Supporting information

In-Situ Microfluidic Fabrication of Multi-Shape Inorganic/Organic Hybrid Particles with Controllable Surface Texture and Porous Internal Structure

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(1) Microfluidic fabrication of pure PLGA particles

Figure S1. SEM images of pure PLGA particles fabricated in a microfluidic flow-focusing device. PLGA dissolved in dichloromethane were used as the dispersed phase whilst aqueous solution containing 90wt% glycerol and 0.5wt% PVA was used as the continuous phase. Scale bars in (a) and (b) are 5μm and 10μm, respectively.

(2) TG-DSC curves of pure PLGA and TiO₂ particles

Figure S2. TG-DSC curves of pure (a) TiO₂ and (b) PLGA particles.
(3) Morphology and size of TiO$_2$ in PLGA/TiO$_2$ particle

![Figure S3. SEM image of TiO$_2$ after acetone treatment of PLGA/TiO$_2$ particle](image)

(4) Porous internal structure of PLGA/TiO$_2$ particles

![Figure S4. SEM images of sliced PLGA/TiO$_2$ particles fabricated with the dispersed phase containing 8 mg/g of TBT and (a) 30mg/g and (b) 50 mg/g of PLGA respectively.](image)

(5) Pore size distribution
Figure S5. Pore size distribution calculated according to Figure 5b (cross-section of PLGA/TiO$_2$ particle).

(6) Fabrication of disklike TiO$_2$ particle

Figure S6. SEM images of disklike TiO$_2$ particle fabricated with the dispersed phase containing 8mg/g TBT.

(7) Microfluidic fabrication of spherical PCL/TiO$_2$ particles

Figure S7. SEM images of PCL/TiO$_2$ particles fabricated using the dispersed phase containing 8mg/g TBT and 30mg/g PCL. The continuous phase was aqueous solution containing 90wt% glycerol and 0.5wt% PVA, and the collection solution was 2% PVA aqueous solution.
(8) EDS analysis on the cross-section of PLGA/TiO$_2$ particle

Table S1. EDS data measured on the cross-section of PLGA/TiO$_2$ particle

<table>
<thead>
<tr>
<th>Element</th>
<th>O</th>
<th>C</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight %</td>
<td>34.18</td>
<td>57.03</td>
<td>8.79</td>
</tr>
<tr>
<td>Atom%</td>
<td>30.23</td>
<td>67.18</td>
<td>2.6</td>
</tr>
</tbody>
</table>

(9) Measurement of contact angle and calculation of interfacial tension

Table S2. Contact angle as a function of n-butanol concentration in the continuous phase

<table>
<thead>
<tr>
<th>Continuous phase</th>
<th>0.5wt% PVA aqueous solution</th>
<th>0.5wt% PVA +0.8wt% n-butanol</th>
<th>0.5wt% PVA +1.6wt% n-butanol</th>
<th>0.5wt% PVA +2.4wt% n-butanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact angle</td>
<td>64.8</td>
<td>54.2</td>
<td>47.0</td>
<td>36.7</td>
</tr>
</tbody>
</table>

As can be found, the contact angle decreases with the increase in the concentration of n-butanol. According to Young Equation:

$$\gamma_{sg} = \gamma_{sl} + \gamma_{gl} \cos \theta$$

The interfacial tension between the PLGA/TBT mixture (actually it should be PLGA/TiO$_2$ film because TBT hydrolyzes very fast on the PLGA/TBT surface) and n-butanol can be calculated as:

$$\gamma_{sl} = \gamma_{sg} - \gamma_{gl} \cos \theta$$

Assume that $\gamma_{gl}$ is constant, $\gamma_{sl}$ decreases with the decrease in contact angle. So the interfacial tension is decreased with the addition of n-butanol.