## **Supporting Information**

## Fabrication of Hierarchical Macroporous Biocompatible Scaffolds by Combining Pickering High Internal Phase Emulsion Templates with Three-Dimensional Printing

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Fitting release profiles by different kinetic models

S-1

First-order model: ref.?

$$\ln(100 - Q_t) = k_1 t + C_1 \tag{1}$$

where  $Q_t$  is the % cumulative release rate of the drug at time t,  $k_1$  and  $C_1$  are the first-order release constants. In this case, the amount of drug released at each time was proportional to the residual drug inside the drug carrier.

Higuchi model: ref.?

$$Q_t = k_H t^{1/2} + C_H (2)$$

where  $k_H$  and  $C_H$  are the Higuchi release constants. In this way, the release drug from the insoluble matrix is proportional to the square root of time. This model indicates that the drug release process is based on Fickian diffusion.

## Hixson–Crowell model: ref.?

$$100^{1/3} - (100 - Q_t)^{\frac{1}{3}} = k_C t + C_H \tag{4}$$

where  $k_c$  and  $C_H$  are the Hixson–Crowell release constants. In this case, the cubic root of the unreleased drug is proportional to time, and the geometrical shape of the drug carriers reduced proportionally with time. This model describes the drug release process as based on drug erosion from drug carriers.

**Table S1**. Correlation coefficients of the linear regression of fitting release profiles by different kinetic models.

| Sample          | First-order model R <sub>1</sub> <sup>2</sup> | Higuchi model R <sub>H</sub> <sup>2</sup> | Hixson–Crowell model R <sub>C</sub> <sup>2</sup> |
|-----------------|---|---|--|
| $P_4S_{2.5}-75$ | 0.369   | 0.573                                     | 0.956  |
| $P_5S_{2.5}-75$ | 0.424   | 0.660                                     | 0.895  |
| $P_6S_{2.5}-75$ | 0.333   | 0.560                                     | 0.999  |

 $R_{1^2}$ ,  $R_{H^2}$ ,  $R_c^2$ : Correlation coefficients of the corresponding kinetic models



Figure S1. Digital photos of W/O Pickering emulsions with different formulations 30 min after emulsification: (1)  $P_6S_{2.5}$ -70, (2)  $P_6S_{2.5}$ -75,(3)  $P_6S_{2.5}$ -80, (4)  $P_6S_{2.0}$ -75, (5)  $P_6S_{3.0}$ -75, (6)  $P_7S_{2.5}$ -75, (7)  $P_5S_{2.5}$ -75, (8)  $P_4S_{2.5}$ -75.



**Figure S2.** SEM micrographs of HmPB scaffolds with different formulations:  $(b^{*_1}, b^{*_2})$ P<sub>6</sub>S<sub>2.5</sub>-75;  $(d^{*_1}, d^{*_2})$  P<sub>5</sub>S<sub>2.5</sub>-75;  $(e^{*_1}, e^{*_2})$  P<sub>4</sub>S<sub>2.5</sub>-75.



Figure S3. SEM micrograph of the surface of the printed line of  $P_6S_{2.5}$ -75.



**Figure S4**. Digital photos of side view (top) and top view (bottom) of HmPB scaffolds for (left) P4S<sub>2.5</sub>-75, (middle) P<sub>5</sub>S<sub>2.5</sub>-75 and (right) P<sub>6</sub>S<sub>2.5</sub>-75.