# Patterned Porous Polymer Film for Localized Capture of Insulin and Glucose-Responsive Release

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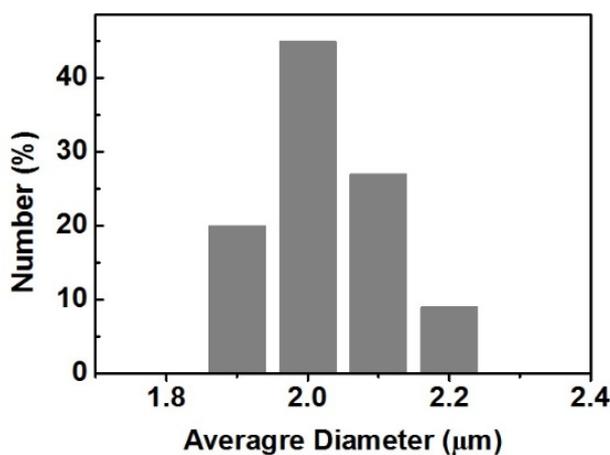


**Fig. S1** Histogram referring to the size-distribution of cavities in PS porous film, where the concentrations of PS and DDA are 6 and 0.5 mg/mL, and the volume of microemulsion is maintained at 5%.
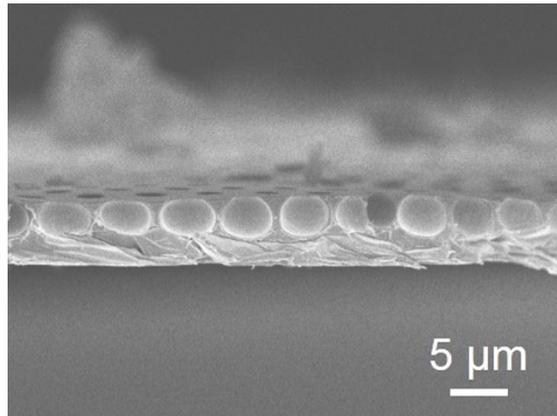
**Fig. S2** SEM images viewed from cross section of PS film prepared by casting the microemulsion solution, where the concentrations of PS and DDA are 6 and 0.5 mg/mL in dichloromethane, and the volume fraction of water in the microemulsion is 5%.
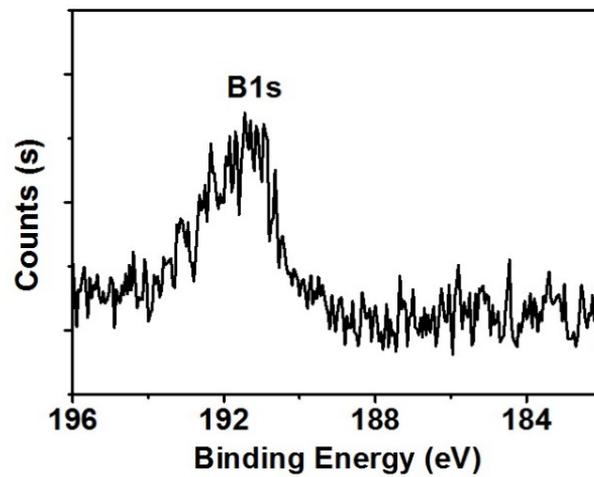


**Fig. S3** XPS spectrum of PBA-PAA/PS porous film.
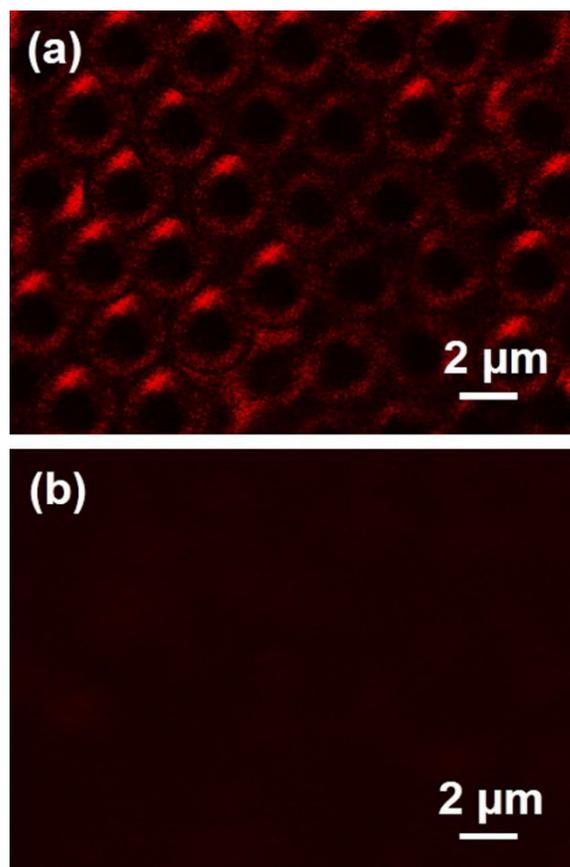
**Fig. S4** CLSM images of (a) Alg-APBA-PAA/PS and (b) APBA-PAA/PS porous film after immersion in CAR aqueous solution.
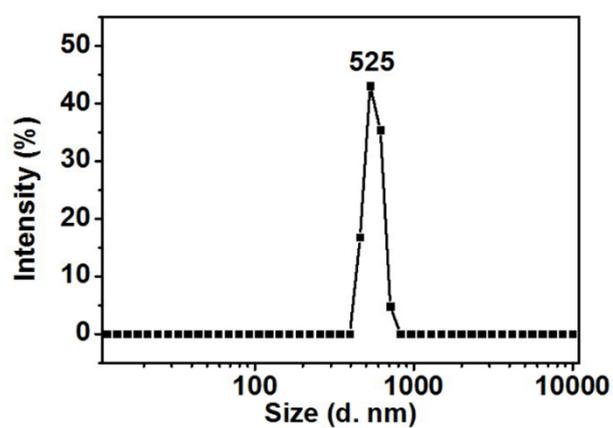


**Fig. S5** DLS plot of insulin aggregates after the immersion of insulin loaded PS porous film in 0.8 M NaCl aqueous solution at pH 5.3.

**Table S1** Frequency of quartz crystal, the porous film, porous film with insulin and porous film after releasing insulin on a quartz crystal, respectively.[a]

| Samples | Frequency of quartz crystal (Hz) | Frequency of porous film adsorption on quartz crystal (Hz) | Frequency of porous film with insulin adsorption on quartz crystal (Hz) | Frequency of porous film release insulin adsorption on quartz crystal (Hz) |
|---|---|---|---|---|
| Film entry 1 | 9017740 | 9017486 | 8993907 | 9016737 |
| Film entry 2 | 9015223 | 9014950 | 8993903 | 9014040 |
| Film entry 3 | 9014314 | 9014024 | 8993440 | 9013093 |

[a] Loading and releasing experiments are accomplished in 0.25 mg/mL insulin for 1 h, and 50 mM glucose solution for 3 h at 25 °C, respectively, and both of the solutions contain 0.8 M NaCl under pH 5.3

**Table S2** Frequency of porous film and porous film with glucose on a quartz crystal, and mass of glucose located on porous film.[a]

| Samples | Frequency of porous film adsorption on quartz crystal (Hz) | Frequency of porous film with insulin adsorption on quartz crystal (Hz) | Mass of loading glucose ($\mu g/cm^2$) |
|---|---|---|---|
| Film entry 1 | 9017645 | 9017492 | 0.834 |
| Film entry 2 | 9018374 | 9018218 | 0.850 |
| Film entry 3 | 9016434 | 9016275 | 0.867 |

[a] Loading experiments are accomplished in 50 mM glucose solution containing 0.8 M NaCl under pH 5.3 for 3 h at 25 °C.

**Table S3** Frequency of porous film and porous film with Alg on a quartz crystal, and mass of Alg located on porous film.[a]

| Samples | Frequency of porous film adsorption on quartz crystal (Hz) | Frequency of porous film with insulin adsorption on quartz crystal (Hz) | Mass of loading Alg ($\mu$g/cm$^2$) |
|---|---|---|---|
| Film entry 1 | 9017739 | 9017598 | 0.768 |
| Film entry 2 | 9018436 | 9018300 | 0.741 |
| Film entry 3 | 9017453 | 9017311 | 0.774 |

[a] Loading experiments are accomplished in 3 mg/mL Alg solution for 3 h at 25 °C.

**Table S4** Frequency of quartz crystal, the porous film, porous film with insulin, and porous film after releasing insulin on a quartz crystal, respectively.[a]

| Samples | Frequency of quartz crystal (Hz) | Frequency of porous film adsorption on quartz crystal (Hz) | Frequency of porous film with insulin adsorption on quartz crystal (Hz) | Frequency of porous film release insulin adsorption on quartz crystal (Hz) |
|---|---|---|---|---|
| Film entry 1 | 9018470 | 9018235 | 8997188 | 9014026 |
| Film entry 2 | 9017690 | 9017430 | 8996381 | 9013642 |
| Film entry 3 | 9017288 | 9017033 | 8995982 | 9013034 |

[a] Loading and releasing experiments are accomplished in 0.25 mg/mL insulin solution containing 0.8 M NaCl under pH 5.3 for 1 h, and 50 mM glucose solution without salt under pH 5.3 for 3 h at 25 °C, respectively.

**Table S5** Mass of insulin aggregates located on and released from the PS film, as well as the efficiency of insulin releasing.[a]

| Samples | Mass of loading insulin (mg/cm$^2$) | Mass of releasing insulin (mg/cm$^2$) | Insulin releasing efficiency (%) |
|---|---|---|---|
| Film entry 1 | 0.114 | 0.091 | 79.8 |
| Film entry 2 | 0.115 | 0.094 | 81.7 |
| Film entry 3 | 0.114 | 0.093 | 81.6 |

[a] Loading and releasing experiments are accomplished in 0.25 mg/mL insulin solution containing 0.8 M NaCl under pH 5.3 for 1 h, and 50 mM glucose solution without salt under pH 5.3 for 3 h at 25 °C, respectively.

**Table S6** Mass of insulin aggregates loaded on and released from the PS film, as well as the efficiency of insulin releasing.[a]

| Samples | Mass of loading insulin (mg/cm$^2$) | Mass of releasing insulin (mg/cm$^2$) | Insulin releasing efficiency (%) |
|---|---|---|---|
| Film entry 1 | 0.120 | 0.118 | 98.3 |
| Film entry 2 | 0.116 | 0.113 | 97.4 |
| Film entry 3 | 0.118 | 0.115 | 97.5 |

[a] Loading and releasing experiments are accomplished in 0.25 mg/mL insulin solution containing 0.8 M NaCl under pH 5.3 for 1 h, and 50 mM glucose solution with 0.8 M NaCl under pH 7 for 3 h at 25 °C , respectively.

**Table S7** Mass of insulin aggregates loaded on and released from the PS film, as well as the efficiency of insulin releasing.[a]

| Samples | Mass of loading insulin (mg/cm$^2$) | Mass of releasing insulin (mg/cm$^2$) | Insulin releasing efficiency (%) |
|---|---|---|---|
| Film entry 1 | 0.119 | 0.117 | 98.3 |
| Film entry 2 | 0.121 | 0.118 | 97.5 |
| Film entry 3 | 0.117 | 0.114 | 97.4 |

[a] Loading and releasing experiments are accomplished in 0.25 mg/mL insulin solution containing 0.8 M NaCl under pH 5.3 for 1 h, and 50 mM glucose solution with 0.1 M phosphate buffer saline under pH 7.4 for 3 h at 25 °C , respectively.
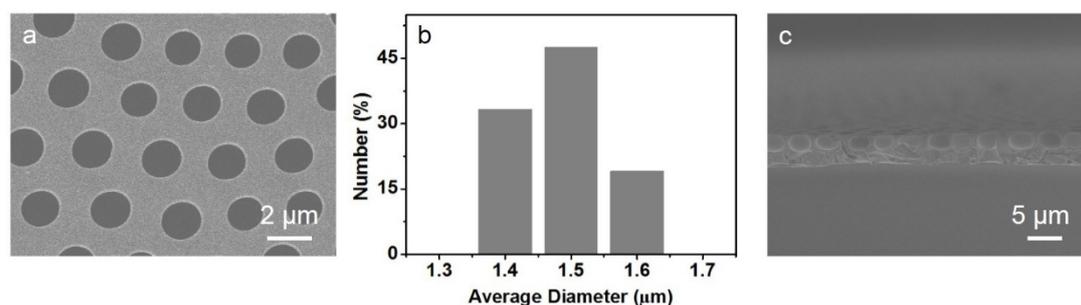


**Fig. S6** SEM images viewed from (a) top surface, (b) histogram referring to the size-distribution of cavities, and (c) cross section of PS porous film, where the concentrations of PS and DDA are 6 and 0.1 mg/mL, and the volume of microemulsion is maintained at 5%.

**Table S8** Frequency of porous film, porous film with insulin, and porous film after releasing insulin on a quartz crystal, respectively.[a]

| Samples | Frequency of porous film adsorption on quartz crystal (Hz) | Frequency of porous film with insulin adsorption on quartz crystal (Hz) | Frequency of porous film release insulin adsorption on quartz crystal (Hz) |
|---|---|---|---|
| Film entry 1 | 9015913 | 8996647 | 9015169 |
| Film entry 2 | 9013797 | 8994898 | 9013053 |
| Film entry 3 | 9012838 | 8993388 | 9011921 |

[a] Loading and releasing experiments are accomplished in 0.25 mg/mL insulin for 1 h, and 50 mM glucose solution for 3 h at 25 °C, respectively, and both of the solutions contain 0.8 M NaCl under pH 5.3

**Table S9** Mass of insulin aggregates loaded on and released from the PS film, as well as the efficiency of insulin releasing.[a]

| Samples | Mass of loading insulin (mg/cm$^2$) | Mass of releasing insulin (mg/cm$^2$) | Insulin releasing efficiency (%) |
|---|---|---|---|
| Film entry 1 | 0.105 | 0.101 | 96.1 |
| Film entry 2 | 0.103 | 0.099 | 96.1 |
| Film entry 3 | 0.106 | 0.101 | 95.6 |

[a] Loading and releasing experiments are accomplished in 0.25 mg/mL insulin for 1 h, and 50 mM glucose solution for 3 h at 25 °C, respectively, and both of the solutions contain 0.8 M NaCl under pH 5.3
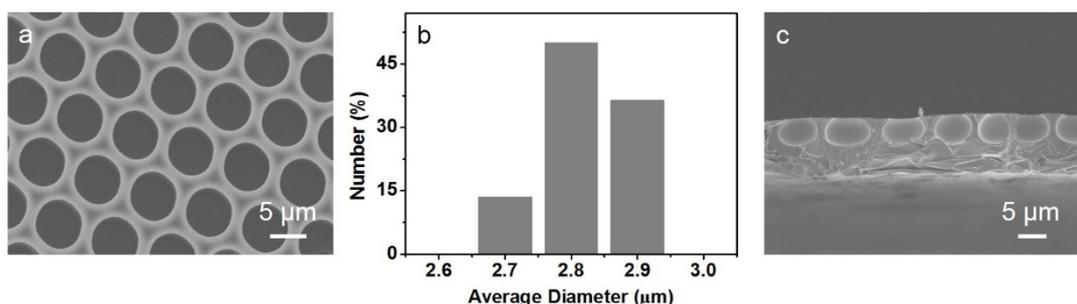
**Fig. S7** SEM images viewed from (a) top surface, (b) histogram referring to the size-distribution of cavities, and (c) cross section of PS porous film, where the concentrations of PS and DDA are 6 and 1 mg/mL, and the volume of microemulsion is maintained at 5%.

**Table S10** Frequency of porous film, porous film with insulin, and porous film after releasing insulin on a quartz crystal, respectively.[a]

| Samples | Frequency of porous film adsorption on quartz crystal (Hz) | Frequency of porous film with insulin adsorption on quartz crystal (Hz) | Frequency of porous film release insulin adsorption on quartz crystal (Hz) |
|---------|------------------------------------------------------------|--------------------------------------------------------------------------|----------------------------------------------------------------------------|
| Film entry 1 | 9017093 | 8990512 | 9015809 |
| Film entry 2 | 9016262 | 8990023 | 9015161 |
| Film entry 3 | 9015184 | 8987478 | 9014083 |

[a] Loading and releasing experiments are accomplished in 0.25 mg/mL insulin for 1 h, and 50 mM glucose solution for 3 h at 25 °C, respectively, and both of the solutions contain 0.8 M NaCl under pH 5.3.

**Table S11** Mass of insulin aggregates loaded on and released from the PS film, as well as the efficiency of insulin releasing.[a]

| Samples | Mass of loading insulin (mg/cm$^2$) | Mass of releasing insulin (mg/cm$^2$) | Insulin releasing efficiency (%) |
|---|---|---|---|
| Film entry 1 | 0.145 | 0.138 | 95.2 |
| Film entry 2 | 0.143 | 0.137 | 95.8 |
| Film entry 3 | 0.151 | 0.145 | 96.0 |

[a] Loading and releasing experiments are accomplished in 0.25 mg/mL insulin for 1 h, and 50 mM glucose solution for 3 h at 25 °C, respectively, and both of the solutions contain 0.8 M NaCl under pH 5.3.

**Table S12** Frequency of quartz crystal, the porous film, porous film with insulin, and porous film after releasing insulin on a quartz crystal, respectively.[a]

| Samples | Frequency of quartz crystal (Hz) | Frequency of porous film adsorption on quartz crystal (Hz) | Frequency of porous film with insulin adsorption on quartz crystal (Hz) | Frequency of porous film release insulin adsorption on quartz crystal (Hz) |
|---|---|---|---|---|
| Film entry 1 | 9017845 | 9017565 | 8994586 | 9016197 |
| Film entry 2 | 9015934 | 9015637 | 8994178 | 9014693 |
| Film entry 3 | 9017937 | 9017668 | 8996733 | 9016580 |

[a] Loading and releasing experiments are accomplished in 0.25 mg/mL insulin solution containing 0.8 M NaCl under pH 5.3 for 1 h at 25 °C , and 50 mM glucose solution with 0.8 M NaCl under pH 5.3 for 3 h at 35 °C , respectively.

**Table S13** Summary of Mass of insulin aggregates loaded on and released from the patterned PS film, as well as their efficiency of insulin releasing.[a]

| Samples | Mass of loading insulin (mg/cm$^2$) | Mass of releasing insulin (mg/cm$^2$) | Insulin releasing efficiency (%) |
|---|---|---|---|
| Film entry 1 | 0.125 | 0.118 | 94.4 |
| Film entry 2 | 0.117 | 0.112 | 95.7 |
| Film entry 3 | 0.114 | 0.108 | 94.7 |

[a] Loading and releasing experiments are accomplished in 0.25 mg/mL insulin solution containing 0.8 M NaCl under pH 5.3 for 1 h at 25 °C , and 50 mM glucose solution with 0.8 M NaCl under pH 5.3 for 3 h at 35 °C , respectively.