

## Electronic Supplementary Information

### Dual-Responsive Multicompartment Nanofibers for Controlled Release of Payloads

Shuai Jiang,<sup>a,b,c</sup> Li-Ping Lv,<sup>a</sup> Katharina Landfester,<sup>a</sup> Daniel Crespy<sup>a,\*</sup>

<sup>a</sup> Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

<sup>b</sup> Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China

<sup>c</sup> University of Chinese Academy of Sciences, Beijing 100049, China

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### Experimental

#### Materials

Tetraethoxysilane (TEOS, Alfa Aesar, 98%), bis[3-(triethoxysilyl)propyl] tetrasulfide (TESPT, Sigma Aldrich, 90%), hexadecane (HD, Sigma Aldrich, 99%), *m*-xylene (Acros Organics,  $\geq 99\%$ ), 2-mercaptobenzothiazole (MBT, Sigma Aldrich, 97%), cetyltrimethylammonium chloride (CTMA-Cl, Acros Organics, 99%), glutaraldehyde (GA, Merck KGaA, 50% aqueous solution), hydrochloride acid (HCl, Sigma Aldrich, 37%), dithiothreitol (DTT, Sigma Aldrich,  $\geq 98\%$ ), and tris(2-carboxyethyl)phosphine hydrochloride (TCEP·HCl, Alfa Aesar,  $\geq 98\%$ ) were used as received. Polyvinyl alcohol (PVA,  $M_w = 125,000 \text{ g}\cdot\text{mol}^{-1}$ , 88 mol% hydrolyzed) and poly(acrylic acid) (PAA,  $M_w = 100,000 \text{ g}\cdot\text{mol}^{-1}$ , 35 wt% in water) were purchased

from Polysciences Inc. Demineralized water was used through all the experiments if not specifically mentioned.

### **Encapsulation of corrosion inhibitor in redox-responsive silica nanocapsules**

Redox-responsive silica nanocapsules loaded with corrosion inhibitors were synthesized by miniemulsion polymerization similarly to a previous procedure.<sup>1</sup> The surface of miniemulsion droplets was used as soft template for the hydrolysis and condensation of alkoxy silanes. Alkoxy silane precursors (1.5 g of TEOS and 0.5 g of TESPT) were first mixed with 125 mg of HD, 1 g of *m*-xylene, and 25 mg of MBT, and then added to 30 mL of a 0.77 mg·mL<sup>-1</sup> aqueous solution of CTMA-Cl. After pre-emulsification under 1000 rpm for 1 h at room temperature, the emulsion was sonicated with ice cooling for 180 s at 70% amplitude in a pulse regime (30 s sonication, 10 s pause) using a Branson 450 W sonifier and a 1/2'' tip. The resulting miniemulsions were stirred under 1000 rpm at room temperature overnight to obtain silica nanocapsules.

### **Preparation of multicompartement nanofibers by colloid-electrospinning**

The fibers were obtained by electrospinning a mixed aqueous solution of PVA, PAA, and silica nanocapsules dispersion. Three fiber samples with different content of PAA (-COOH:-OH = 0:1, 1:1 and 2:1) were prepared and named NF-0, NF-1 and NF-2, respectively. Firstly, 15 wt% PVA aqueous solution was prepared by dissolving PVA in distilled water at 80 °C with vigorous stirring for 5 h. The electrospinning solution was prepared by mixing the 15 wt% PVA solution, the nanocapsules dispersion, and 35 wt% PAA solution at a weight ratio of 2.75:2.25:0, 1.62:2.25:1.13, and

1.15:2.25:1.60. Electrospinning was carried out using a model fabricated by IME Technologies with an applied voltage of 15 kV, a working distance between the spinneret and the collector of 10 cm, and a feeding rate of 0.2 mL·h<sup>-1</sup>. For studying the release of payloads, fibers were collected for 12 h. The diameter of electrospun nanofibers was estimated by counting at least 100 nanofibers from SEM micrographs.

### **Crosslinking of the electrospun nanofibers**

The electrospun nanofibers were first carefully detached from the aluminum foil collector. The detached non-wovens were then exposed to GA/HCl vapor in a vacuum desiccator under 6\*10<sup>-1</sup> MPa for 1 h. 1 mL of 50 wt% GA aqueous solution was used as source of GA vapor. 20 μL of 37 wt% HCl aqueous solution was used as source of HCl vapor for catalyzing the crosslinking reaction between -CHO of GA and -OH of PVA. Afterwards, the crosslinked nanofibrous mats were exposed to air flow in the fume hood for 24 h before use in order to remove the residual GA and HCl.

### **Controlled release of MBT from nanofibers**

To study the pH and redox-responsive release of MBT from electrospun nanofibers, 24 mg of nanofibers and 1 mL of buffer were placed into a dialysis bag (MWCO 14000) with both ends sealed. Afterwards, the dialysis bag was immersed in 9 mL of buffer. Buffers with pH value of 2, 6, and 9 were used. Buffers with 0, 0.07, 0.7, and 7 mmol·L<sup>-1</sup> TCEP·HCl (corresponding to ratio of TCEP:TESPT = 0:1, 0.3:1, 3:1, and 30:1, respectively) were used in solutions with pH values of 2 and 6. In the case of pH = 9, the same molar concentration of DTT was used instead of TCEP·HCl. After given time intervals, 0.4 mL of the solution outside the dialysis bag was taken out for

UV-Vis measurements. An equal amount of fresh reducing agent/buffer solution was added to keep the volume constant. The concentration of released MBT was determined by monitoring the absorption of the peak  $\lambda_{\max} \sim 311$  nm by UV-Vis spectroscopy. A calibration curve drawn by measuring a series of MBT solutions with known concentrations was used.<sup>2</sup>

### **Characterization methods**

The hydrodynamic diameter of silica nanocapsules was evaluated by dynamic light scattering (DLS) using a Nicomp particle sizer (Model 380, PSS, Santa Barbara, CA) at a fixed scattering angle of 90°. The shell thickness of obtained nanocapsules was estimated by counting at least 100 capsules from TEM micrographs. The morphologies of silica nanocapsules and nanofibers were examined with a Gemini 1530 (Carl Zeiss AG, Oberkochen, Germany) scanning electron microscope (SEM) operating at 0.35 kV and a Jeol 1400 (Jeol Ltd, Tokyo, Japan) transmission electron microscope (TEM) operating at an accelerating voltage of 120 kV. SEM and TEM samples of silica nanocapsules were prepared by casting the diluted nanocapsule dispersions on silicon wafers and 400-mesh carbon layer-coated copper grids, respectively. The samples of nanofibers for SEM and TEM were prepared by depositing electrospun nanofibers on silicon wafers and copper grids, respectively. The UV-Vis absorption spectra were recorded with a Perkin Elmer Lambda 25 UV-Vis spectroscopy.

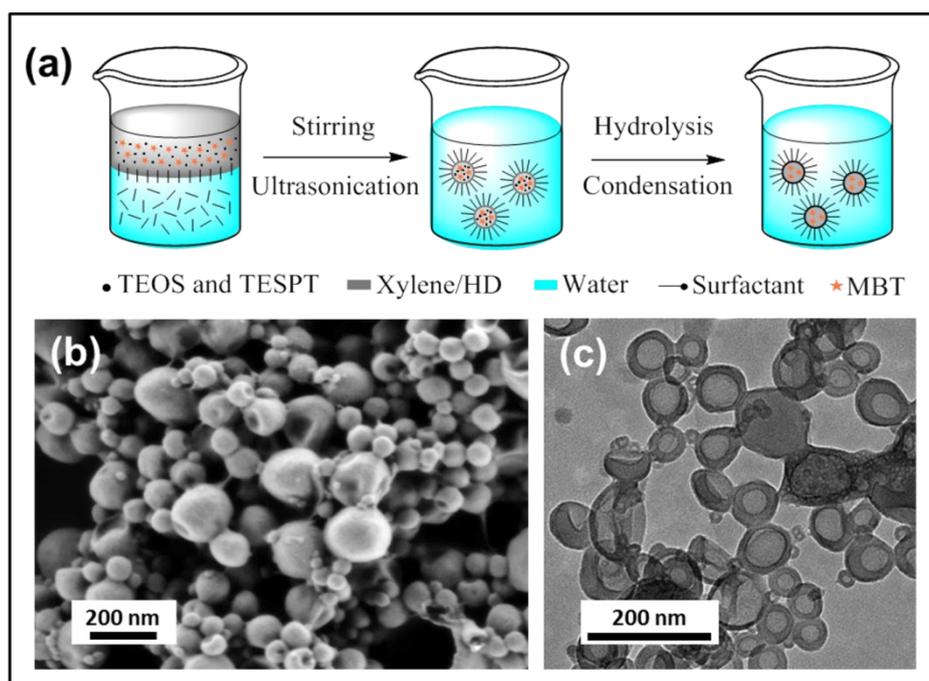
The loading efficiency of MBT in silica nanocapsules was estimated by UV-vis spectroscopy. 0.5 mL of the miniemulsion was first mixed with 0.5 mL of 35 g·L<sup>-1</sup>

NaCl solution to destabilize the capsules dispersion. The mixture was centrifuged at 4000 rpm for 15 min to separate the capsules from the dispersion. The supernatant was analyzed by using UV-vis spectroscopy according to a preliminary calibration at ~ 331 nm and compared to the theoretical loading amount.

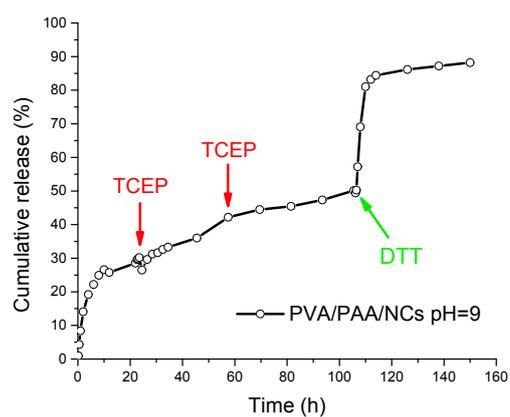
To measure the swelling degree of nanofibers, dry samples were weighed and immersed in different buffer solutions (pH = 2, 6, and 9). The equilibrium was considered to be reached when the weight of the wet sample did not significantly change. The weight of swollen samples was measured after the excessive water on the surface was removed with filter paper. The swelling degree of the fibers content is defined as follows:

$$\text{Swelling degree} = \frac{m_s - m_o}{m_o} \times 100\% \quad (\text{S1})$$

where  $m_s$  and  $m_o$  are the weights of the samples in the swollen and dried states, respectively.



**Figure S1.** (a) Schematic illustration of miniemulsion process for preparing silica nanocapsules; (b) SEM and (c) TEM micrographs of redox-responsive silica nanocapsules.



**Figure S2.** The reducing effect of TCEP and DTT on the release of MBT from PVA/PAA nanofibers at pH = 9.

## References

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