

Construction of Anti-Counterfeiting Pattern On The Cellulose Film By In-Situ Regulation Strategies

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Abstract

Cellulose and its derivatives films are increasingly used in paper, packaging, and other fields, but there is limited research on its films with anti-counterfeiting patterns. Here, we demonstrate an approach to prepare cellulose film with a micro-millimeter scale pattern by lithium chloride (LiCl) crystal template, which grows out by the *in-situ* generation in the film formation process. The surface morphologies of the as-prepared film were systematically controlled by regulating the solution viscosity (η) and the surrounding temperature. The imprinting of LiCl crystal was retained on the film surface after rinsing. Moreover, the crystallinity of patterned film was significantly improved, and about 62 MPa increased tensile strength than the film without a pattern. Especially, these patterns were similar to fingerprint size, which had exhibited an excellent function to unlock fingerprint locked phones and showed a potentiality in the anti-counterfeiting yield.

1. Introduction

Due to the great coding capacity and extensive application, visually (Braeckmans et al. 2003; Han et al. 2012; Huang et al. 2010) and spectrally (Lee et al. 2010; Lee et al. 2014) encoded taggants have proven tempting as 'identifiers' to convey information about tagged items. On the other hand, most designs are insufficiently appropriate as 'security tags' for verification since these taggants are prone to cloning threats. Hypothetically, any deterministic encoding system eventually leads to counterfeiting by definition and code replication. As a result, a nondeterministic encoding system is required for robust authentication to ensure distinct and fundamentally irreproducible code outcomes.

A physical object with an intrinsic, unique, fingerprint-like property is known as a physical unclonable function (PUF). A random pattern with various features achieves its individuality. (i) It is constructed on the object's microstructure being randomly disordered throughout the production procedure; (ii) It is simple to construct yet impossible to duplicate, even by the producer; (iii) It is simple to understand yet difficult to anticipate.; and (iv) It is entirely unclonable by characterization. Due to the desirable encoding features, basic information about the tag does not have to be hidden for unclonable functions to work. They merely depend on the uniqueness of their physical properties. The uniqueness should initiate from the usual variance in the PUF production protocol. The utilization of biomimetic fingerprint-like structures was one of the most important ways for synthesizing PUF anti-counterfeiting materials. Liquid crystals and the random wrinkling of polymer films both contained artificial fingerprint-like features that may be read out via imaging. Nakayama et al. (Ohtsubob 2012) showed that the photo-polymerized ultraviolet (UV)-curable liquid crystals produce polarized patterns fixed in a random texture. Furthermore, Bae et al. (Bae et al. 2015) designed unique artificial fingerprints coated with disc-shaped polymer particles by randomly wrinkling silica films with remarkable encoding capability. Unfortunately, it is limited by a sensitive identification technique with 80% reliability, subjected to manual verification in practical application.

Recently, sensitive recognition technologies were improved and fused into PUF design. For example, Tian et al. (Tian et al. 2016) developed a material having electromagnetically sensitive areas by covering a randomly folded polymer sheet with plasmonic nanostructures. The plasmonic film was encoded with Raman tags that give bright surface-enhanced Raman scattering (SERS) signals. The inclusion of Raman tags offer stochastic chemical patterns on top of the nondeterministic structural patterns, expands the PUF key's encoding capability and the number of potential responses. However, they still suffer from some limitations, such as (i) orientation-sensitive optical codes (Baughman et al. 2002), (ii) short lifespan of fluorescent material (Feng et al. 2019), and (iii) narrow-ranged product applicability (Buchanan et al. 2005). Moreover, its patterned size mainly focused on the micro-nano level, and difficult to produce a clear visual appearance and judge anti-counterfeiting. On the other hand, overt macro-features let users authenticate the authenticity of a pack. Such characteristics are highly obvious and complicated, but they are difficult to duplicate. As a result, PUF taggants are not yet versatile enough for an industry scalable authentication technique. Meanwhile, above the materials of anti-counterfeiting taggants were mainly from the petroleum-based polymer matrix, which has caused serious white pollution. But, bio-based polymers could overcome this shortcoming, which had been widely applied in the packaging and other yields (Cazón and Vázquez 2021; Liu et al. 2021). Cellulose is one such renewable and degradable natural polymer (Mahmud et al. 2021), which film has high mechanical strength, excellent hydrophilic properties, good thermal resistance, and a good potential to replace petroleum-based films (Azeredo et al. 2017; Zhao et al. 2019). Surprisingly, limited reports were found regarding the macro-pattern on the surface of cellulose films as anti-counterfeiting code.

Previously, we prepared patterns on the cellulose film by convection of solution (Zhong et al. 2020). Herein, the *in-situ* growth of LiCl crystal on the surface of natural cellulose film at different temperatures was investigated, and the growth mechanism was explored systematically (Scheme 1). Meanwhile, various morphology of LiCl crystals was produced by controlling the solution's viscosity and temperature. It was observed that the morphology of LiCl crystal could be completely retained on the surface of cellulose film after rinsing and got the different macroscopic patterned film. This method was easy to operate and did not need complicated instruments and equipment. The pattern on the surface of natural cellulose film is crisp, complex, and difficult to reproduce, which exhibited a potential application in anti-counterfeiting.

2. Experimental

The quartz glass plate substrates (20 cm × 15 cm) were purchased from Lianyungang Ryo Quartz Products Co. Ltd., Jiangsu, China. Cellulose (degree of polymerization, DP ≈ 1400, 700, 400) was purchased from Xuzhou Lierkang Health Materials Co. Ltd., Fushan, China. Anhydrous LiCl was obtained from Shanghai Mclin Biochemical Technology Co. Ltd., Shanghai, China; and N, N-dimethyl acetamide (DMAc) was purchased from Guoyao Pharmaceutical Group Co. Ltd., Jiangxi, China. Carboxymethyl cellulose (CMC, DP=700) and Tri-cellulose acetate (DP=700) were purchased from Haidong Qinghua Co. Ltd., Zhangjiagang, China;

In preparing patterned cellulose films, a dissolution method was initially adopted to prepare cellulose solution, according to our previous reports (Zhang et al. 2021a; Zhang et al. 2021b). Then, the solution was poured onto a clean glass plate. A smooth glass rod with copper wire at both ends was used to scrape the plate's casting solution. The glass plate was then inserted into the baking oven, where the temperature was set for 70, 80, 90, 100, and 120 °C, respectively. After about two hours, the DMAc had been evaporated completely, and a polarizing optical microscope (POM) observed the crystal morphology of LiCl on the surface of cellulose film. The glass plate was then immersed in a water bath to remove the residual LiCl crystals and DMAc. After the LiCl/DMAc was removed entirely, the wet film was taken out and dried naturally at room temperature. The print of LiCl crystals was retained on the cellulose substrates even after rinsing. Finally, the pattern on the cellulose film was engraved by eliminating LiCl crystal and monitored by stereo-microscope. Similarly, the solution of CMC and Tri-cellulose acetate and patterns were achieved.

During the characterization, the viscosity of cellulose solution was measured by a digital viscometer (NDJ-5S, Pingxuan Scientific Instruments Co. Ltd., Shanghai, China). A stereo microscope (XTL-770E, Chang Fang Instruments Co. Ltd., Shanghai, China) was used to track the film formation process and take pictures. The morphology of crystals in the film was observed by a polarizing microscope (Nicon LV100POL, Japan). Alpha-Step IQ (2D benchtop surface profiler), HRP 350 series provides comprehensive surface metrology analysis and surface topography control solutions.

3. Results And Discussion

The films with divergent like a LiCl crystal were obtained in Figure 1 (a₁, a₂, and a₃). The concentration of the film-forming solution was 1.0, 1.5, and 2 wt %, respectively. The DP of cellulose was about 700. It was noticed that the setting of growth temperature at 90 °C, the crystal size was decreased with the increase of cellulose concentration. Cellulose film retained crystal morphology print after rinsing (Figure 1: b₁, b₂, and b₃). The daisy and chrysanthemum-like crystals appeared on the film's surface when the DP of cellulose was 1400 (Figure 1: a₅ and a₆), while the size was also different due to the solution concentration variation.

Considering the formation process of the crisp daisy and chrysanthemum-like print, we further investigated the effect of temperature (80-120 °C) on the morphology of LiCl crystal (Figure S1 and S2). It was observed that the size of the pattern increased first and then decreased in the process of increasing temperature from 80 °C to 120 °C (Figure S3). Meanwhile, an increasing number of branching was obtained with the increasing temperature (Figure S1 and S2). However, few regular patterns were obtained once the temperature was lowered than 90 °C (Figure S1 and S3). It showed that the formation of a perfect crystal needed enough activation energy.

Moreover, the print clarity was improved with the increase of concentration (viscosity) or DP according to the stereo-microscope picture (Figure S1 and S2) and characterization of surface profilometer (Figure 2: E₄ and E₅, Table S2 and S3). The main reason was that the growing DP and concentration could increase

the viscosity of the solution, thus improving the matrix stability, which was conducive to stabilizing the arrangement of LiCl crystal. The higher temperature was beneficial to LiCl crystals' growth and formed a relatively perfect patterned structure under relatively stable substrates.

To further verify the effect of different viscosity (0.031, 2.02, and 19.94 Pa. S) on the morphology of LiCl crystal, the variable cellulose concentrations (1.0, 2.0, and 4.0 wt %) with DP of 300 were used to produce patterned films using the same technique at 100 °C. While the viscosity was increased, the morphology of LiCl crystals on the cellulose film surface was changed from a divergent pattern (Figure 2: A and A₁) to a daisy-like pattern (Figure. 2: B and B₁). The pattern became curlier when concentration was increased to 4.0 wt % (Figure. 2: C and C₁). It means that the pattern can be regulated by changing the cellulose solution concentration at a specific temperature. Moreover, it was observed that the petal width for daisy or line for divergent and the ridge height were different, although these films had a similar pattern. The characterization of the surface profilometer (Figure 2: E₁ and E₂, Table S2 and S3) exhibited the width between the neighboring ridge and ridge height at a distance of 1 mm and 2 mm from the center. Furthermore, it was identified that the width between the neighboring ridge and ridge height would continue to increase with increasing distance from the center. This trend was similarly observed with the increase of the cellulose solution viscosity (Figure 2: E₄ and Table S2). However, only a little difference was observed on the height ridge and the width between neighboring ridges when the temperature was raised to 100 °C (Table S3). We understand that by changing the combination of concentration, temperature, and viscosity, many patterns of different heights and widths could be generated. The crisp pattern was like the unique characteristics of the fingerprint from humans (Figure 2: E₃), which may be used for anti-counterfeiting field.

During the experiment, it was observed that various LiCl morphologies could be formed. Besides, their print can be retained on the surface of cellulose film even after rinsing. To further explore the effect of the substrate on LiCl crystals' formation, we first investigated the growth process of its crystal from the evaporation of the pure solvent (DMAc, without cellulose) at different temperatures. As shown in Figure S4, the morphologies of LiCl crystals were almost the same octahedral structure at different temperatures and concentrations of LiCl after evaporation. However, it was evident that the size of the LiCl crystal increased with the increase of temperature and concentration (Figure S4.b). A similar phenomenon was also observed in a previous report while NaCl crystal morphology was produced with the assistance of other compounds such as formamides and urea (Zhang et al. 2011). Since both LiCl and NaCl belong to the cubic crystal system, it explains a similar growth mechanism. The carbonyl oxygen in acetamide had a strong interaction with lithium ions, thus stabilizing the surface of the LiCl crystal (1 1 1), leading to the formation of the octahedral crystal (Figure S4.c). This control experiment also exhibited that the cellulose solution induced some influence on the growth of LiCl crystal.

We further studied the effect of the types of matrix and solvent on the formation of patterns. In contrast, CMC (containing hydroxyl group) and tri-cellulose acetate (little hydroxyl group) were selected as growth matrix for LiCl crystal, where solvents were DMAc and a different solvent, respectively. The morphology

evolution of LiCl crystals in LiCl/DMAc and LiCl/water solvent systems was compared and discussed for the CMC matrix. Cubic crystals could also be formed in the CMC matrix regenerated from LiCl/water at 100 °C, almost the same as pure solvent systems. At the same time, divergent patterns were only produced in the CMC matrix regenerated from LiCl/DMAc, which was similar to that from cellulose substrate (Figure S5: a and b). The formation processing of LiCl crystal could be observed on the surface of CMC films regenerated from solution due to its slower growth rate. It was recorded at 20 s, 60 s, and 120 s for 0.5 wt % (Figure 3: a₁, b₁, c₁) and 2.0 wt % (Figure 3: a₂, b₂, c₂) CMC solution, respectively. The pattern started from cubic LiCl crystals, evolved into the octahedral structure, and finally formed divergent or similar structures. For Tri-cellulose acetate substrates, a similar result was also obtained, although it had no hydroxyl groups.

The above experimental phenomena further revealed that the interaction between LiCl and amide solvent was the prerequisite of forming diversity morphology on a cellulose film. Accordingly, the LiCl crystal growth in the cellulose matrix and its influencing factors was schematically presented in Figure 3 (I, II, III). The solvent evaporated slowly when the temperature was relatively lower (T=70, 80 °C). The cellulose solution was easy to flow and could not provide a stable matrix for the further growth of LiCl crystals at a low viscosity. Meanwhile, there was not enough activation energy for forming a perfect crystal at a low temperature. Consequently, the LiCl crystals were disseminated as particles in the matrix (Figure 3I). While the solution viscosity was increased, the cellulose solution provided a stable matrix for the growth of the LiCl crystal. The free LiCl molecule released by the evaporation of DMAc began to rearrange and gradually grew along a crystal plane of LiCl to form an octahedral structure. After that, these octahedral LiCl crystals could aggregate and form dendritic LiCl crystals on the film surface (Figure 3II). With the further increase of temperature (T=90, 100, 120 °C), enough growth activation energy could be provided. Meanwhile, the evaporation rate of the solvent accelerated increased the solution viscosity and stability. Finally, the perfect crystal could be formed, such as divergent, daisy, chrysanthemum, and other morphologies.

The XRD curves of cellulose film with different patterns mainly showed the characterization peaks at $2\theta = 12^\circ, 20^\circ$ (cellulose II) (Figure 4:a) (AlfredD. French. 2020; Xing L et al. 2018). The crystallinity order of film formed at different conditions was as follows: Dendritic film (80 °C) > Divergent film (90 °C) > Daisy film (100 °C) > Film without a pattern (25 °C). It could be seen that cellulose crystallinity was increasing firstly and then decreasing when the temperature ranged from 25-100 °C. The daisy-like film (100 °C) showed higher toughness among the patterned films. The tensile strength of films formed at high temperatures (80, 90, and 100 °C) was improved, more obviously comparing the film at 25 °C. The main reason was that LiCl was more easily crystallized due to the solvent evaporation quickly at higher temperatures (Figure S2 and S3). Crystal LiCl could be a nucleating agent during the film formation, which improved the crystallinity of cellulose film and favored the increase of tensile strength.

Interestingly, the pattern on the cellulose film exhibited an excellent anti-counterfeiting function similar to the fingerprint. As shown in Figure S6, the forefinger fingerprint was collected and stored on the phone. The phone locked was readily unlocked by the fingerprint printed on the pattern (Figure S6:c). But it was

not unlocked by finger with patterned cellulose film. However, it was not worked after the pattern was collected and stored on the phone (Figure 4c and Video 1). In addition, the anti-counterfeiting function was sustained after one year. In this process, thirty trials were given every month and found all responsive in one second (Figure S7). It is also worth noting that the artificially fingerprinted taggant held up well in harsh conditions such as low (-20 °C) or high temperature (60 °C) (Figure S7), RH>65, and exposure time < 1h. The results showed that cellulose film with these patterns could be used as an anti-counterfeiting key like a fingerprint.

4. Conclusion

In conclusion, a dendritic, daisy, diverging, chrysanthemum-like pattern on the cellulose surface was firstly successfully prepared by *in-situ* regulation of the morphology of LiCl crystal. The morphology of the LiCl crystal could be regulated by the changing temperature and viscosity of the solution. Moreover, the interaction between LiCl and amide solvent was the prerequisite of forming diversity morphology on a cellulose film. The patterned film exhibited higher crystallinity and tensile strength. The patterns on the film could be collected by phone and used as unlock triggers. Furthermore, countless points of temperature and viscosity, including their possible combination, could form hundreds of billions of patterned films with different heights and widths of the ridge, which should be used in anti-counterfeiting fields like a fingerprint from the human.

Declarations

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Scheme

Scheme 1 is available in the Supplemental Files section

Figures

Figure 1

Polarization microscopic (yellow) before rinsing and stereo-microscope picture (green) after rinsing on the surface of cellulose films formed at temperature for 90 °C (DP=700, a_1 , b_1 for 1.0 wt. %; a_2 , b_2 for 1.5wt. %; a_3 , b_3 for 2.0 wt. %), (DP=1400, a_4 , b_4 for 1wt. %; a_5 , b_5 for 1.5 wt. %; a_6 , b_6 for 2.0 wt %).

Figure 2

A (DP=300, 1.0 wt % for cellulose solution), B (DP=300, 2.0 wt % for cellulose solution), C (DP=300, 4.0 wt % for cellulose solution), Polarization microscopic picture (yellow: A, B, C) before washing and Stereo-microscope picture (green: A_1 , B_1 , C_1) after washing at temperature for 100°C. E_1 and E_2 for surface roughness measurements of lines aa_0 and a_1a_2 . E_3 for the model of fingerprints. E_4 and E_5 for change of the height and width of the ridge with the increase of viscosity and temperature.

Figure 3

Polarized microscope image of the growth process for LiCl crystals on the surface of CMC films from different concentration at the temperature for 100 °C, ($a_1 \sim c_1$, C= 4.0 wt %); ($a_2 \sim c_2$, C=12.0 wt %). Schematic illustration for the growth process of LiCl crystal on the surface of the cellulose film (I, II, III).

Figure 4

(a) XRD patterns of cellulose films with different patterns, (b) Mechanical properties of cellulose film with different patterns, (c, d, e) pattern information stored on the phone used as the key of unlocking.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Scheme1.png](#)
- [SupportingInformation.docx](#)
- [video1.mp4](#)