Supporting information

Magnetic Self-healing Hydrogel

Yaling Zhang[a], *Bin Yang*[a], *Xiaoyong Zhang*[a], *Liangxin Xu*[a], *Lei Tao**[a], *Shuxi Li*[a] *and Yen Wei**[a,b]

[a] Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China;

[b] Key Lab of Organic Optoelectronic & Molecular Engineering of Ministry of Education, Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China;

Tel: +86-010-62792604; E-mail: leitao@mail.tsinghua.edu.cn, weiyen@tsinghua.edu.cn

Experimental section

1. Materials and characterizations

Chitosan (Jinan Haidebe Bioengineering, degree of deacetylation: 85%), carboxyl group modified Fe_3O_4 nanoparticle (99.9%, 20 nm, Beijing DK nano technology Co.LTD) were used as purchased. DF-PEG was synthesized as our previous report[1]. Other reagents were purchased from Sinopharm Chemical Reagent and used without further purification. The magnet used in current work is an NdFeB magnet.

Rheology analyses are performed on a TA-AR G2 rheometer with parallel plate geometry (20 mm in diameter) at 25 ^{o}C.

2. Methods

2.1 Preparation of chitosan-Fe_3O_4 ferrofluid.

A typical preparation of chitosan-Fe_3O_4 ferrofluid is as followed:
Chitosan solution (3%, w/w) was prepared by dissolving 0.30 g of chitosan powder into 10 mL of acetic acid (2%, v/v) aqueous solution, then Fe_3O_4 nanopowder (0.30 g) was added into the chitosan solution, followed with sonication for 1 hour to generate targeting black homogenous sticky chitosan-Fe_3O_4 ferrofluid (Fig. S1a). This chitosan-Fe_3O_4 ferrofluid was found to respond rapidly to an external magnetic field, That is, the whole mixture instead of only Fe_3O_4 particles moved with a magnet. It is noticeable that the ferrofluid is stable, even kept within a magnetic field for 1 week, and the ferrofluid could still maintain homogeneous appearance.

2.2 Preparation of magnetic hydrogel

As a typical method, 40 μL of DF-PEG aqueous solution (20%, w/w) was added to 400 μL of chitosan-Fe_3O_4 ferrofluid, and the hydrogel was formed quickly with vortexing (room temperature, < 2 min) (Fig. 1).

2.3 Rheology analyses

The rheology analyses of the hydrogel were performed as our previous reports. For example, chitosan-Fe_3O_4 ferrofluid (400 μL) was spread on the parallel plate (diameter = 20 mm) of the rheometer, then DF-PEG (40 μL) solution was added evenly on the surface of the ferrofluid solution, the storage moduli G' and loss moduli G'' were immediately collected as a function of time to monitor the gelation process (Fig. 1). As a control, chitosan solution without magnetic nanoparticles was also used to form hydrogel, and the G', G" were recorded with same fashion.
Self-healing analyses were carried out with pre-made hydrogels through vortexing method to obtain the homogenous hydrogel much quicker (Fig. 2).

2.4 Magnetic properties

The Fe_3O_4 nanoparticles afford additional magnetic property to the hydrogel. The magnetic interaction between a home hold NdFeB magnet and a hydrogel in a plastic tube could even conquer the gravity of hydrogel and the tube. (Fig. S1b). Meanwhile, the magnetic hydrogels could also be driven by a normal laboratory magnetic stirrer (Video S1).

2.5 Self-healing analyses

The self-healing experiments were carried out following our previously reported.
A ~1.0 cm diameter hole was artificially punched in the middle of a ~2.0 cm diameter round hydrogel disk, and then photos were taken at different time intervals to monitor the self-healing process. Additionally, quantitatively analyses of the self-healing process were carried out through rheology measurements using strain sweep and

continuous oscillation methods, respectively.

2.6 Magnetism and Self-healing property cooperation

A hydrogel round disk was cut into several pieces and put in a water solution, these hydrogel fragments could be gathered quickly using a magnet, after approximate 10 min, the magnet was removed and the hydrogel pieces were found to regenerate an integral hydrogel (Fig. 3).

2.7 Cytotoxicity evaluation of the DF-PEG

Cytotoxicity evaluation of DF-PEG on Hela cells was determined by MTT assay. Briefly, cells were seeded in 96-well microplates at a density of 5×10^4 cells mL^{-1} in 160 μL of respective media containing 10% FBS for 24 h (37 ℃, 5 % CO_2), then the cells were incubated with 0.5, 1.0, 3.0, 6.0, 9.0 mg mL^{-1} of DF-PEG for another 24 h. The cells were washed with PBS for three times, and 100 μg of MTT dye dissolved in 200 μL of DMEM cell culture media was added to each well and incubated for 4 h. Plates were then analyzed with a microplate reader (VictorIII, Perkin-Elmer). Measurements of dye absorbance were carried out at 490 nm. The values were proportional to the number of live cells. The percent reduction of MTT dye was compared to controls (cells not exposed to DF-PEG), which represented 100% MTT dye reduction. Five replicate wells were used for each control and test concentrations per microplate, and the experiment was repeated three times. Cell survival was expressed as absorbance relative to that of untreated controls. Results are presented as mean ± standard deviation (SD). Same molecular weight PEG was also assayed using the same method.

Supporting data

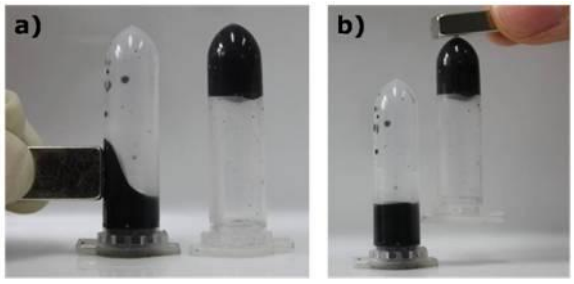

Figure S1. Photos of a) chitosan-Fe_3O_4 ferrofluid and prepared hydrogel, b) magnetic property of the prepared hydrogel.

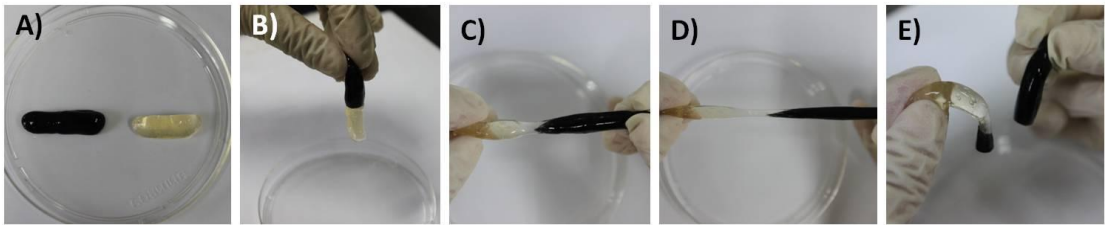

Figure S2. Photos of the self-healed gels under stretching, A) two hydrogel strips (black: Fe_3O_4 contained magnetic hydrogel, transparent: hydrogel without Fe_3O_4), B) self-healed hydrogel after contacting two strips for 1 minute, C, D) continuous stretching of the self-healed hydrogel, E) broken hydrogel with no fracture at the self-healed interface.

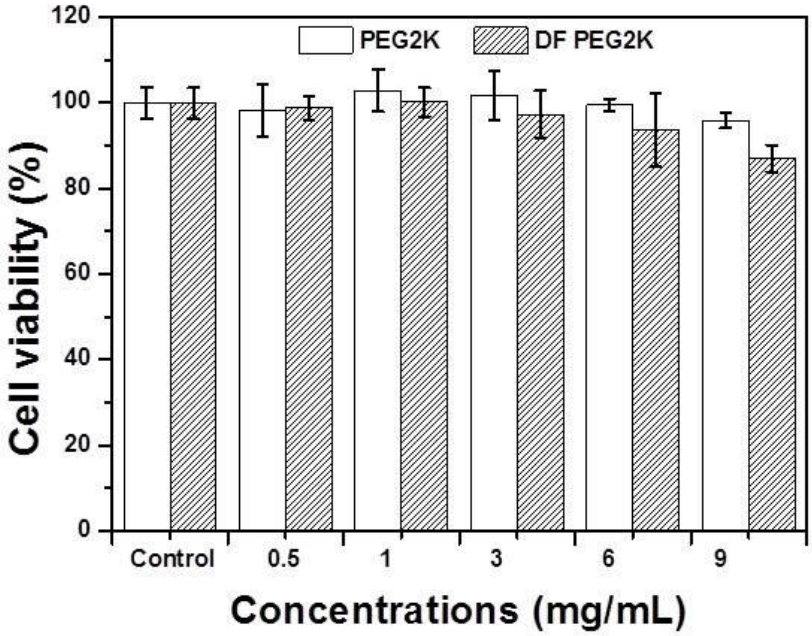

Figure S3. Cytotoxicity evaluation of the synthetic DF-PEG.

(1) Y. Zhang, L. Tao, S. Li and Y. Wei *Biomacromolecules* 2011, **12**, 2894.