

**Keywords:** cancer hormone therapy, diethylstilbestrol, targeted delivery, reactive oxygen species

### Acknowledgements

The authors acknowledge financial support from the Czech Ministry of Health (#16-30544A) and of Education, Youth and Sports (# KONTAKT LH14292, 7F14009, LM2015064; #POLYMAT LO1507) and the Czech Grant Foundation (#13-08336S).

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doi:10.1016/j.jconrel.2017.03.047

### Fabrication and characterization of coaxial electrospun multicomponent fibrous graft for vascular tissue engineering

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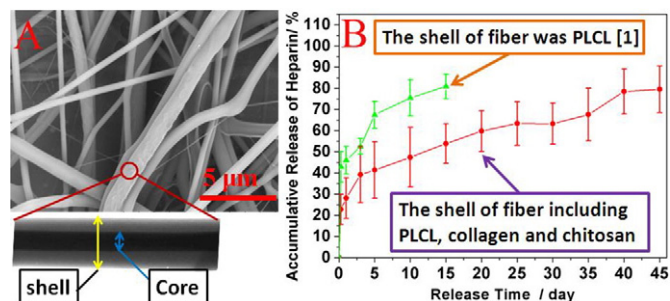
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Grafts loading with heparin have been demonstrated to possess antithrombotic performance. However, the heparin released too fast which did not match the endothelialization rate, resulting in graft occlusion ultimately. Fabrication of core-shell fibrous vascular graft which heparin was encapsulated into the inside of the fibers via coaxial electrospinning became a great choice, and the early research showed partial improvement has been achieved [1, 2]. In our recent study, heparin as a core could be encapsulated into multicomponent fibrous graft (including collagen, chitosan and poly(L-lactide-ε-caplacton) (PLCL)) through coaxial electrospinning (Fig. 1A). With three different compositions as shell, heparin could be greatly scattered inside of three different fibers. The results showed that heparin could be sustained released over 45 days, as well as lower initial burst release compared to early reports (Fig. 1B) [1]. This kind of graft could keep releasing heparin sustainably, partially because of the different degradation rates of collagen, chitosan and PLCL. Moreover, these three blend components probably improved efficiency of heparin encapsulation during electrospinning procedure, which contributed to a low initial burst release. Therefore, this kind of graft has great potential for vascular tissue engineering.

**Keywords:** coaxial electrospinning, sustained release, heparin, vascular tissue engineering



**Fig. 1.** (A) SEM and TEM of coaxial electrospun fibers with heparin loaded. (B) Accumulative release of heparin from different grafts.

### Acknowledgements

The authors are grateful for the financial support from the National Natural Science Foundation of China (31500784), China Postdoctoral Science Foundation Funded Project (2015M580790), and Program of Introducing Talents of Discipline to Universities (B16033).

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doi:10.1016/j.jconrel.2017.03.048

### Photon-triggered polymersome rupture under temporal, spatial and spectral control

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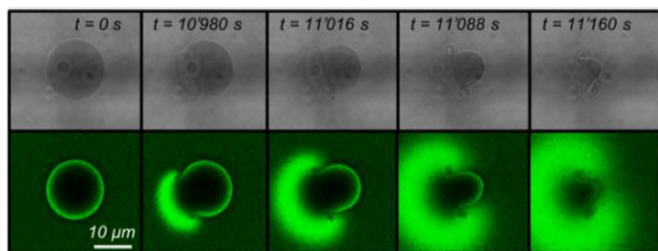
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Polymersomes are robust self-assembled vesicular structures that are widely studied in a variety of domains from nanomedicine to artificial cell design [1]. Control over their membrane diffusion properties and structural integrity is crucial for their future development [2]. In particular, a high level of control is mandatory in drug delivery applications where species have to be released at the right place and time. Here, we present a high precision method allowing programmed vesicle rupture with full control in time, space and excitation wavelength for selective cargo-release.

We designed an easy and tunable protocol for light-driven specific polymersome rupture controlled in time and space, which combines the advantages of utilizing light as a trigger and the fast release of components from bursting vesicles. Our system is based on laser excitation of hydrophilic dyes loaded in the lumen of distinct giant poly(butadiene)-*b*-poly(ethylene oxide) polymersomes. Upon excitation,

the fast generation of reactive oxygen species leads to an increase of the internal osmotic pressure that can not be compensated fast enough, resulting in subsequent vesicle rupture (Fig. 1). This process allows for a precise and fast release of entrapped species from different compartments. Additionally, such a selective mechanism allows discrimination between two types of vesicles within a group of many and successive triggered release of their content without altering the remaining vesicles. This unique mechanism is shown to selectively rupture polymersomes with high precision, and even to deliver small polymersomes and liposomes.



**Fig. 1.** Confocal microscopy images of controlled rupture of a polymersome under laser irradiation.

**Keywords:** triggered rupture, polymersomes, cargo-release, self-assembly, light stimulus

#### Acknowledgements

This work was funded by the French Ministry of Research and Education and the Agence Nationale de la Recherche (ANR program NO-SynthCell).

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doi:10.1016/j.jconrel.2017.03.049

#### *In vivo* visualized degradation of injectable hydrogel by real-time fluorescence tracking

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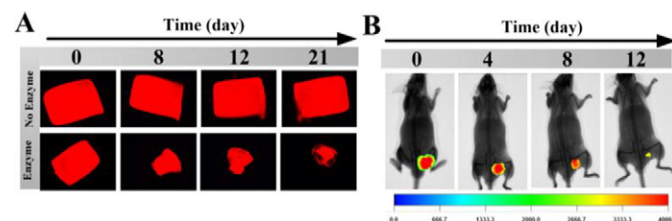
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Real-time and non-invasive monitoring the *in vivo* degradation of hydrogel via fluorescence image is valuable to design suitable degradation rate matching with tissue regeneration rate and to screen of hydrogel for signal molecular and cells delivery [1]. Fluorescence tracking the degradation of hydrogels is simple and inexpensive. Fluorescent hydrogel shows intrinsic fluorescent properties either via covalent linkage of fluorescent dyes (FITC and Rhodamine) to their polymer backbones or in combination of

quantum dots. However, fluorescent dyes and quantum dots have several drawbacks such as poor photostability, photobleaching, and potential toxicity. We developed UV crosslinkable, injectable chitosan for the preparation of patterned cell-laden microgels for tissue engineering and rapid transdermal curing hydrogel for localized drug delivery [2], and high yield synthesis of biocompatible carbon nanodots (CNDs) for cell imaging and mercury ion detection [3].

To visualize degradation of injectable hydrogel *in vivo*, we proposed CNDs with advantages of good photostability and non-photobleaching as fluorescent probes. CNDs with size of 3 nm show maximum emission wavelength of 457 nm when  $\lambda_{ex}$  was 375 nm. Red chitosan hydrogel with encapsulated CNDs maintained the original size and the area of fluorescent signal merely changes 10%. CNDs hardly leached or diffused in the absence of enzyme, however the size of red hydrogel and the area of fluorescent signal decreased significantly (80%) at day 21 in presence of enzyme (Fig. 1A). Fig. 1B shows the real-time and non-invasive visualization degradation of injectable chitosan hydrogel *in vivo*. The injectable hydrogel with encapsulated CND under skin was shown by the red area with clear boundary in mouse. The relationship between fluorescence lessening and degradation time was established by quantitative analysis of fluorescence images, which shows similar degradation curve to that obtained by the weight loss method. Injectable chitosan hydrogel was hardly detected by fluorescent signal at day 12, which demonstrated a faster degradation *in vivo* than *in vitro* (day 21).



**Fig. 1.** CNDs serving as fluorescent probe for quantitative assessment visualized degradation of injectable hydrogel *in vitro* (A) and *in vivo* (B).

**Keywords:** *In vivo* degradation, carbon nanodots, injectable hydrogel, fluorescence tracking

#### Acknowledgements

The authors thank the financial support from 51372051, 51321061, 2012CB339300, 2016TS03, 2013RFLXJ023, HIT.IBRSEM.201302.

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doi:10.1016/j.jconrel.2017.03.050