Supporting Information

## One-Step Fabrication of Polymeric Hybrid Particles with Core-Shell, Patchy, Patchy Janus and Janus Architectures via Microfluidic- Assisted Phase Separation Process

Xiaodong Cao<sup>1, 2, 3</sup>, Wenxiu Li<sup>1, 2,3</sup>, Ting Ma<sup>1, 2</sup>, Hua Dong<sup>1,2,3,\*</sup>



Figure S1. Optical images of monodisperse PLGA/PCL droplets collected at the outlet of microfluidic devices. The solvents used in (a) and (b) were dimethyl carbonate and dichloromethane, respectively.



**Figure S2.** SEM images of cross-sectioned core-shell and patchy PLGA/PCL particles produced with different mass ratios of PLGA and PCL: (A) 7:3, (B) 5:5, (C) 3:7 and (D) 2:8. Dichloromethane was used as the solvent of the dispersed phase and the flow rates of the dispersed phase and continuous phase were 0.25 and 0.45 mL h<sup>-1</sup>, respectively.



**Figure S2.** SEM images and size distribution of PLGA/PCL particles reported in the text: 1-A, 1-B, 1-C and 1-D correspond to particles shown in Figure 1(A-D), 2-A, 2-B and 2-C correspond to particles shown in Figure 2(A-C), 3-A and 3-B correspond to particles shown in Figure 3(A-B).

Particle type & label	Average diameter (μm)	Coefficient of variation (%)
Corel-shell (1-A)	45.1	3.40
Corel-shell (1-B)	47.0	2.70
Patchy (1-C)	52.5	4.50
Patchy (1-D)	48.8	2.17
Patchy Janus (3-A)	30.8	3.30
Patchy Janus (3-B)	35.4	2.00
Janus (2-A)	32.1	4.00
Janus (2-B)	28.4	4.25
Janus (2-C)	36.7	3.70

Table S1. Average diameter and coefficient of variation for various particles

Note: Average particle size and size distribution was measured by choosing randomly fifty particles in SEM images.

 Table S2. Calculation of interfacial tension between PLGA and PCL in dimethyl carbonate

 system

Materials	Testing systems	Contact angle ( <sup>O</sup> )	Surface energy (mN/m)	Interfacial tension (mN/m)
PLGA	Water-PLGA	85.5	27.29	- 7.48
	Diiodomethane-PLGA	44.5	37.28	
PCL	Water-PCL	102.7	11 76	
	Diiodomethane-PCL	38.8	44.70	

Additional note: PLGA and PCL solutions were first spin-coated on clean glass slides to form a uniform film after solvent evaporation. Then, two standard probe liquids (pure water and diiodomethane) with well-known surface energy ( $\gamma_L$ ), dispersive ( $\gamma_L^d$ ) and polar component ( $\gamma_L^p$ ), were dropped on the surface of polymer film for contact angle measurements (OCA15, Data Physics Instruments GmbH). According to the classic Owens-Wendt-Kaelble (OWK) equation,

$$\gamma_L(1+\cos\theta) = 2\sqrt{\gamma_S^d \gamma_L^d} + 2\sqrt{\gamma_S^p \gamma_L^p}$$

The dispersive  $(\gamma_S^d)$  and the polar component  $(\gamma_S^p)$  of PLGA and PCL could be obtained, and their surface energy were calculated as  $\gamma_S = \gamma_S^d + \gamma_S^p$ . The interfacial tension between PLGA and

PCL is the D-value between the surface energy of PLGA and PCL. These data were summarized in Table S2.