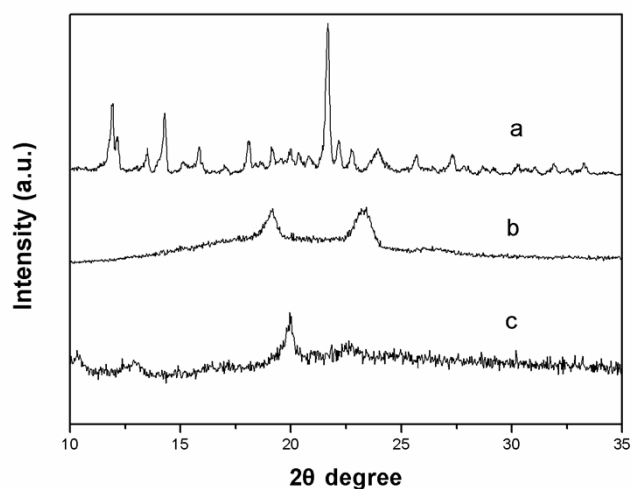


Figure S3 X-ray diffraction patterns of (a) α -CD. (b) PEI-PEG. (c) PEI-PEG/ α -CD particles.

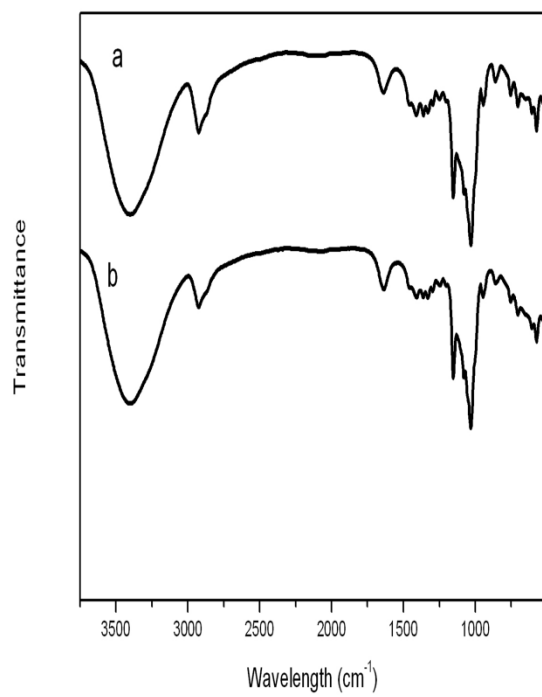


Figure S4 FT-IR spectra of (a) PEI-PEG/ α -CD, (b) PEI-PEG/ α -CD/ Fe_3O_4 .

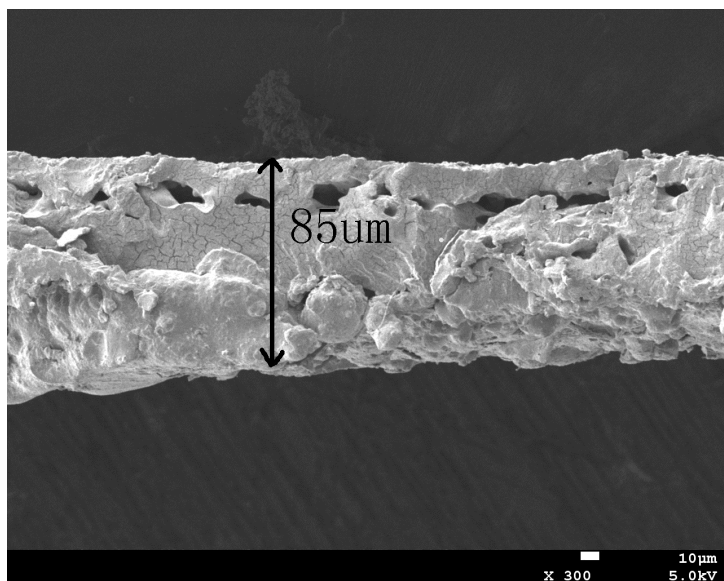


Figure S5 Cross-sectional SEM image of the Alg/(PEI-PEG/ α -CD/ Fe_3O_4) film.

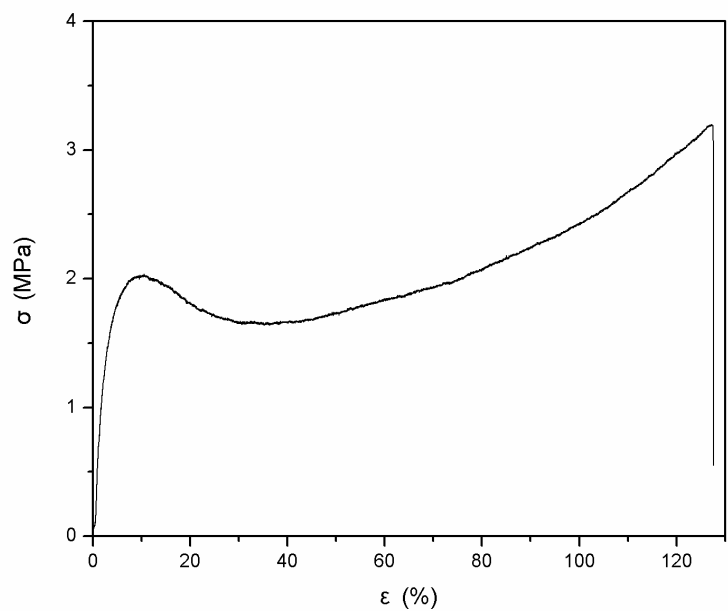


Figure S6 The stress-strain curve of the Alg/(PEI-PEG/ α -CD/ Fe_3O_4) film

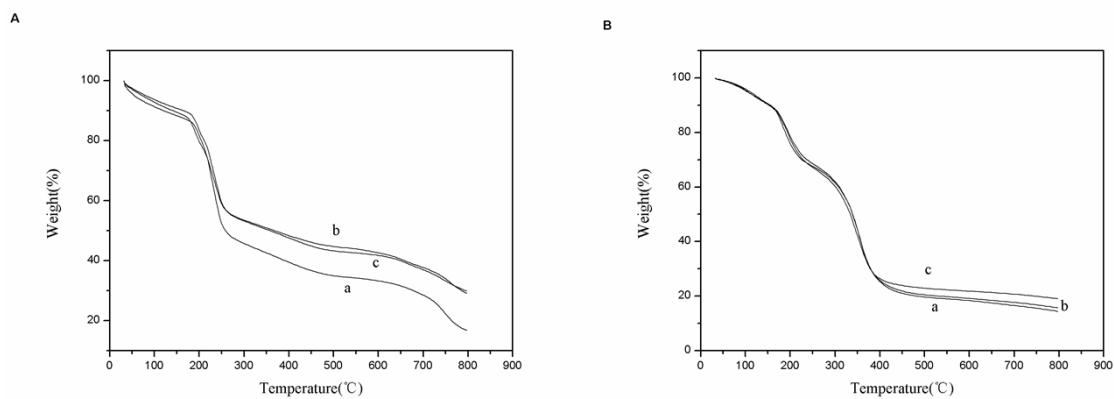


Figure S7 TGA curves of the A) three samples of Alg/ Fe_3O_4 film prepared by casting method B) three samples of Alg/(PEI-PEG/ α -CD/ Fe_3O_4) film.

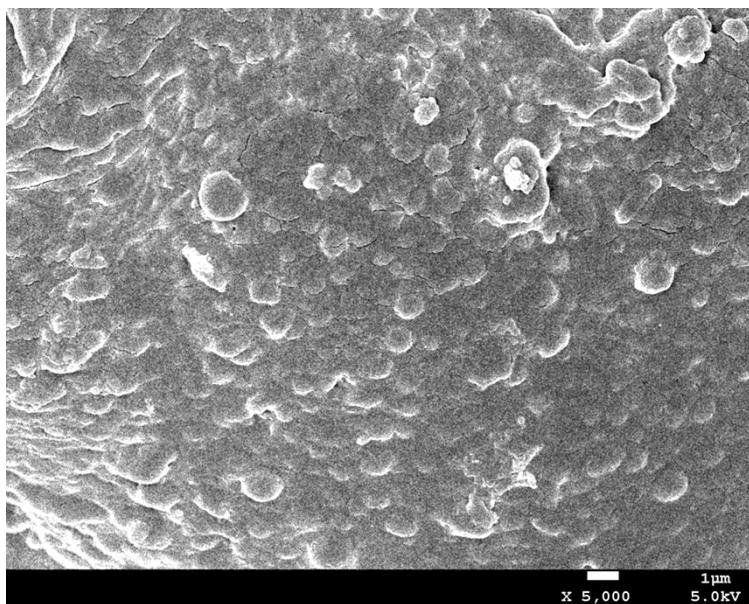


Figure S8 Surface SEM image of Alg/(PEI-PEG/ α -CD/ Fe_3O_4) film

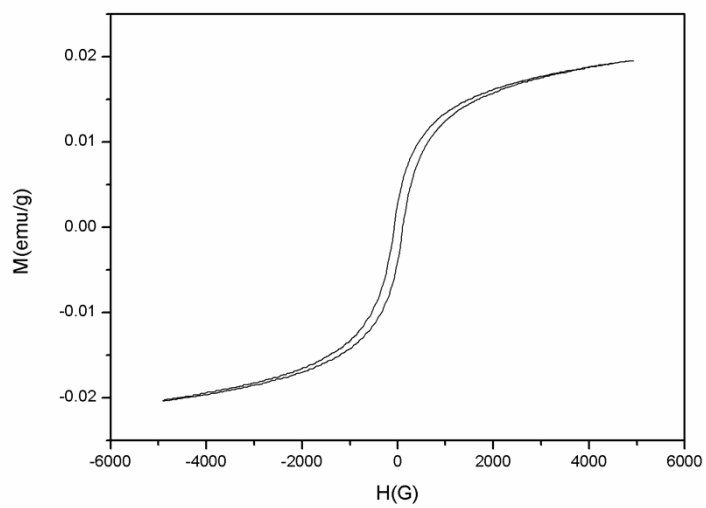


Figure S9 Room temperature magnetic hysteresis loops of Alg/(PEI-PEG/ α -CD/ Fe_3O_4) film.

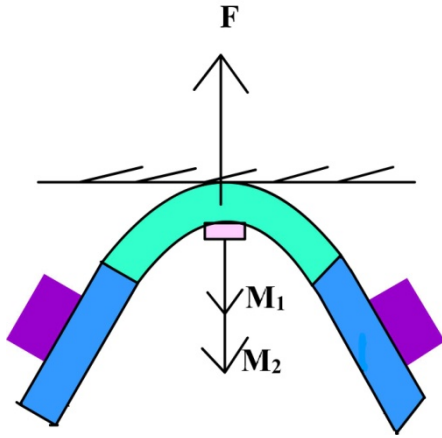


Figure S10 Schematic illustration of the forces that are generated by the films in the magnetic field. M_1 is the gravity of the walking device, M_2 is the gravity of the weights which were pasted on the film, F is the forces that are generated by the films in the magnetic field.

In order to get the forces that are generated by the films in the magnetic field, we paste weights in the middle of the bending film until the critical point that the walking device can not get off the substrate, the gravity of the weights which were pasted to the film and the walking device were the force that are generated by the films in the magnetic field.

The total weight of M_1 and M_2 is 0.3097 g, so the forces that are generated by the films in the magnetic field: $F = (M_1 + M_2) \times g = 3.035mN$

Measurements

The ^1H NMR spectra was measured on an Advance Bruker 600 NMR spectrometer at 600 MHz. Transmission electron microscopy (TEM) observations were performed on a Jeol JEM-100CX electron microscope at an accelerating voltage of 80 kV. Zeta potential of aggregates was measured with a Zetasizer model Nano-ZS, Malvern Instruments, England, and the concentration of all samples were 0.5%. Scanning electron microscopy (SEM) observations were performed on a Jeol JSM-5900LV electron microscope at an accelerating voltage of 20 kV. The X-ray diffraction measurements were performed by using Cu-K α irradiation with PHILIP X'Pert MPD. Tensile strength measurements at room temperature were carried out on a universal tensile tester (INSTRON 5567). The strain rate was 0.6 mm min^{-1} in all experiments.

Reference

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