## **MATERIALS SCIENCE**

# $S$  - aiau, a aiau, a . **in periodic Liesegang-type structures**

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**C** i.e., a i.e.u,  $i \times a$  u,  $i \times j \times j$ ,  $j \times k$  ,  $k \times k$  and  $k \times k$  and  $k \times k$  and  $k \times k$  order  $k \times k$ **morphologies and structural hierarchy. Periodic structures are formed by either molecules or nanoparticles. On the premise of new directing factors and materials, an emerging frontier is the design of systems in which the precipitation are nanoparticles are nations and molecules and molecules are solvent evaporation from a suspension from a suspensio cellulose nanocrystals (CNCs) and L-(+)-tartaric acid [L-(+)-TA] causes phase separation and precipitation, which, being coupled with a reaction/diffusion, results in rhythmic alternation of CNC-rich and L-(+)-TA–rich rings. The CNC-rich regions have a cholesteric structure, while the L-(+)-TA–rich bands are formed by radially aligned elon-** $\mathsf{a}$ uddles. The moving edge of the pathology of the path  $p$  finite  $\mathsf{a}$  finite  $\mathsf{$ **control of periodicity by variations**. This work expanditions would be about self-organizing  $\mathbf{v}_i$  about self-organizing  $\mathbf{v}_i$  about self-organizing  $\mathbf{v}_i$  about  $\mathbf{v}_i$  self-organizing  $\mathbf{v}_i$  about  $\mathbf{$  $r$ eaction-diffusion-diffusion-diffusion-design offers a strategy  $r$  of  $\mathbf{a}$  and  $\mathbf{a}_1$  and  $\mathbf{a}_2$  and  $\mathbf{a}_3$  and  $\mathbf{a}_4$  and  $\mathbf{a}_5$  and  $\mathbf{a}_7$  and  $\mathbf{a}_8$  and  $\mathbf{a}_7$  and  $\mathbf{a}_8$  and  $\mathbf{a}_9$ 

#### **INTRODUCTION**

Self-organization and self-assembly in non-equilibrium systems are  $a_j$  universal process that occurs in living matter  $(1, 2)$ ,  $e_{j, \alpha} e_{j, \alpha} a_{j, \alpha}$ and mineral environments ( ), as the science ( ), and industry science of  $\mathbf{a}$  $t$ rial settings (5). I<sub>n p</sub>articular, particular, pa systems provide a fascinating example of highly ordered, spatial or  $s_p$ atio $\frac{1}{2}$ statu $\frac{1}{2}$ structures as a result of the synergy between transports  $\frac{1}{2}$ of chemical species and chemical reactions. For example, periodic ring patterns have been observed in seeingly unrelated systems,  $\mathbf{r}_i$  $e_n$  in crystallizing low-molecular weight compounds ( ), polymer films ( ), polymer films ( ), polymer films ( ), formed from solutions ( , ), equivalent polymerization mixtures ( ), and even in human tissues (*10*). In crystallizing polymer melts, the formation of ring-banded spherulites due to the helicoidal twisting of radial lamellae is a commonly observed phenomenon (*11*).

 $\mathrm{A}$  special class of reaction-diffusion-diffusion-diffusion-diffusion-diffusion systems is that in  $\mathrm{A}$  is that in  $\mathrm{A}$ heterogeneous precipitation pattern forms. In a reaction-diffusion experiment conducted by Liesegang in the late 19th century, a reaction between two water-solution electrolytes results in spatially a spatially a spatially  $\mathbb{R}$ periodic ring-type bands of a precipitating salt (*12*). Periodic precipi- $\tan^{-1}$  the  $\tan^{-1}$  the rates of the rates of the precipitation process and reactant mass transport, resulting in a reactant-exhausted in a reaction of the context of the context  $\mathbf{u}$  (*1*).

 $\mathsf{Q}$  the projection periodic structures can be divided into two groups. In the classical Liesegang-type experiments, the system consists of two interactions  $\mathcal{C}$  is a constant or operator  $\mathcal{C}$ 

 $\mathcal{L}_s$ d,  $\mathbf{c}_k$  arged nanoparticles (NPs),  $\mathcal{L}_s$  are initially spatially spatially spatially separated in  $\mathcal{L}_s$  $( \ , I \ )$ . Pattern formation of the diffusion of the due to diffusion of the diffusion of these compositions of the theorem in the diffusion of the diffus nents toward each other, leading to the first precipitation band When the product of local concentrations of the reagence of the reagence of the reagence of the reagence the r solubility product. The precipitation process decreases the reagent concentrations in the precipitation  $\mathcal{L}$  or also faster than the diffusion can the diffusion can the diffusion can the diffusion can be diffusion can increase them, causing dependence of  $\alpha$  and  $\alpha$  reagents in the reagents in the reagents in the reagents in  $\mathbf{r}_i$ ring the first precipitation band. A new precipitation band. A new precipitation band. A new precipitation band.  $\partial \mathbf{a}_{\alpha \beta}$  ,  $\mathbf{b}_{\alpha \beta}$  , and solutions on concerning again. The repeated again. The repeated again. The repeated again tition of the process  $f_{\alpha}$  is the process yields periodic precipitate bands. In the precipitate bands. In the process  $f_{\alpha}$ the second group of experiments, periodic ring-type structures for  $\tau$ a system that in a spatially has a spatially uniform distribution of components but undergoes phase separation or crystallization (*15, 1)*. Chemical organization via periodic periodic precipitation of the new model of the new model of the periodic pr stably for y classical cabines with fights of morphologies with ordered morphologies with ordered more substit  $a_n$ ,  $d_{n-1}$  ta,  $\dot{a}$  it  $d_n$  (

 $\mathbf{M}_{\hat{\mathbf{a}}}$  a r<sub>p</sub>  $_{\hat{\mathbf{a}}}$  100 s 300 nm and diameter of 10 s 20 nm (2), , all the recently attracted great interest of the soft matter  $\mathbf{r}_i$ als science community because of the their ability to organize into cho- $\mathbf{r} \cdot \mathbf{r}$ lig (C<sub>i</sub>) i<sub>nte</sub>ric case (2). Upon drying, a<sub>nteri</sub>c CNC  $s_{\text{ref}}$  or molecular with  $\mathbb{X}$  and  $\mathbb{X}$  and  $\mathbb{X}$  is  $s_{\text{ref}}$  or  $(2, 2)$ , polymers (*0, 1*) and N s (*2, )* formed *i* a C<sub>h</sub> i *a*<sub>1</sub>*3* i<sub>1</sub>*s*<sub>**1**</sub>*s***<sub>1</sub>***i***<sub>1</sub><b>***s*<sub>*f***</sub>**</sub>  $\mathcal{A}_i$  ,  $\mathfrak{z}$  be (With intrinsic defects) or random disordered morphologies; however, periodic precipitation bands have not been reported.  $I$  the present work, we show that upon solvent work, we see that upon solvent  $\mu$ aqueous l-(+)-TA/CNC mixture undergoes phase separation and sub $s_{\rm eff}$  exploring italian, being coupled with a diffusion-driven with a diffusion-driven with a diffusion-driven process, results in a rhythmic alternation of CNC-rich and CNC- $\mathcal{A}_\bullet$  (  $\mathcal{A}_\bullet$  ), I-(+)-TA–1), The corrichator regions. The CNC-rich regions. **.** a 37, Ma  $\qquad$  A 2, 4, A 6  $\qquad$  is NC  $\qquad$  6  $\qquad$  a  $\qquad$ , ) 6 75

 $\begin{array}{lllllllllllll} \textbf{a} & \textbf{a} & \textbf{a} & \textbf{a} & \textbf{b} \\ \textbf{a} & \textbf{a} & \textbf{a} & \textbf{b} & \textbf{c} \\ \textbf{a} & \textbf{a} & \textbf{a} & \textbf{b} & \textbf{c} \\ \textbf{a} & \textbf{a} & \textbf{a} & \textbf{b} & \textbf{c} \\ \textbf{c} & \textbf{b} & \textbf{c} & \textbf{c} & \textbf{c} \\ \textbf{c} & \textbf{c} & \textbf{c} & \textbf{c} & \textbf{$ 

the radial direction in the TA-enriched phase. The topography of the surface of the composite film was examined using atomic force

aninal direction of the radial direction, the structures formed by  $\epsilon$  $\text{CNC} \text{ a }$  and  $\text{A} \text{a }$  and  $\text{A} \text{a }$  along  $\text{A} \text{a }$  and  $\text{A} \text{a }$  and  $\text{A} \text{a }$  $\mathbf{a}$ ally reconstructed at the nanoscale solely by two-dimensional solely by two-dimensional solely  $\mathbf{a}$  $(2D)$  optical polarimetry characterization, providing and interesting and in example of complex organization of  $\mathcal{E}_{\mathbf{a}}$  organization or  $\mathcal{E}_{\mathbf{a}}$  $f \in \mathbb{R}^{\mathbb{N} \times \mathbb{N}}$  studies.

 $S_{\rm s}$  and  $\epsilon$  -ray scattering (SAX). Was probe the structure to probe the struc  $\mathbf{a}^{\mathbf{t}}$  is a  $\mathbf{A}/\mathbf{CNC}$  finite  $\mathbf{a}$  in the transmission mode (Fig. 5A). And  $\frac{1}{2}a$  and  $\frac{1}{2}a$  m/s  $\frac{1}{2}a$  entire film area for  $A$  space  $\alpha$  ,  $\alpha$  ,  $\alpha$  ,  $\alpha$  space  $S$  and  $\alpha$   $\alpha$   $\alpha$  space  $S$  $q$ analysis analysis using the variation of the scattering intensity intensity intensity intensity intensity in  $\mathbf{F}$ ric (0)  $\mathbf{X}_k$  gra $\mathbf{A}$  , gancy co (cric  $\mathbf{X}_k$ imgrafined with detector plane with  $\alpha$  th respect to the horizontal direction; Fig. 5B).  $M$ ore specifically, we compute  $\mathcal{L}$  and  $\mathcal{L}$  or  $\mathcal{L}$  or  $\mathcal{L}$  or  $\mathcal{L}$  . The  $\mathcal{L}$ function (ODF), (), which reflects the probability of the scatterers  $\frac{1}{2}$  or aligned in a particular direction (*40, 11*) and is calculated as calculated as calculated as calculated as  $\frac{1}{2}$ *f*(

$$
E + F \rightarrow 2F, \nu_7 = k_7, k_7 = 10^3 \tag{8}
$$

Where , , , , , , and are the concentrations of the concentrations of the concentrations of the chemical species  $\mathbf{r}$ . A, B, C, D, E, and F,  $\mathbf{r}_i$ ,  $\mathbf{r}_j$  and  $\mathbf{r}_j$  be an extending step function; and \* and \* are the threshold concentrations for the for and  $A-CNC$ ,  $r^2s^2s^2s$ ,  $r\sin^2(G_1, 5a_0, 6)$ . The value  $\sim$  in Eq. 1 is calculated using stoichiometric coefficients and reacchiometric coefficients  $\mathbf{a}^*$  **far.**  $a$ ,  $r_i = \sum_{j=1}^7 \left( v_j^r - v_j^l \right) v_j$ ,  $\mathbf{A}$   $\mathbf{c}^* \mathbf{c}$   $v_j^r \mathbf{a}$   $\mathbf{c}$   $v_j^l \mathbf{a}^* \mathbf{c}$   $\mathbf{a} \cdot \mathbf{a}$   $\mathbf{c}$ ,  $\mathbf{a} \cdot \mathbf{a}$   $\mathbf{c}$ ,  $\mathbf{a}$   $\mathbf{c}$ etric coefficients of the the three compound at the right- at the right-  $\alpha$  $\mathcal{A}_s$ es in the the the the spectral is the reaction, reaction rate of  $r$  $\mathbf{a} \in \mathbb{R}^n$  , c...  $\mathbb{E}_\mathbf{a}$  and  $\mathbb{R}^n$  2 and  $\mathbb{R}^n$  and  $\mathbb{R}^n$  autocatalytic forma- $\mathbf{a} = \mathbf{A}_{\mathbf{A}}$ , ri $\mathbf{a}_{\mathbf{A}}$ ,  $\mathbf{A}_{\mathbf{A}}^{\mathbf{A}}$  .  $\mathbf{a}_{\mathbf{A}}$ ,  $\mathbf{e}_{\mathbf{A}}$  of  $\mathbf{a}_{\mathbf{B}}^{\mathbf{A}}$ . Equation 3 describes the process of the formation of  $\mathbf{A}_s$  and  $\mathbf{A}_s$  are  $\mathbf{A}_s$  and  $\mathbf{A}_s$  and  $\mathbf{A}_s$ model comprises the concentration threshold-limited steps (Eqs. 5) and 6),  $\mathbf{A}$  is graphic described the formation of TA-CNC can be  $\mathbf{A}\text{-CNC}_{\epsilon+1}$  and  $\mathbf{A}\text{-CNC}_{\epsilon+1}$ c<sub>lust</sub> in the CNC-enriched phase (Eqs. 7and 8). Figure 510 shows the schematic representation of the mechanism.  $\mathbf{y}$  or  $\mathbf{F}_\mathbf{z}$  are set of  $\mathbf{z}$  and  $\mathbf{z}$  of partial equations (Eq. 1) numerical equations ically by using the method of lines technique on an equipment grid on an equipment  $\alpha$ in a polar coordinate system (*45*). The finite difference spatial dis cretization method was combined with a forward Euler method for the integration in time of the set of ordinary differential equations.  $\mathbf{u}_1 \cdot \mathbf{a}_2 \cdot \mathbf{b}_3$  in  $\mathbf{a}_3$  in  $\mathbf{a}_4$  in  $\mathbf{a}_5$  in  $\mathbf{a}_7$  in  $\mathbf{a}_8$  in  $\mathbf{a}_7$  (  $\mathbf{b}_8$  (  $\mathbf{b}_9$  = 1.0, (  $\mathbf{b}_9$ ),  $(0, 0) = 0, (0, 0) = 0, (0, 0) = 1.0, (0, 0) = 0,$  and  $(0, 0) = 0, (0, 0) = 0$  $\mathbf{t}$ ,  $\mathbf{t}$ ,  $\mathbf{t}$  and initial experimental conditions, when  $\mathbf{t}$  and  $\mathbf{t}$  and  $\mathbf{t}$  and  $\mathbf{t}$  conditions, when  $\mathbf{t}$  $(D)$  were uniformly distributed in the mixed suspension. To investigate  $D$ passion, William formation, we fash  $\frac{1}{2}$  B as  $\frac{1}{2}$  = 0 as  $= 0$ , i.e.,  $( = 0, 0) = 1.0$ ...  $\epsilon_1 \cdot \epsilon_2 = \epsilon_1 \cdot \epsilon_2$  Dirichlet bounds ary conditions for all chemical species at  $\alpha$  and  $\alpha$  and  $\alpha$  $\mathcal{A}$  contains is the simulation of the simulation domain.

 $F_{ij}$  is 6. Note that the numerical model model model model  $F_{ij}$  reproduced  $F_{ij}$  reproduced  $F_{ij}$ the experimental findings: The threshold-limited phase separation  $\mathbb{R}$  $A_a$  CNC  $(E_t . 5a_0 6)$  produced periodic TA-richard CNCrich ring-type regions (Fig. 6, A  $a \in B$ , respectively). The model predicted a finite constant velocity of the moving from  $\mathbf{r}_i$  the moving from  $\mathbf{r}_i$  $\mathbf{q} \cdot \mathbf{q}$  and  $(\mathbf{F}_1, 2\mathbf{K})$  due to reactions described by Eqs. 2 to 8 (see  $\mathbf{w}$ , 1).

#### **DISCUSSION**

Generally, in multiple proponent precipitation of  $\mathcal{L}^{\mathbf{r}}$  and governed system governed systems.  $\boldsymbol{x}$  and sizes of the sizes of the same range, they in the same range range range  $\boldsymbol{x}$ 

 $\begin{array}{ccccccccc} .a_{1}^{-1}aa' & .aa_{2},a_{2}^{-1}a_{3}^{-1}a_{4}^{-1}a_{5}^{-1}a_{6}^{-1}a_{7}^{-1}a_{8}^{-1}a_{8}^{-1}a_{9}^{-1$ 

or 1,5 + 3 (i) i = 4.224.0<br>Ji in , , e, mime , an/CNC+ ii, ii, ere , easy 10, 0<br>4.24 iv. .5NC6(Hj., 371E)4 . i. b<sub>i + 1</sub>. en/Geli ...ii(0.005 , 9 1845 5901 & e ...ei asmi, )0. h<sub>i</sub> ees<sub>tel</sub>est. I e am  $\mathcal{O}(\overline{A}) = \mathcal{O}(\overline{A})$ 

 $f: \mathbb{R}^4$  for (A41001 H :F),  $\mathbb{R}^4$  and  $\mathbb{R}^4$  with  $f: 480$ , 23  $480$ . 23 .  $T_{\rm eff}$  by a figure of samples for SEM imaging of the composite composite  $\alpha$  $\mathbf{a}$ . Alexandre deposition and  $\mathbf{a}$  droplet of TA/CNC ( = 4.5)  $s_{\rm tot}$  suspension on  $\alpha$  single water and deposite de provincial de provincial de provincial de provincial de provincia  $\sin^2\beta$ siti $\sin^2\theta$  was was water and  $\sin^2\theta$  with with with with  $\sin^2\theta$  with  $\sin^2\theta$ filtered compressed air. The samples were imaged using the FEI  $\mathbf{q}$  and FEG 250 end in environmental scanning electron microscope un $d_{\rm eff}$  is  $d_{\rm eff}$  at 3 kV. The silvers of obtain  $\mathbb{R}$  is  $d_{\rm eff}$ with deposited films with a diamond-tipped glass cutter. We cut that with a diamond-tipped glass cutter. The cut The fractured films affixed to the silicon wafers were mounted on .) میں مائی استعمال میں ایک ایک ایک مقابض ا AFM experiments were called positive contributions for  $\mathcal{C}_\mathbf{a}$  for  $\mathcal{C}_\mathbf{a}$  and

 $\bullet$ ,  $\bullet$ ,  $\bullet$ ,  $\bullet$  A/CNC (

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### **Self-organization of nanoparticles and molecules in periodic Liesegang-type structures**

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