



**Fig. S1** SEM images of PLGA/PCL microspheres with increased total concentration of PLGA plus PCL (a) and slowed rate of solvent evaporation (b).

The increased total concentration of PLGA plus PCL would inhibit the movement of molecular chains of PLGA on the surface. Therefore, more small islands of PLGA and less large ones were formed (Fig. S1a). If the rate of solvent evaporation was slowed down, the PLGA molecular chains were provided more time to move and assemble into large islands (Fig. S1b). When the assembly proceeded further, the islands would aggregate with each other, even forming the skin-like structure. These results demonstrated that the generation of island-sea topography on the surface of PLGA/PCL microsphere originated from the movement and assembly of PLGA chains.

**Table S1** The GPC analysis of degraded microsphere.

	PLGA	PCL	PLGA/PCL		
			14 d	21 d	31 d
$M_w$ (Daltons)	35,908	86,025	64,767	92,754 9,235	46,490

The result of GPC further revealed the degradation of PLGA/PCL microspheres. As a whole, the  $M_w$  of the microsphere decreased with degradation. At the time of 21 d, two separate peaks were obtained. This was due to the loss of chains with low molecular weight in PCL, producing the 92,754 peak, and the break of chains in PLGA, producing the 9,235 peak.