Colloid Polym Sci (2007) 285:827–832
DOI 10.1007/s00396-006-1626-0

SHORT COMMUNICATION

Kinetic aspects in the drying dissipative crack patterns of colloidal crystals

Tsuneo Okubo · Miyuki Nozawa · Akira Tsuchida

Received: 28 August 2006 / Accepted: 19 November 2006 / Published online: 20 January 2007

Abstract Kinetics of the dissipative structure formation in the course of drying the colloidal crystals of silica spheres (103 nm in diameter) in aqueous deionized suspension on a rinsed cover glass has been studied by the close-up video observation. The patterns of the broad ring of the hill accumulated with the spheres coexisted with the many spoke-like cracks. The characteristic convection flow of the spheres and the interactions between the spheres and substrate were important for the pattern formation. Cracks formed suddenly in the course of drying along the outside edge first, then toward the center, and stopped around the middle point between the outside edges and the frontier of suspension area. The further growth of the cracks took place at the adjacent place of the previous crack side by side and cooperatively. After the fast formation of these cooperative spoke-like cracks was completed, then all the crack lines further developed very slowly and simultaneously toward the center with the similar rate as that of the movement of the drying frontier of the suspension area toward center. Rates of the fast and slow modes of crack formation were 6.2 mm/s and 0.0098 mm/s, respectively, at the sphere concentration of 0.033 in volume fraction.

T. Okubo (✉)
Institute for Colloidal Organization,
Hatoyama 3-1-112,
Uji, Kyoto 611-0012, Japan
e-mail: okubotsu@ybb.ne.jp

T. Okubo
Cooperative Research Center, Yamagata University,
Johnan 4-3-16,
Yonezawa 992-8510, Japan

M. Nozawa · A. Tsuchida
Department of Applied Chemistry, Gifu University,
Gifu 501-1193, Japan

Keywords Drying dissipative structure · Crack formation kinetics · Colloidal silica spheres · Spoke-like crack

Introduction

Generally speaking, most structural patterns in nature form via self-organization accompanied with the dissipation of free energy and in the non-equilibrium state. Among several factors in the free energy dissipation of aqueous colloidal suspensions, evaporation of water molecules at the air–water interface and the gravitational convection are very important. To understand the mechanisms of the dissipative self-organization of the simple model systems instead of much complex nature itself, the authors have studied the *convectional*, *sedimentation*, and *drying* dissipative patterns of colloidal suspensions as systematically as possible.

Drying dissipative patterns have been studied for suspensions and solutions of many kinds of colloidal particles [1–13], linear-type polyelectrolytes [14], polymers [15, 16], ionic and non-ionic detergents [9, 17, 18], and gels [19] mainly on a cover glass. The macroscopic broad ring patterns of the hill, accumulated with the solutes in the outside edges, always formed. For the non-spherical particles, the round hill formed in the center area in addition to the broad ring. Macroscopic spoke-like cracks or fine hills including flickering spoke-like ones were also observed for many solutes. The convection of water and the solutes at the different rates under gravity and the translational Brownian movement of the latter were important for the macroscopic pattern formation. Furthermore, beautiful fractal patterns such as branch-like, arc-like, block-like, star-like, cross-like, and string-like ones were observed in the microscopic scale. These microscopic drying patterns were reflected from the *shape*, *size* and/or *flexibility* of the solutes themselves. Microscopic patterns also formed by the translational Brownian diffusion of the solutes and the electrostatic and the hydrophobic interactions between solutes and/or between the solutes and substrate in the course of the solidification. One of the very important findings in our experiments is that the primitive vague patterns were formed already in the suspension state before dryness and they grew toward fine structures in the course of solidification.

Recently, the *sedimentation* dissipative patterns in the course of drying suspensions of colloidal silica spheres and green tea (Ocha) have been studied in a glass dish, a watch glass, and others [20–22]. The broad ring patterns were formed within several 10 min in suspension state by the convectional flow of water and the colloidal particles. The sedimentary particles were suspended above the substrate and always moved by the external force fields including convectional flow.

The *convectional* dissipative structures, which were formed in the initial course of drying, were studied for Chinese black ink and 100% ethanol suspensions of colloidal silica spheres in our laboratory [10, 23]. The existence of the small circle-like *convection cells* proposed by Terada et al. [24–26], for the first time, was supported. Vigorous cell convectional flow was observed for both of Chinese black ink and the ethanol suspension with the naked eyes, and the convectional patterns changed dynamically with time.

In this work, the rates of drying crack pattern formation of colloidal crystals of silica spheres have been measured on a video-tape observation in the macroscopic scale. The authors were excited to observe the cooperated dynamic events of the pattern formation.

Experimental

Materials

Colloidal silica sphere sample, CS82 (103 nm in diameter, ±19 nm in the dispersion from the mean diameter), was a gift from Catalysts and Chemicals Tokyo. The colloidal samples were deionized with a mixed bed of cation- and anion-exchange resins (AG501-X8(D), 20–50 mesh, Bio-Rad) *more than 10 years*. It takes a long time before complete deionization is achieved because the deionization proceeds between the two solid–liquid phases one after another, i.e., between colloidal particles and water and then water and the resins. The exhaustively deionized suspension thus obtained was semi-transparent and emitting the strong bluish iridescent colors, which supports clearly the formation of the crystal-like distribution of the spheres, *colloidal crystals*, with the extended electrical double layers. The water used for the sample purification and preparation was purified by a Milli-Q reagent grade system (Milli-RO5 plus and Milli-Q plus, Millipore, Bedford, MA).

Observation of the dissipative crack structures

A 5 to 70 μl of the aqueous CS82 suspension was dropped carefully and gently on a micro cover glass (30×30 mm, thickness no. 1, 0.12 to 0.17 mm, Matsunami Glass, Kishiwada, Osaka) in a dish (60 mm in diameter, 15 mm in depth, Petri, Tokyo). The cover glass was rinsed with chromic acid–sulfuric acid mixture for 24 h before use. The contact angle for the pure water was 11±0.5° from the drop profile of water on the rinsed cover glass. A micro-pipet (Multi-pet Plus, Eppendorf UK) was used for the dropping. Observation of the drying patterns was made for the film formed after the suspension was dried up completely on a cover glass in a room air-conditioned at 25 °C and 50 to 60% in humidity. The humidity was not regulated in our experiments. Concentrations of the colloidal spheres ranged from 3.33×10^{-6} to 0.0333 in volume fraction.

Time-resolved dissipative structures were observed with a digital HD microscope (type VH-7000, Keyence, Osaka) and vide-tape recorder (WV-ST1, Sony). Macroscopic close-up pictures were also taken on a Canon EOS 55 camera with macro-lens (EF 50 mm, f=2.5) and a life-size converter EF.

Results and discussion

Drying patterns of colloidal crystals on a rinsed cover glass

Drying patterns of the deionized aqueous suspensions of CS82 spheres at sphere concentrations ϕ (volume fraction)= 3.33×10^{-6}, 3.33×10^{-5}, 3.33×10^{-4}, 0.00333, 0.0167, and 0.0333 were observed on a rinsed cover glass in this work, although the pictures showing these were omitted. The broad rings were observed for all the suspensions. The spoke-like cracks, however, appeared only for the high sphere concentrations at 0.0167 and 0.0333 in volume fraction. The number of the spoke-like cracks and also the angle between the adjacent cracks, θ, decreased and increased, respectively, as sphere concentration increased. The similar concentration effect on the θ values has been reported on an unrinsed cover glass [7, 8]. It should be mentioned here that the initial area of the liquid and the number of the spoke-like cracks on a rinsed cover glass in this work were strikingly large compared with those of CS82 spheres on an unrinsed cover glass [7, 8].

Figure 1 shows the typical drying pattern of colloidal crystal of CS82 spheres on a rinsed cover glass at the concentration of 0.033 in volume fraction. Clearly, the broad ring patterns at the outside edges of the film and the many lines of spoke-like cracks were observed. A main cause for the broad ring formation is the convection flow of water and the colloidal particles in the different rates, where the rate of the latter is slower than that of the former under gravity. Especially, the flow of the particles from the center area toward the outside edges in the lower layer of the liquid drop, which was observed on a digital HD microscope directly from the movement of the very rarely occurred aggregates of the particles, is important [10]. The convection flow is enhanced by the evaporation of water at the liquid surface, resulting lowering of the suspension temperature in the upper region. When the particles reach the edges of the drying frontier at the outside region of the liquid, a part of the particles turn to upward and go back to the center region. However, the movement of the most particles may stop at the frontier region by the disappearance of water. This process must be followed by the broad ring accumulation of the particles near the round edges. It should be noted that the broad ring formation has been observed for all the solutions and suspensions examined by our group [7–19] and by other distinguished researchers [1–6]. Figure 1 shows that the spoke-like cracks developed crossing the broad ring area and separated a part of the film into the long flakes.

Figure 2 shows the extended picture of the broad ring area shown by the square *a* of Fig. 1. The broad ring is shown as the blue band area, where the spoke-like cracks are quite few compared with those in the thin film area shown in the lower part of the figure. This supports that the number of cracks decreased as the film thickened. The rigidity of the dried film determines the actual number of the cracks. As was discussed previously [7, 8], the cracks are originated with the spoke-like lines of the repeated hills and valleys formed with the very small cell convections in the normal direction to the spoke lines found by Terada et al. [24–26], for the first time, in the suspension state. It is highly plausible that so many spoke-like lines exist potentially in all the area of the film including the broad ring part and the actual number of the crack lines is determined by the rigidity of the dried film. In Fig. 2, the crack lines parallel to the broad ring are also observed. It was clarified that the parallel crack lines developed from right-hand side toward left-hand side first and turned to grow toward the central region of the film, which will be discussed in detail below using Fig. 7.

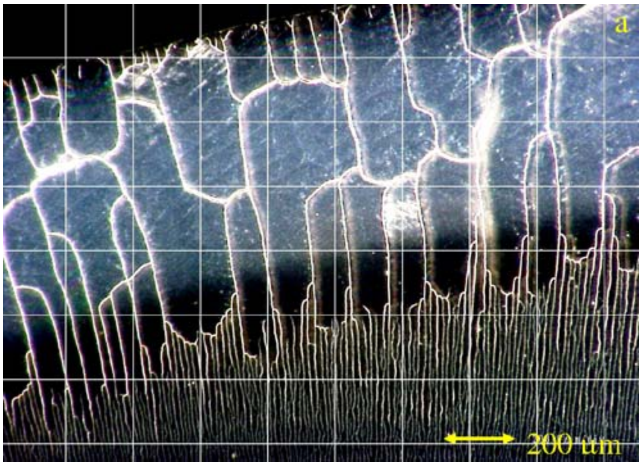

Fig. 2 Drying dissipative patterns of colloidal crystals of CS82 spheres on a rinsed cover glass at 25 °C. Part *a* of Fig. 1 is extended, in water, 70 μl, ϕ=0.033, exposure time=1/45 s, iris=3.5

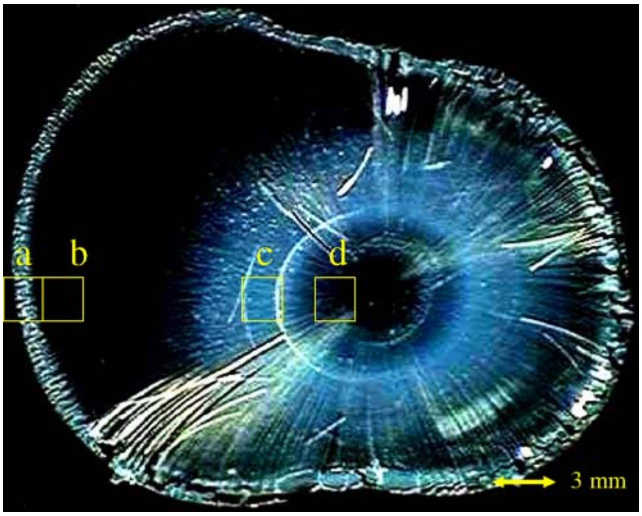

Fig. 1 Drying dissipative patterns of colloidal crystals of CS82 spheres on a rinsed cover glass at 25 °C. In water, 70 μl, ϕ=0.033, exposure time=1/45 s, iris=3.5

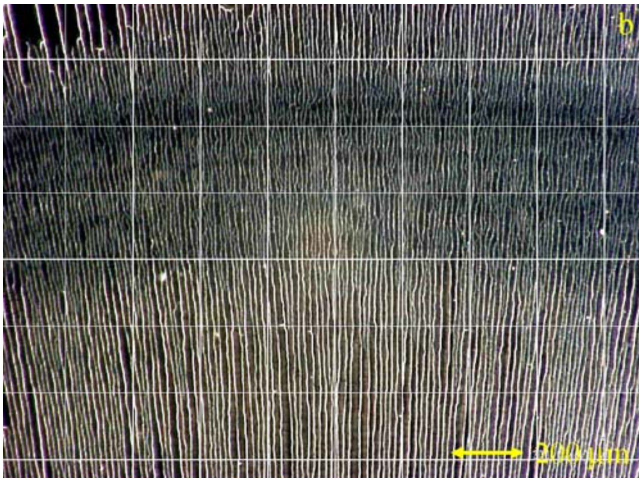

Fig. 3 Drying dissipative patterns of colloidal crystals of CS82 spheres on a rinsed cover glass at 25 °C. Part *b* of Fig. 1 is extended, in water, 70 μl, ϕ=0.033, exposure time=1/45 s, iris=3.5

Figure 3 shows the extended picture of the area *b* shown in Fig. 1. Very fine and slightly curved lines, keeping the inter-line distances between 10 to 20 μm, are impressively beautiful. This figure clearly shows again that the spoke-like lines of the hills and valleys observed by Terada et al. by the convection of spheres are so fine and dense. Figure 4 shows the extended pictures of the area *c* rather close to the center. In this paper, it is interesting to note that the vague spoke-like lines were also observed between the clear crack lines. This supports the idea that the stress of film raised at the step of drying are compensated by making cracks and the number of the cracks decrease as the rigidity of the film increases. It should be mentioned here that the appearance of the broad two circle lines upper and lower in the figure is deeply correlated to the transition time in the crack line formation kinetics, which will be discussed later using Figs. 7 and 8. Figure 5 shows the extended picture at the area very close to the center of the film in Fig. 1. It is impressive that the fine lines continue throughout the whole course from the outside edges to the center. It should be mentioned here that the spoke-like lines in this work are very dense compared with the previous work on the colloidal crystals of silica spheres [7, 11]. This is clearly due to the difference of the thickness of the dried film, i.e., the film on a rinsed cover glass in this work is much extended and thinner compared with those on an unrinsed cover glass in the previous papers.

Figure 6 shows the picture of the long flake separated naturally from the dried film at 20 μl of the amount of the initial suspension. Figure 6 shows also the thickness distribution of the flake measured by the charge-coupled device (CCD) observation (open circles) and by the laser microscopy (crosses). Clearly, the film of the broad ring area is thick around the outside edges, and the central region of the film is extremely thin. The shape of the section of the long flake is like the section of airplane's wing and beautiful. The angles between the adjacent spoke-like cracks (θ) were also shown by triangles in Fig. 6. Clearly, increase in the thickness of the dried film (d) is resulted in increase in the θ values except the central area of the dried film. This correlation was also observed so often for colloidal silica and polystyrene spheres on an unrinsed cover glass and explained with change in the elastic modulus of the film [7, 8], as was discussed above. In the central area, however, the common relationship between d and θ did not hold at all. This observation is not common because so many cracks appeared in the central area when 70 μl of suspension was dried up as is shown in Fig. 5. Causes for the discrepancy are not clear yet. It is highly plausible that there existed much more potential cracks, which was not observed clearly experimentally.

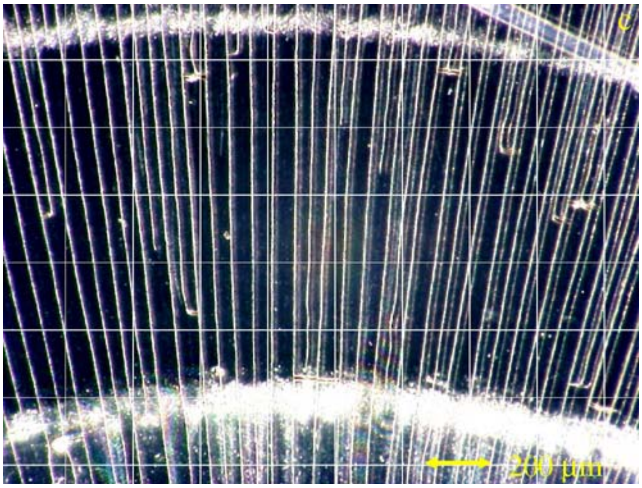

Fig. 4 Drying dissipative patterns of colloidal crystals of CS82 spheres on a rinsed cover glass at 25 °C. Part *c* of Fig. 1 is extended, in water, 70 μl, ϕ=0.033, exposure time=1/45 s, iris=3.5

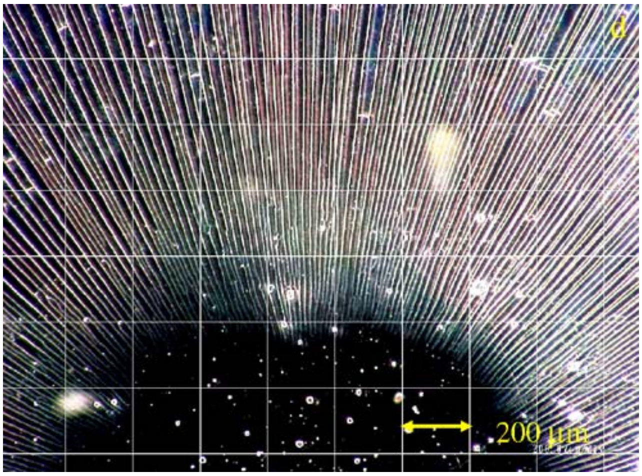

Fig. 5 Drying dissipative patterns of colloidal crystals of CS82 spheres on a rinsed cover glass at 25 °C. Part *d* of Fig. 1 is extended, in water, 70 μl, ϕ=0.033, exposure time=1/45 s, iris=3.5

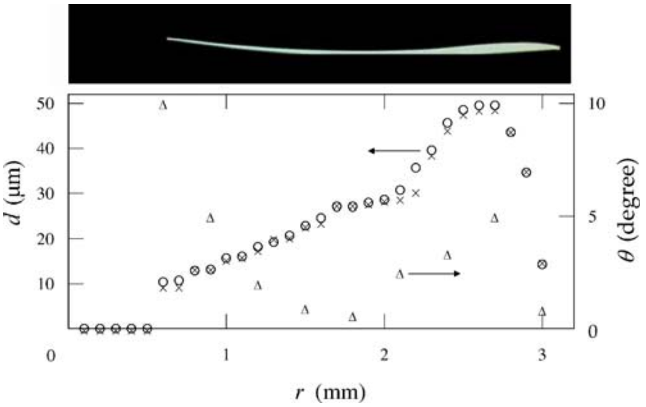

Fig. 6 Thickness (d) and inter-neighbored cracks angle (θ) of the dried film as a function of radius (r) at 25 °C. In water, 20 μl, ϕ=0.033, *open circle* CCD microscope, *cross* laser microscope

Kinetics of the crack growth of colloidal crystals on a rinsed cover glass

Figure 7 shows the growth processes of the cracks with time. At t=13 s, only the outside edges were dried up, but most area was the blue suspension state. At t=18 min 15 s, the cracks started to grow. The parallel crack lines developed first from right-hand side toward left-hand side and then turned to grow further toward the central region. It is interesting to note that the growth of the cracks was very fast and stopped around the middle point between the outside edges and the frontier of the suspension area. It is highly plausible that the black area between the growth stopping points and the suspension frontier is wetted with water, although the area looks like dried up with the naked eyes. The black area where the cracks appeared is, therefore, really dried up area. When the growth of the preceding crack line stopped, the growth of the new crack took place at the left-hand side neighbor cooperatively. The growth again stopped at the middle point. Then, another crack repeated further to grow at the left-hand side neighbor, and so on. After all the cracks were completed around the middle points, they grew toward the center area very slowly and simultaneously with the similar rate as the withdrawal of the suspension frontier. The fast and slow growth rates of the crack formation were determined from the plots of the lengths of the cracks against time as shown in Fig. 8a and b, and 6.2 mm/s and 0.0098 mm/s,

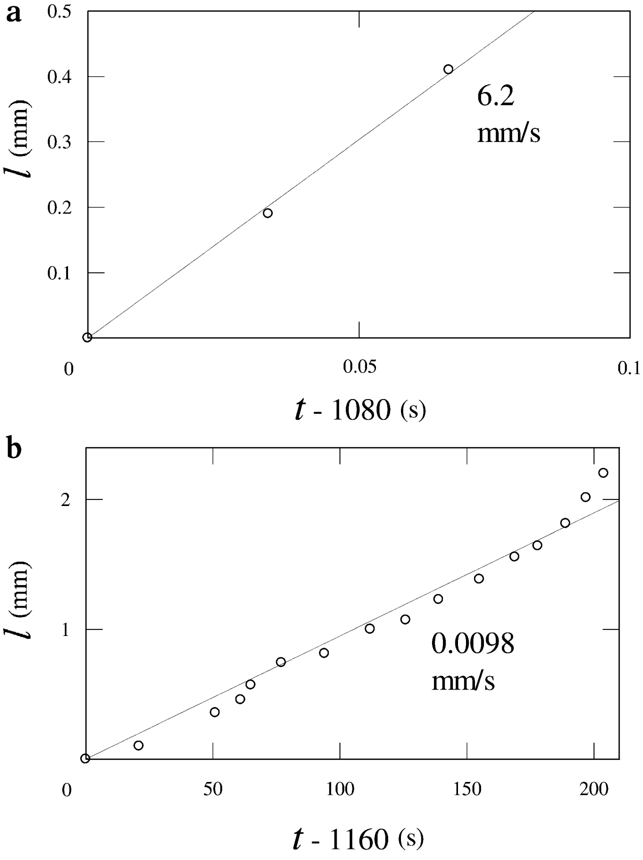

Fig. 8 Fast (**a**) and slow crack growth rate plots (**b**) of colloidal crystals of CS82 spheres on a rinsed cover glass at 25 °C. In water, 10 μl, ϕ=0.033

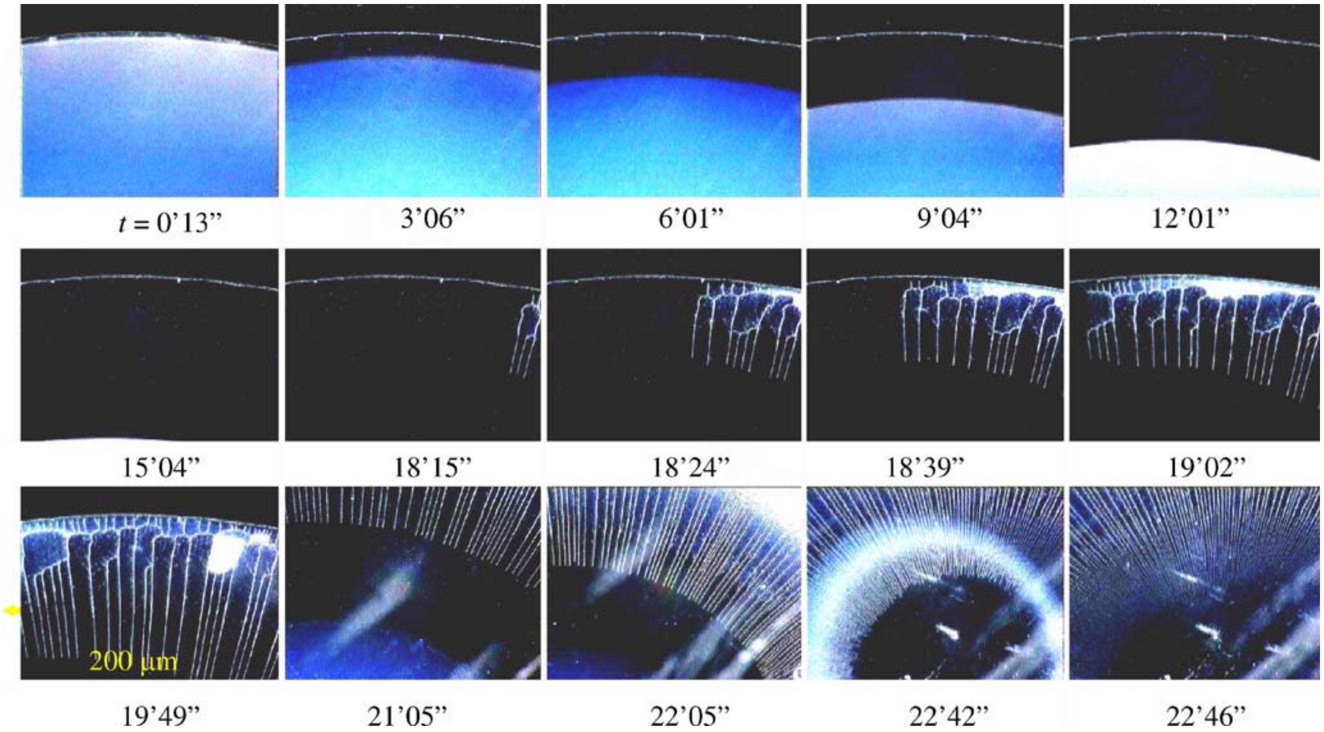

Fig. 7 Processes of the drying dissipative patterns of colloidal crystals of CS82 spheres on a rinsed cover glass at 25 °C. In water, 10 μl, ϕ=0.033

respectively. The former rate was about 630-fold faster than the latter.

Influences of initial liquid amount set on a rinsed cover glass

In this work, the liquid amount set on a rinsed cover glass (Q) varied between 5 and 70 μl. The initial area of the liquid at ϕ=0.033 on the cover glass (S) increased quite linearly from 28 to 284 mm^2 as Q increased from 5 to 70 μl at 25 °C. However, it should be noted that the absolute values of S were rather sensitive to the temperature and humidity of the room of laboratory in each experiments and also to the delicate difference in the degrees of the rinse of the cover glasses used. The angles between the adjacent spoke-like cracks (θ) coincided to each other irrespective of the liquid amount when the normalized θ values, θ/θ_{max}, were plotted against the normalized r values, r/r_{max}, although the graph demonstrating this observation was omitted in this paper.

Acknowledgment Financial supports from the Ministry of Education, Culture, Sports, Science and Technology, Japan and Japan Society for the Promotion of Science are greatly acknowledged for Grants-in-Aid for Exploratory Research (17655046) and Scientific Research (B) (18350057), respectively. Catalysts and Chemicals Co. is thanked deeply for providing the colloidal silica sphere samples used in this work.

References

1. Vanderhoff JW (1973) J Polym Sci Symp 41:155
2. Nicolis G, Prigogine I (1977) Self-organization in non-equilibrium systems. Wiley, New York
3. Ohara PC, Heath JR, Gelbart WM (1997) Angew Chem 109:1120
4. Maenosono S, Dushkin CD, Saita S, Yamaguchi Y (1999) Langmuir 15:957
5. Nikoobakht B, Wang ZL, El-Sayed MA (2000) J Phys Chem 104:8635
6. Ung T, Litz-Marzan LM, Mulvaney P (2001) J Phys Chem B 105:3441
7. Okubo T, Okuda S, Kimura H (2002) Colloid Polym Sci 280:454
8. Okubo T, Kimura K, Kimura H (2002) Colloid Polym Sci 280:1001
9. Okubo T, Kanayama S, Kimura K (2004) Colloid Polym Sci 282:486
10. Okubo T, Kimura H, Kimura T, Hayakawa F, Shibata T, Kimura K (2005) Colloid Polym Sci 283:1
11. Okubo T, Yamada T, Kimura K, Tsuchida A (2005) Colloid Polym Sci 283:1007
12. Yamaguchi T, Kimura K, Tsuchida A, Okubo T, Matsumoto M (2005) Colloid Polym Sci 283:1123
13. Okubo T, Kimura K, Tsuchida A (2006) Colloids surf B Biointerfaces, doi 10.1016/j.colsurfb.2006.10.012
14. Okubo T, Kanayama S, Ogawa H, Hibino M, Kimura K (2004) Colloid Polym Sci 282:230
15. Shimomura M, Sawadaishi T (2001) Curr Opin Colloid Interface Sci 6:11
16. Okubo T, Yamada T, Kimura K, Tsuchida A (2006) Colloid Polym Sci 284:396
17. Kimura K, Kanayama S, Tsuchida A, Okubo T (2005) Colloid Polym Sci 283:898
18. Okubo T, Shinoda C, Kimura K, Tsuchida A (2005) Langmuir 21:9889
19. Okubo T, Itoh Emi, Tsuchida A, Kokufuta E (2006) Colloid Polym Sci 285:339
20. Okubo T (2006) Colloid Polym Sci 284:1191
21. Okubo T (2006) Colloid Polym Sci 284:1395
22. Okubo T (2006) Colloid Polym Sci 285:331 CPS449, doi 10.10097/s00396-006-1576-6
23. Okubo T (2006) Colloid Polym Sci, 285:225 CPS396, doi 10.1007/s00396-006-1555-y
24. Terada T, Yamamoto R, Watanabe T (1934) Sci Paper Inst Phys Chem Res Jpn 27:173
25. Terada T, Yamamoto R, Watanabe T (1934) Sci Pap Inst Phys Chem Res Jpn 27:75
26. Terada T, Yamamoto R (1935) Proc Imp Acad Tokyo 11:214