## **Supplementary information**

#### Staged Phase Separation in I-I-N Triphase Region of Platelet–Sphere

#### **Mixtures**

## Mingfeng Chen<sup>a</sup>, Min He<sup>a</sup>, Pengcheng Lin<sup>a</sup>, Ying Chen<sup>a</sup>,

## Zhengdong Cheng\* b,c,d

<sup>a</sup> Soft Matter Center, Guangdong Provincial Key Laboratory on Functional Soft Condensed Matter, School of Materials and Energy, Guangdong University of Technology, Guangzhou, 510006, China

<sup>b</sup> Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX, 77843-3122, USA.

<sup>e</sup> Mary Kay O'Connor Process Safety Center, Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX, 77843-3122, USA

<sup>d</sup> Materials Science and Engineering, Texas A&M University, College Station, TX, 77843-3003, USA.

# 1. Scanning electron and transmission electron micrographs of

## ZrP platelets and silica spheres

Fig. S1 shows the scanning electron and transmission electron micrographs of the platelets and spheres used in the experiments. The diameters of ZrP and silica were  $704.3\pm105.6$  and  $116.4\pm11.8$  nm, respectively. Thus, the size ratio q was  $0.2310\pm0.0576$ .



Fig. S1 (a) Scanning electron micrograph of ZrP crystal. Transmission electron micrographs of the (b) ZrP monolayers and (c) silica spheres

### 2. Observation of staged phase separation

A series of samples with volume fraction of ZrP nanolayers  $\phi_{ZrP}$  ranging from 0.0066 to 0.0138 and silica sphere  $\phi_S$  ranging from 0 to 0.0041, were prepared. The phase separations of most samples for 144 h after preparation are presented in Figs. S2 to S7. The samples were observed by placing the samples between two cross-polarized polymer films and images were

taken at various time points using a Cannon digital camera. Only the I-N phase transition occurred when the added  $\phi_S$  were 0, 0.0014, and 0.0023 (Figs. S2 –S4). By contrast, an I-N-I triphase demixing emerged when the added  $\phi_S$  was increased to 0.0032 (Figs. S5–S7). Sample A is shown in Fig. S6, while samples B and C are shown in Fig. S7.



Fig. S2 Photograph of ZrP/Silica suspension between crossed polarizers. The volume fraction of silica φ<sub>S</sub> is 0. The volume fractions of ZrP φ<sub>ZrP</sub> from left to right are 0.0066, 0.0072, 0.0078, 0.0084, 0.0090, 0.0096, 0.0102, 0.0108,0.0114, 0.0120, 0.0126, 0.0132, and 0.0138. The error bar for them is ±0.0001. From top to bottom, the time points of the sample after preparation are (a) 0, (b) 48, (c)96, and (d)144 h.



Fig. S3 Photograph of ZrP/Silica suspension between crossed polarizers. The volume fraction of silica  $\phi_S$  is 0.0014±0.0003. The volume fractions of ZrP  $\phi_{ZrP}$  from left to right are 0.0066, 0.0072, 0.0078, 0.0084, 0.0090, 0.0096, 0.0102, 0.0108,0.0114, 0.0120, 0.0126, 0.0132, and 0.0138. The error bar for them is ±0.0001. From top to bottom, time points of the sample after preparation are (a) 0, (b) 48, (c) 96, and (d) 144 h



Fig. S4 Photograph of ZrP/Silica suspension between crossed polarizers. The volume fraction of silica  $\phi_S$  is 0.0023±0.0003. The volume fractions of ZrP  $\phi_{ZrP}$  from left to right are 0.0066, 0.0072, 0.0078, 0.0084, 0.0090, 0.0096, 0.0102, 0.0108, 0.0114, 0.0120, 0.0126, 0.0132, and 0.0138. The error bar for them is ±0.0001. From top to bottom, the time points of the sample after preparation are (a) 0, (b) 48, (c) 96, and (d)144 h.



Fig. S5 Photograph of ZrP/Silica suspension between crossed polarizers. The volume fraction of silica  $\phi_S$  is 0.0032±0.0003. The volume fractions of ZrP  $\phi_{ZrP}$  from left to right are 0.0066, 0.0072, 0.0078, 0.0084, 0.0090, 0.0096, 0.0102, 0.0108,0.0114, 0.0120, 0.0126, 0.0132, and 0.0138. The error bar for them is ±0.0001. From top to bottom, the time points of the sample after preparation are (a) 0, (b) 48, (c) 96, and (d)144 h.



Fig. S6 Photograph of ZrP/Silica suspension between crossed polarizers. The volume fraction of silica  $\phi_S$  is 0.0036±0.0003. The volume fractions of ZrP  $\phi_{ZrP}$  from left to right are 0.0066, 0.0072, 0.0078, 0.0081,0.0084,0.0087 0.0090, 0.0096, 0.0102, 0.0108,0.0114, 0.0120, 0.0126, 0.0132, and 0.0138. The error bar for them is ±0.0001. From top to bottom, the time points of the sample after preparation are (a) 0, (b) 48, (c) 96, and (d)144 h.



Fig. S7 Photograph of ZrP/Silica suspension between crossed polarizers. The volume fraction of silica  $\phi_S$  is 0.0041±0.0003. The volume fractions of ZrP  $\phi_{ZrP}$  from left to right are 0.0066, 0.0072, 0.0078, 0.0084, 0.0090, 0.0096, 0.0102, 0.0108, 0.0114, 0.0120, 0.0126, 0.0132, and 0.0138. The error for them bar is ±0.0001. From top to bottom, the time points of the sample after preparation are (a) 0, (b) 48, (c) 96, and (d) 144 h.



Fig. S8 High-brightness and high-contrast magnified micrographs of the samples. (a) Magnified micrograph of sample A after 24 h of preparation shows the weak boundary between the gas and liquid phases. (b) Magnified micrograph of sample C after 24 h of preparation shows many small light spots dispersed in the suspension.

## 3. The determining of equilibrium experimental and calculated

## phase fraction

To calculated the fraction of the phase, the tri-phase triangle was converted in a system of number density. A lever rule in tri-phase coexistence region were utilized<sup>1</sup>, as presented in Fig 1a. The calculated fraction of the phase was presented in table 1.

To determine the experimental equilibrium phase fractions, we have measured the fraction of the phase as functions of time. Since the gravity compressed the sample continuously, we can only estimate the fraction of the three phases by the method as Fig.1b shows below. For which, we assumed the phase reached equilibrium when the change of the fraction of phases became small. Actually, the phases will be compressed by gravity slowly until compaction. And the equilibrium fractions of the three phases were obtained, then normalized. the values are presented in table 1.



Fig.S9 (a) the tri-phase triangle with axis of number density of ZrP and silica. According lever rule,

for state point A, the fraction of gas phase f(G)=|HA|/|HO|, the fraction of liquid f(L)=|IA|/|IP|, and fraction of nematic f(N)=|JA|/|JQ|. similar calculations were done to state points B and C. (b) measured phase fractions as function of time.

### 4. Kinetic maps from free-energy landscape

Poon et al. introduced the kinetic maps from free-energy landscapes in binary spherepolymer colloidal mixtures with tri-phase coexistence. In this method, a generic link was constructed between the phase pathways and the free-energy landscape<sup>2</sup>. The phase transition pathways were categorized into several types and confirmed preliminarily using the phaseseparation processes in colloid–polymer mixtures. Kinetic maps were drawn by traced the lowest cotangential points (stable phase boundaries, correspond to the bold line in Fig.S10) and the other two minimums (metastable line(dashed) and the spinodal line(dotted)). Similar in the platelet-sphere colloidal mixture, the phase diagram can be divided into the same kinetic regions (A to M) as shown in Fig.S10. Region F-J (F, G,H,I,J), L and M overlayered with the tri-phase region, which indicates the homogeneous sample located in this overlayered regions may separate through the pathways of these kinetic types.



Fig.S10 The schematic of the  $(\phi_{ZrP}, \mu_S)$  phase diagram in platelet-sphere colloidal mixtures. The phase diagram was divided by the stable phase boundaries (bold curve), metastable phase line (dashed line) and spinodal line (dotted line) into different kinetic regions (A to M), where the pathways are distinguishably different. Point-dashed line outlines the three phases coexistence. The horizontal solid line which labelled in  $\mu$ tr s is the three phase three phase three phase coexistence line.

The phase separation pathways in the tri-phase region are presented in fig. S11, which were labeled by the following symbols: formation a new phase ( $\bigcirc$ ), spinodal decomposition into a pair of new phases (s), the phase in the final equilibrium state ( $\blacksquare$ ), which are (from left to right) gas, liquid, and nematic, respectively. Time is from up to bottom vertically. The upward arrow represents the latter phase can not form until the former occurred, the downward represents

once the former occurred, the latter must follow. If there is no arrow, the two phase may happen in ether order.



Fig.S11 the Pathways of different kinetic regions (F-J, L, M) which eventually achieve three phases equilibrium.

Pathways:

F, a nematic phase can nucleate straightly from the homogenized sample. However, it also contains the possibility of forming an intermediate metastable liquid phase and then nucleating a nematic phase from it.

G, first, spinodal decomposition takes place into a metastable gas and a metastable liquid phase first, and then a nematic separated from these two meta-phases.

H, a gas phase is separated from the homogenized sample, meanwhile, a metastable liquid phase is formed. Then a nematic phase can be separated out from the gas and/or liquid phase.

I, this pathway contains many possibilities and is of the most mystery. The gas phase can separate out from the homogenized sample or the metastable nematic phase, and the nematic phase can nucleate from the metagas or metaliquid phases.

J, a metastable nematic phase nucleates from the homogeneous sample, and a metastable liquid phase is formed, then the gas phase is separated out from the nematic or liquid phase.

L, this pathway also has many possibilities. The gas phase may separate out from the metastable liquid phase at two different times (the gas phase may be separated from the metaliquid phase after it separated out a nematic phase), and the nematic phase can separate from the metastable liquid or the metastable gas phase.

M, a nemtic phase nucleates from the homogenized phase first, as soon as possible, a gas phase is separated out from the metastable liquid phase, since the gas phase is required by the nucleation of the nematic phase.

#### Reference:

1. R. Dehoff, CRC Press, 2006, 273-274.

2. R. M. Evans, W. C. Poon and F. Renth, *Phys Rev E*, 2001, **64**, 031403.