

Cellulose as an Eco-Friendly and Sustainable Material for Optical Anticounterfeiting Applications: An Up-to-Date Appraisal

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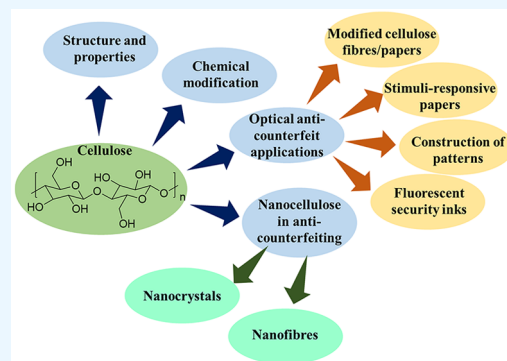
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ABSTRACT: The falsification of documents, currency, pharmaceuticals, branded goods, clothing, food products, and packaging leads to severe consequences. Counterfeited products can not only pose health risks to consumers but also cause substantial economic losses that can negatively impact the global markets. Unfortunately, most anticounterfeiting strategies are easily duplicated due to rapid technological advancements. Therefore, innovative and cost-effective antiforgery techniques that can offer superior multilevel security features are continuously sought after. Due to the ever-growing global awareness of environmental pollution, renewable and eco-friendly native biopolymers are garnering wide attention in anticounterfeiting applications. This review highlights the potential use of cellulose-based eco-friendly materials to combat the counterfeiting of goods. The initial section of the review focuses on the structure, properties, and chemical modifications of cellulose as a sustainable biomaterial. Further, the topical developments reported on cellulose and nanocellulose-based materials used as fluorescent security inks, films, and papers for achieving protection against counterfeiting are presented. The studies suggest the convenient use of cellulose and modified cellulose materials for promising optical antiforgery applications. Furthermore, the scope for future research developments is also discussed based on the current critical challenges in the fabrication of cellulose-based materials and their anticounterfeit applications.



1. INTRODUCTION

Forged goods, especially consumer products, microelectronics, pharmaceuticals, food items, currency, security documents, etc., cause substantial economic loss and affect governments, companies, and customers.^{1–3} As per the World Health Organization statistics, a high proportion of medications and pharmaceutical products, (~10%) globally and even higher (~25%) in developing countries, are counterfeits, which can impact consumers' health.⁴ Though there are several anticounterfeit measures, the duplication or replication of products is increasing at an alarming pace. Therefore, there is a dire need to improve anticounterfeit technology to prevent the distribution of counterfeit products worldwide.

Most anticounterfeit techniques rely on patterns easily recognized through visual inspection but are difficult to forge. In this context, security printing has garnered immense attention with approaches that exploit unique optical features for not only data encryption and decryption in printing and packaging industries but also to check the originality of products. The security features can be detected either visually or by using an appropriate instrument, upon illumination with a suitable light source or by application of various stimuli, including pH, solvents/chemicals, temperature, pressure, etc. and are ideal for information storage, encryption, and anticounterfeit applications. More and more researchers try

to create greater design options for data encryption and decryption to ensure multilevel data security by changing the stimulation mode, and also the decryption conditions do not damage the protected documents or objects. The demanding requirements of repeatability and processability are also constraints to the wide and practical applications of stimuli-responsive materials.⁵ Besides, there are other features including printed patterns such as holograms, barcodes, stamps, watermarks, colored fibers, fluorescent/optical variable/temperature variable inks, and colorimetric labels which helps in authentication.^{6–8} Though these are attractive approaches because of less cost and are easily applied in real life, they are not very effective as they provide only a primary level of security. Moreover, these conventional security features can be easily duplicated due to the continuous progress in high-quality printing technologies.⁹ Advanced multilevel protection can be achieved through intricate processes, using

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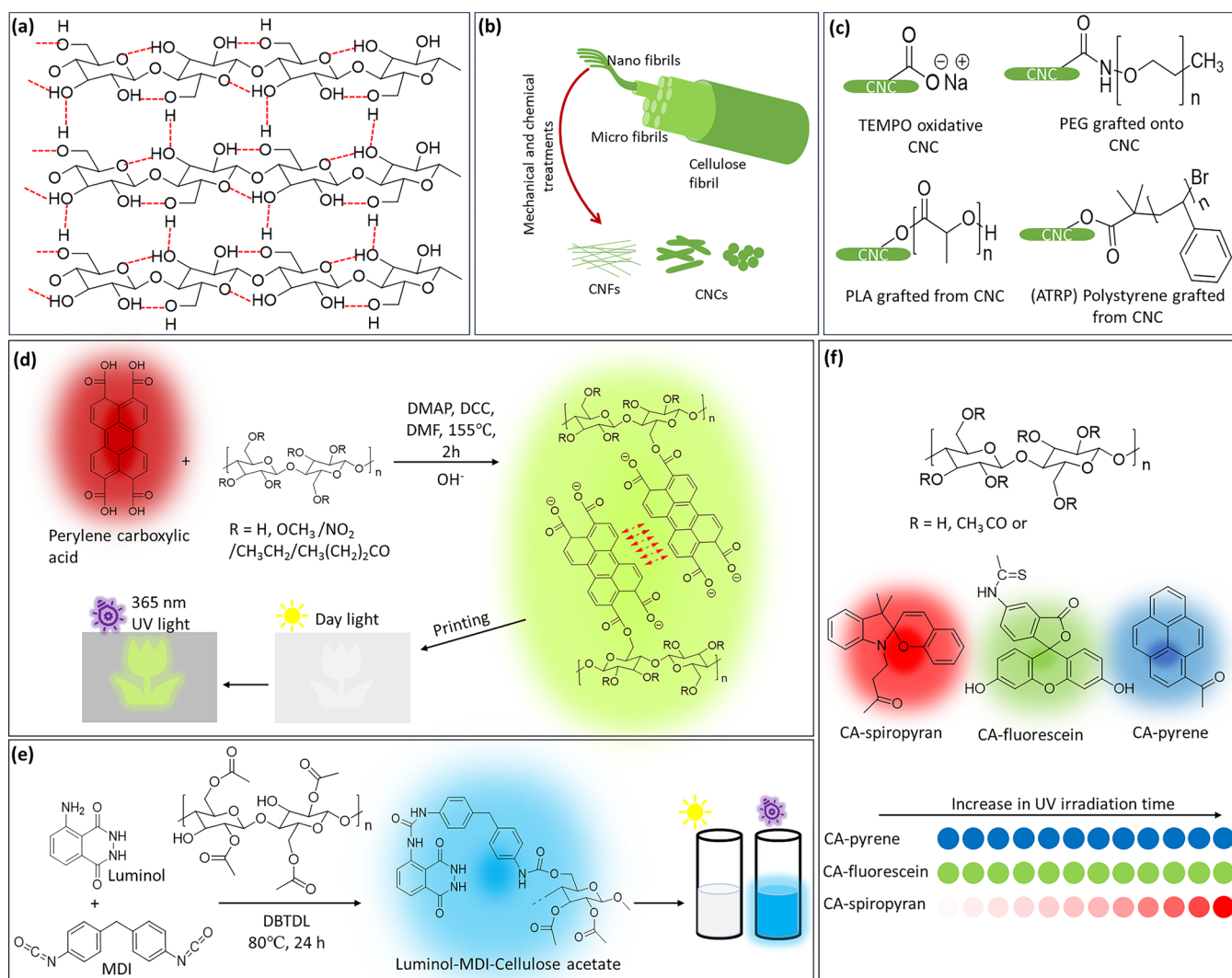


Figure 1. (a) Structure of cellulose depicting H-bonds within the polymer, (b) schematic illustration of cellulose fibers and nanocellulose, and (c) small molecule modification and polymer grafting of cellulose. Anchoring and dilution effect of cellulose–ACQ fluorophore conjugates with intense solid-state emission: (d) cellulose–perylene and (e) cellulose acetate–MDI–luminol composites and their fluorescent inks. (f) Dynamic trichromatic fluorescent materials with photoinduced fluorochromism for phototunable full-color emission.

suitable printing techniques in combination with different inks that offer dual fluorescence, up-conversion from the infrared, opalescence (iridescence), response to stimuli, etc. using various smart materials.¹⁰ In the recent past, secondary and multiple levels of protection technologies such as radio frequency identification (RFID) technology, laser coding, 3D holographic imaging technology, and molecular coding are widely used as they are unique and difficult to forge. However, relatively complex authentication or identification processes and the requirement of expensive equipment limit the use of many security materials in practical applications.

Anticounterfeiting approaches based on innovative fluorescent materials, including organic dyes, lanthanide-based materials, carbon dots (CDs), etc., have immense security potential.^{3,11–15} Nevertheless, poor thermal stability, photobleaching, and strong matrix-induced luminescence quenching severely impede the extensive industrial application of luminescence-based anticounterfeiting technologies. Therefore, highly scalable and easy-to-authenticate technologies based on eco-friendly functional materials with unique intrinsic optical features for anticounterfeiting remain challenging.¹⁶ Amidst

the usage of nonbiodegradable materials for security applications, and thereby the mounting concerns on environmental pollution, much research has been focused on natural polymeric materials that offer veritable prospects for future survival. The shortage of nonrenewable resources and intensification of environmental pollution have garnered increasing attention in developing naturally available polysaccharide-based materials¹⁷ for anticounterfeiting applications. Polysaccharides are biopolymers of carbohydrates synthesized by plants, animals, and humans that consist of glucose as the monosaccharide unit.¹⁸ Most of the natural polysaccharides, including starch, chitosan, gelatin, and cellulose, have been reported as resins or binders in security inks, films, papers, and composite materials in the anticounterfeiting arena.^{19,20} The use of cellulose as an abundantly available natural polysaccharide significantly reduces the product cost and offers a stronger commercial attraction in practical uses, especially in the packaging industry.

2. CELLULOSE AS A SUSTAINABLE AND ECO-FRIENDLY MATERIAL: STRUCTURE AND PROPERTIES

Cellulose ($C_6H_{10}O_5$)_n is the most abundant organic polymeric material derived naturally from plants; the most common and pure natural sources are cotton seed hairs, bamboo, and wood.²¹ This renewable high molecular weight polysaccharide can be isolated from a cellulose–lignin composite by chemical pulping, subsequent separation, and purification processes. Cellulose is an environment-friendly raw material because it undergoes microorganism-assisted biodegradation.^{22,23} Cellulose differs from synthetic polymers by virtue of its distinct polyfunctionality, high chain stiffness, and sensitivity toward the hydrolysis and oxidation of the chain-forming acetal groups, which determine its chemical properties and handling.²² Among the four different cellulose polymorphs, the naturally occurring one has β -D-glucose monosaccharide units connected through β -acetal linkages between C-1 and C-4 of adjacent glucose units. Due to the equatorial conformation of these glucose residues, the linear polysaccharide backbone adopts an extended, rigid, rod-like conformation, in addition to its chiral nature. The three hydroxyl (–OH) groups present in each monomeric glucose unit engage in strong inter- and intramolecular hydrogen bonding (H-bonding) networks with oxygen atoms on the neighboring or same chain (Figure 1a). Moreover, these H-bonds align the individual polymeric chains firmly to form microfibrils having high mechanical strength. Depending on the chemical and mechanical preparation approaches, different forms of cellulose materials, such as cellulose fibers, microfibrillated cellulose (MFC), and nanoscale cellulose, including cellulose nanofibers (CNF) and cellulose nanocrystals (CNC), with different fiber dimensions are perceived (Figure 1b).^{24–26}

The properties of cellulose mainly depend upon the degree of polymerization (*n*) which ranges between 10,000 and 15,000, depending on the plant source. Accordingly, the chemical composition and physical properties of cellulose-based materials can vary. The intrinsic properties, good biocompatibility and biodegradability, facile chemical modifiability, high transparency, good toughness, better moldability, and intriguing luminescence of cellulose-based systems, are very striking and have garnered extensive research attention. The eco-friendly carbohydrate is easily accessible and is used as an environmentally friendly raw material in paper, textile, and cosmetic industries and also in several other applications^{27,28} including alternative energy sources,²⁹ biodegradable wound dressings,³⁰ modern composite materials,^{31,32} or optoelectronics.³³ Moreover, the hydroxyl groups abundantly present on the polymer structure allow the conjugation of various moieties, and these modified cellulose products have been widely utilized as adsorbent materials, chemical sensors, bioimaging agents, ultraviolet (UV) shielders, and in anticounterfeiting.³⁴

3. CELLULOSE: CHEMICAL MODIFICATION STRATEGIES

The chemical modification of cellulose can be easily performed by facile chemical reactions,^{25,35} and these surface modifications do not significantly affect the chemical composition and crystalline nature of cellulose fibers. Modified cellulose generally preserves high tensile strength and biodegradable characteristics. Cellulose has a large number of active surface

hydroxyl groups, which account for its hydrophilic nature. However, preparing smart polymer composites using hydrophilic cellulose fillers is challenging due to their lower dispersion and compatibility issues with many hydrophobic polymers. In the recent past, several chemical strategies were followed to transform the surface groups for improving the hydrophobicity of cellulose: (i) substituting hydrophilic hydroxyl functionalities by introducing small molecules, and (ii) polymer “grafting onto” and “grafting from” approaches through atom transfer radical polymerization (ATRP), ring-opening polymerization (ROP), etc., have been successfully employed.³⁶

Substitution of primary hydroxyl groups on cellulose with small molecules is advantageous due to the possibility of diverse chemical reactions, high grafting efficiency, conducive reaction conditions, and optional functional groups for further structural modification. The three primarily used chemical reaction strategies are esterification, oxidation/amidation, and silanization. Esterification is generally performed by an acylation process with carboxylic acid anhydride using 4-dimethylaminopyridine or strong acid as catalyst. Introduction of aldehyde vs carboxylic acid onto cellulose surface is also possible through oxidation reactions, with the most commonly used being 2,2,6,6-tetramethylpiperidinyloxy radical (TEMPO) oxidation.^{37,38} The product generated during TEMPO oxidation with highly reactive carboxylic groups has also become a popular precursor for surface functionalization of cellulose. The surface oxidation of cellulose and nanocellulose obtained from wood can be achieved through selective catalytic oxidation of C-6 hydroxyl groups under moderate aqueous conditions. Further, commercial coupling agents—silanes—that contain an alkoxy silane group can modify the biopolymer by forming covalent bonds at one end and tailoring with suitable functional groups at the other to suit a given matrix.³⁹ Other chemicals such as titanate⁴⁰ and triazine derivatives^{41,42} can also react with cellulose.

Cellulose grafting is yet another emerging and efficient approach to endow the biopolymer matrix with improved interfacial interactions through physical entanglement or chemical/H-bonding. The surface-initiated ROP is the most suitable “grafting from” strategy that aids in solvent-free industrial fabrication, controllable grafted chain lengths, and high grafting densities.⁴³ This approach is mainly used to prepare poly(lactic acid) (PLA)-grafted cellulose. The facile and commercially scalable “grafting onto” free-radical-initiated reaction strategy can assist in manufacturing cellulose-based sustainable and biodegradable composites with improved mechanical properties. An example is the grafting reaction using dicumyl peroxide as a radical initiator to form a C–C bond between the methylene groups of CNCs and the methine groups of PLA. Reversible addition–fragmentation chain transfer polymerization (RAFT), ATRP, and click chemistry are other mild and attractive chemical approaches that have showcased immense prospective in the construction of polymer-grafted cellulose enabling high grafting efficiency.^{44–46} The modifications of cellulose using small molecules and polymers are presented in Figure 1c.

Although the chemical modification of cellulose has been largely explored, the limited choice of solvents to conduct these reactions is yet another challenge. Though cellulose is hydrophilic, strong intermolecular H-bonding, high polarity, and hydrophobic interactions limit its solubility in water and commonly used organic solvents. Therefore, special solvents

including *N*-methylmorpholine-*N*-oxide (NMMO), dimethyl sulfoxide (DMSO)/tetrabutylammonium fluoride trihydrate (TABF), *N,N*-dimethylacetamide (DMAc)/lithium chloride (LiCl), and ionic liquids are used for chemical modification of cellulose.⁴⁷

4. OPTICAL ANTICOUNTERFEIT APPLICATIONS OF CELLULOSE-BASED MATERIALS

Cellulose can be used either as it is or modified structurally through chemical/physical processes, grafting or by simply mixing with suitable material for anticounterfeiting application. The application of cellulose can be expanded to the optical field by incorporating conventional fluorophores such as quantum dots, polymer dots, rare-earth materials, dyes, etc. into the cellulose matrix, resulting in remarkably luminescent soft materials. These cellulose-based fluorescent composites can be beneficial in anticounterfeiting and security printing due to (i) excellent processability inherent to cellulose, enabling easy preparation of fluorescent inks from traditional fluorophores, (ii) exceptional film-forming capability of cellulose, making them compatible with different substrates including glass, plastics, metals, and ceramics, (iii) Förster resonance energy transfer (FRET) that can be realized by a simple blending process, and (iv) stimuli-responsive chiral behavior of the polymer chain. The following section illustrates various reports on the application of cellulose-based materials in anticounterfeit applications.

4.1. Fluorescent Security Inks. Security inks are used to introduce safety features to protect printed documents, currency notes, labels, or packaging against fraudulent reproduction. Many standard anticounterfeiting inks are associated with several drawbacks such as poor light fastness, long-term toxicity, and high cost, thereby impeding their real-life applications. Biopolymer cellulose-based security inks can be an eco-friendly and cost-effective alternative with superior properties, as discussed below.

4.1.1. Fluorescent Inks from Cellulose–ACQ Luminophore Conjugates. It is well-established that the emission of certain fluorescent materials is quenched in their solid state or concentrated solutions as they aggregate together to form excimers or exciplexes to trigger aggregation-caused quenching (ACQ).⁴⁸ These ACQ materials are therefore not recommended for preparing fluorescent materials for solid-state anticounterfeiting. However, the presence of ACQ fluorophores in small amounts in host materials can offer required solid-state fluorescence because they emit intensely in dilute solutions. In addition, this low concentration of ACQ luminogens will not significantly change the intrinsic characteristics of the host material including processability, solubility, biocompatibility, mechanical features, and biodegradability.⁴⁹ With this background, few studies are reported wherein the ACQ luminogens have been incorporated into the cellulose backbone to prepare fluorescent security inks.

Tian et al. effectively conjugated a perylene derivative as conventional ACQ luminogen to cellulose for preparing pH-responsive inks that display excellent solid-state fluorescence emission.⁵⁰ The carboxyl groups of the perylene derivative were esterified to C-6 hydroxyl groups of cellulose/cellulose acetate/cellulose acetate butyrate/cellulose nitrate/ethyl cellulose, as shown in Figure 1d. The 7% degree of substitution and alkaline environment (pH = 13.6) suppressed the aggregation of the ACQ luminophore–cellulose conjugate to display an intense greenish-yellow fluorescence with 58% quantum yield.

This bright emission has been attributed to (i) the restricted mobility of the perylene derivative when bonded covalently to the cellulose skeleton and (ii) the destruction of the H-bonding and π – π stacking. In turn, electrostatic repulsion is established among perylenes due to the ionization of the residual carboxylic acid functionalities into a negatively charged carboxylate ion on the conjugates in the alkaline medium. Thus, the synergistic influence of anchoring and dilution due to cellulose chains and the ionic repulsion of the ACQ luminophores inhibit their aggregation and hence the self-quenching of fluorescence. The cellulose–peryrene conjugate is readily dissolved in dimethylformamide (DMF) and processed into pH-responsive ink to obtain different patterns on paper, glass, steel, and polymer substrates for security printing. In addition to the strong fluorescence, this material retained the good processability intrinsic to cellulose and can be easily processed into different printing patterns, coatings, films, and fibers.

Nawaz et al. fabricated cellulose acetate-based innovative material by chemically connecting ACQ–fluorophore luminol onto the cellulose acetate backbone using 4,4'-methylene diphenyl diisocyanate (MDI) as a cross-linking agent.⁵¹ The intramolecular charge transfer phenomenon in the extended conjugated structure of the cellulose acetate–MDI–luminol composite led to bright aqua blue fluorescence, as presented in Figure 1e. The covalent attachment and subsequent immobilization of luminol onto the cellulose chains and the diluting effect induced by the biopolymer structure hindered their aggregation and subsequent self-quenching of fluorescence. The polymer composite was dissolved in DMSO and used as an ink to draw patterns and develop security barcodes, which could be effectively used for information encryption applications. Besides, QR codes constructed using the material were efficiently utilized for practical applications. Moreover, different weight ratios of polymer blends were used to prepare flexible and strong fluorescent films and coatings, which showed aqua blue fluorescence upon UV illumination, and could be used for food packaging. In addition, the material can be applied to ensure the safety and integrity of bank currency notes, bank cards, documents, brands, etc.

Tian and co-workers reported a feasible and economical method to realize tunable multicolor fluorescent materials with advanced level security features for anticounterfeiting.⁵² They could achieve full-color phototunable fluorescent materials that rely on trichromacy and dynamically tunable FRET phenomena by covalently coupling spiropyran, fluorescein, and pyrene with cellulose acetate. These trichromatic materials, cellulose–spiropyran (red) which displayed photoinduced fluorochromic behavior, cellulose–fluorescein (green), and cellulose–pyrene (blue), could be readily converted into printing inks as they retained the exceptional processability of the biopolymer, as shown in Figure 1f. Dynamically tunable FRET between the donors (green and blue) and the acceptor (red) was perceived by simply blending the inks using these three trichromatic materials. Various fluorescence colors and intensities were achieved by finely tuning the blending ratio of the RGB components and their excitation intensity as well as irradiation time. These cellulose-based fluorescent composite materials could meet excellent reversibility, stability, and versatility in material processing and are beneficial in security printing due to their (i) phototunable reversibility based on the noncontact and nondestructive authentication method, (ii) easily formulated fluorescent inks with excellent processability, (iii) simple

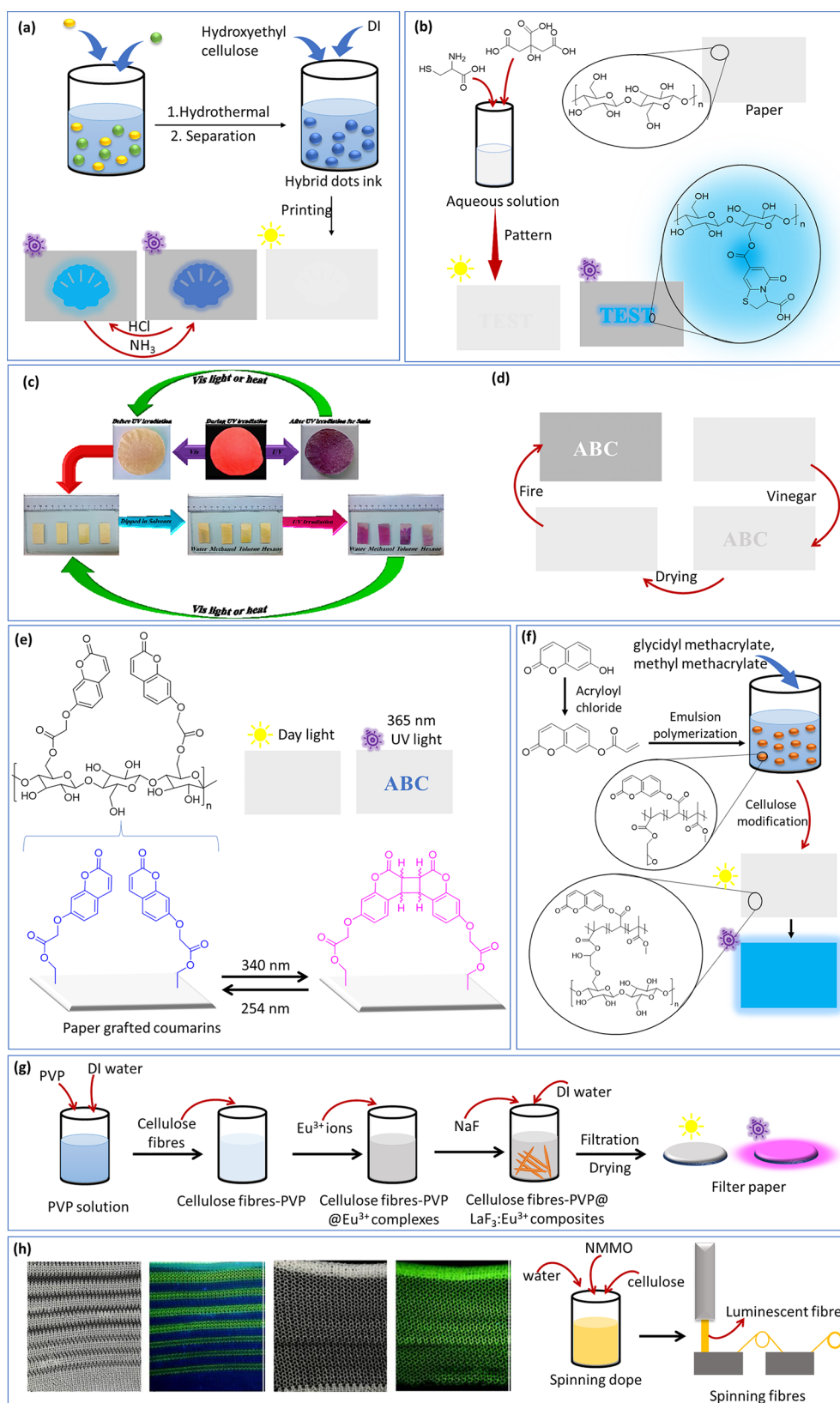


Figure 2. (a) Color-switchable hydroxyethyl cellulose hybrid dots ink. (b) Citric acid–cysteine as an invisible security ink on cellulose substrate. (c) Photochromic stimuli-responsive paper for anticounterfeiting. Reprinted with permission from ref 59. Copyright 2016 Elsevier. (d) Cellulose fiber–hydroxyapatite nanowire secret paper for information protection. Photoresponsive cellulose–coumarin papers with (e) blue and (f) cyan emissions upon UV light excitation for hidden and reversible optical data storage as well as anticounterfeit application. (g) Cellulose fiber–PVP@LaF₃:Eu³⁺ composite fluorescent paper. (h) Lyocell process and photographs of knitted fabrics fabricated using modified cellulose fibers under daylight and luminescent green upon 254 nm UV irradiation. Reprinted with permission from ref 74. Copyright 2019 Elsevier.

blending-enabled FRET process, (iv) controllable ratio of the RGB components using an inkjet printer, and (v) more information conveyed due to dynamic fluorescence in full-color space. The team demonstrated remarkable applications of RGB trichromatic conjugate inks by printing patterns that could emerge as a dynamic image upon 365 nm UV illumination. Moreover, the color tone could gradually transit from blue to full color with prolonged UV exposure and return to the original blue color under visible light. The fluorescent printing patterns are extremely hard to replicate, forge, and reverse engineer. Besides, the complex dynamic nonlinear dependency between the fluorescent inputs and outputs has been well-utilized as an encryption algorithm. Furthermore, the broad substrate compatibility expands the applicability of these cellulose-based full-color fluorescent composites in security printing, information encryption, dynamic anticounterfeiting, etc. Fascinatingly, attractive features including wide-spectrum full-color emission and dynamic color and intensity properties can be fine-tuned using external stimuli.

4.1.2. Fluorescent Inks from CDs Using Hydroxyethyl Cellulose as Binder. There are several reports on anticounterfeiting applications of CDs.^{53–56} However, their inks display several limitations: (i) fluorescence upon a single wavelength UV excitation with low-level security application, (ii) ACQ when deposited on metal, plastic, glass, and silicon substrates, and (iii) easily washed off with water. In order to address these drawbacks, an eco-friendly, nontoxic, and inexpensive security ink with durable and high-level covert features was formulated by Fu et al.⁵⁷ They combined hydrothermally prepared silicon/carbon hybrid dots with a hydroxyethyl cellulose binder to effectively prevent the ACQ of hybrid dots. The water-dispersible colorless ink displayed widespread practicability attributed to the combined merits of hydroxyethyl cellulose and hybrid dots. Customized patterns could be screen-printed onto various substrates including cellulosic paper, cotton fabric, polyethylene terephthalate (PET) film, silicon wafer glass, and metal to detect a blue fluorescence under a 365 nm UV source. The prints also displayed outstanding fastness due to hydroxyl and amino groups available in the ink components. Moreover, acid/base-dependent switchable fluorescence color imparted higher-level security feature to the prints. The cyan fluorescence of the patterns observed upon exposure to hydrochloric acid gas changed back to blue when placed in the presence of ammonia gas as presented in Figure 2a. These security features of the hydroxyethyl cellulose hybrid CDs ink were demonstrated using an invisible inkjet-printed QR code that could be read as a fluorescent blue code under UV light illumination. Additionally, the hidden information could be read using a QR code recognizer or smartphone to realize a double anticounterfeit protection. The ink can impart high-level covert security protection to food packaging, apparels, and documents based on the pH-dependent fluorescence color switching of the printed patterns.

4.2. Construction of Patterns on Cellulose Paper. Cellulose-based materials are commonly used in commodity packaging. Therefore, Chen et al. reported a facile, relatively low-cost, and green technique to chemically modify cellulose using citric acid–cysteine ink to safeguard authentic products.³⁴ Under high temperature, citric acid and cysteine generate conjugated thiazole pyridine carboxylic acid (TPA) that exhibits high fluorescence quantum yield as well as good biocompatibility. The concentrated aqueous mixture of citric

acid and cysteine can penetrate the amorphous regions of cellulose to facilitate its chemical modification without any dissolution. Upon further multidehydration reaction of the ink that occurs during the drying process, the TPA formed gets conjugated to cellulose to permanently mark concealed information on packaging, which can be observed under 365 nm UV irradiation (Figure 2b). Therefore, a citric acid/cysteine aqueous solution can be conveniently utilized as an invisible ink on cellulose-based substrates for anticounterfeit printing. Furthermore, the strong chemical conjugation between cellulose and TPA delivered an antirinsing property to retain the pattern on the film surface, despite repeated rinsing with water. Thus, TPA-modified cellulose powders, fibers, papers, and films can be an excellent alternative anticounterfeit strategy. Yet another attractive feature is water being the only solvent used during the reaction and postprocessing, not only eliminating pollution but also reducing the manufacturing cost.

Jing et al. demonstrated a micro-millimeter scale pattern on cellulose film using a LiCl crystal template that grows out via in situ generation during the film formation process.⁵⁸ The LiCl crystal imprint remained on the paper to display antirinsing properties. Amazingly, these patterns, which are similar to fingerprint size, showed potential in the anticounterfeiting field as they could remarkably function to unlock fingerprint-locked phones.

4.3. Stimuli-Responsive Papers. Stimuli-responsive papers based on photo- and solvatochromic behaviors offer beneficial features upon UV irradiation for anticounterfeit applications.

4.3.1. Through Noncovalent Interactions. Abdollahi et al. demonstrated a green strategy for the fabrication of stimuli-responsive paper using a ring-opening reaction between microcrystalline cellulose matrix and spiropyran containing epoxy-functionalized photochromic latex obtained through semicontinuous emulsion polymerization.⁵⁹ The photochromic efficiency of these papers was achieved through the preservation of the spiropyran moiety from degradation in the highly polar cellulose matrix. The photoresponsive papers could show reversible color changes upon alternating UV and normal light irradiation, as depicted in Figure 2c. Moreover, the colored papers could repeatedly revert back to the original colorless form upon application of heat or visible light. These smart papers displayed intense color changes in wet conditions when immersed in water and methanol due to H-bonds and dipolar interactions but a different color when they are dry. The merocyanine open-ring form of the spiropyran moiety enabled color changes when exposed to polar and nonpolar solvents. These smart papers also own significant photostability and photofatigue resistance with prospective use in anticounterfeiting and confidential documents.

Chen et al. reported an encryption–decryption method based on the color-changing secret paper fabricated from cellulose fibers and ultralong network-structured hydroxyapatite nanowires.⁶⁰ The aqueous suspension containing nanowires and a paper sheet former was used to prepare the secret paper with an integrated porous networked structure, wherein the nanowires wrap around to fill the spaces between the cellulose fibers through H-bond interactions. Inexpensive and environment-friendly white vinegar was conveniently used as an invisible security ink to encrypt and store covert information on the white secret paper, as displayed in Figure 2d. Fascinatingly, the information can be read in gray–white

color within a short response time of <10 s upon exposure to fire as the decryption key. The unwritten areas on the secret paper turned black due to the generation of combustion residues of cellulose fibers. The secret paper could be applied in covert information protection as it does not collapse during the fire-assisted decryption process because of high thermal stability and excellent fire resistance of the nanowires. Similarly, Hu et al. used a fluorescent molecule to prepare a flexible cellulose paper film by drop cast method which served as a blank storage device.⁶¹ The data written using a metal bar showed no change in emission unless it was fumed with ethyl acetate. These simple encryption–decryption techniques can be used for data recording.

4.3.2. Through Covalent Bonding. With the exception of bar codes and RFID tags, most of the widely used anticounterfeiting techniques, including special inks, watermarks, holograms, security threads, intaglio printing and microtaggants negatively affect the paper, although they are visible to naked eyes. Therefore, storing covert information without affecting the paper is immensely vital for tracking, antiforging and security applications. In recent years, physical or chemical modification of cellulose has been achieved using stimuli-responsive small molecules, both organic and inorganic. However, the ability of such stimuli-sensitive materials to covalently bond with cellulose papers provides several benefits over physical modification or simple doping. Excellent resistance to photofatigue and photobleaching, good photostability, reduced aggregate formation, and leakage in the case of light-sensitive materials are a few fascinating advantages.⁶² Therefore, covalently modified cellulose papers are of interest as they provide access to robust tamper-proof materials but do not compromise the physical appearance of the paper. Moreover, the hidden information is not easily erased by solvents while using invisible photoluminescent inks. Yet another ambitious objective in short-lived data storage is to develop external stimuli-responsive materials with reversible properties for erasing and rewriting through covalent modifications to cellulose.

D'Halluin et al. developed covalent photopatterning of a smart reversible photoresponsive cellulose paper for hidden as well as reversible optical data storage.⁶³ Photoresponsive coumarin unit was covalently grafted to every ten glucose unit of cellulose paper via the esterification process. Short-lived optical data was stored through covalent means using the attractive strategy that relies on the light-mediated reversible dimerization of coumarin grafted onto the cellulose paper surface. Coumarin photodimerized to produce cyclobutane dimer⁶⁴ through a [2 + 2]-cycloaddition upon irradiation at 340 nm and cycloreversed upon exposure to 254 nm light source, as shown in Figure 2e. This unique hidden and reversible optical data storage approach could find immense applications as smart devices for tracking, QR codes, and anticounterfeiting applications.

Similarly, Delavari et al. used 7-acryloxy coumarin (7-AC) as a binder to chemically modify cellulose fibers.⁶⁵ Epoxy-functionalized fluorescent polymer nanoparticles were prepared by copolymerizing 7-AC with glycidyl methacrylate and methyl methacrylate through emulsion polymerization. The hydroxyl groups of the water-dispersed cellulosic paper pulp were chemically modified by a ring-opening reaction with surface epoxy groups of the prepared nanoparticles. The nanoparticle-modified cellulose papers exhibited a bright cyan emission when excited at 315 nm and were used to prepare

fluorescent anticounterfeiting inks and papers, as shown in Figure 2f.

4.4. Lanthanide(III) Ion-Modified Cellulose Fibers/Papers. Fluorescent fibers with unique and captivating luminescent features have been widely explored in trade-marking and anticounterfeiting.^{66,67} In the recent past, typical fluorophores such as rhodamine, azo dyes, fluorene, etc. have been developed as synthetic modifiers for fluorescent fibers.⁶⁸ However, luminescent dye-based fluorescent fibers are non-environmentally friendly, expensive, and have poor photostability, which limit their industrial applicability. Recently, research efforts have been dedicated to developing eco-friendly, low-cost, and color-tunable fluorescent fibers.⁶⁹ Biopolymer cellulose can be used as reinforcement fiber and matrix material. These reinforcement fibers not only are recyclable and biodegradable but also display excellent fiber–matrix adhesion and good mechanical performance.

Luminescent complexes based on trivalent lanthanide (Ln) ions have emerged as competing candidates for anticounterfeiting applications during the past decade, attributed to their fascinating properties. They display narrow absorption/emission bands covering the visible and near-infrared (NIR) regions, broad-range and intense fluorescence, high color purity, long fluorescence lifetime, relatively low toxicity, dopant ion-based multicolor and up-conversion luminescence, high resistance to photobleaching, as well as temperature and pressure treatment, favorable structural, optoelectronic, and magnetic features.^{70–72}

Wang et al. reported a green technique to prepare photoluminescent cellulose fibers-PVP@LaF₃:Eu³⁺ through in situ chemical deposition of lanthanum (La³⁺), europium (Eu³⁺), and fluoride (F⁻) ions onto the surface of bleached hardwood pulp cellulose fibers using an aqueous solution of polyvinylpyrrolidone (PVP) as the coupling agent.¹⁶ The PVP chains with –C–N–C=O groups covering the surface of the fibers enabled strong static adsorption of the organic/inorganic material. The highly flexible composite paper was white under daylight, and the fluorescent red emission of the photoluminescent paper under 365 nm light irradiation remained stable for 15 days with good acid and alkali resistance. The fluorescence intensity can be controlled by tuning the amount of Eu³⁺ and La³⁺ ions in an aqueous medium. The fluorescent paper with good writable and printable properties could be used for large-scale security applications, including packaging, labels, or display materials, as shown in Figure 2g.

It is well-established that, compared to their bulk counterparts, nanomaterials exhibit different optical, thermal, mechanical, and magnetic properties ascribed to the increased surface area, higher number of defects, crystal lattice strains, and unsaturated coordination sites.⁷³ Therefore, Skwierczynska and co-workers fabricated cellulose fibers modified with La(III) ion (LaF₃:Ce³⁺, Gd³⁺, Eu³⁺, CeF₃:Tb³⁺, and CePO₄:Tb³⁺)-doped inorganic luminescent nanoparticles.⁷⁴ The fibers were prepared through the lyocell process, wherein cellulose dissolved in an aqueous solution of NMMO was spun using a dry–wet method. The introduction of nanoparticles into the cellulose matrix enabled not only good mechanical properties but also multicolored bright fluorescence emission: green in case of Tb³⁺-doped fluoride and phosphate-modified fibers and red for Eu³⁺-doped fluoride, when irradiated with 200–300 nm UV light. These fibers can be used to mark security documents and produce value papers for special purposes, including identity cards, driving licenses, passports, etc. Luminescent

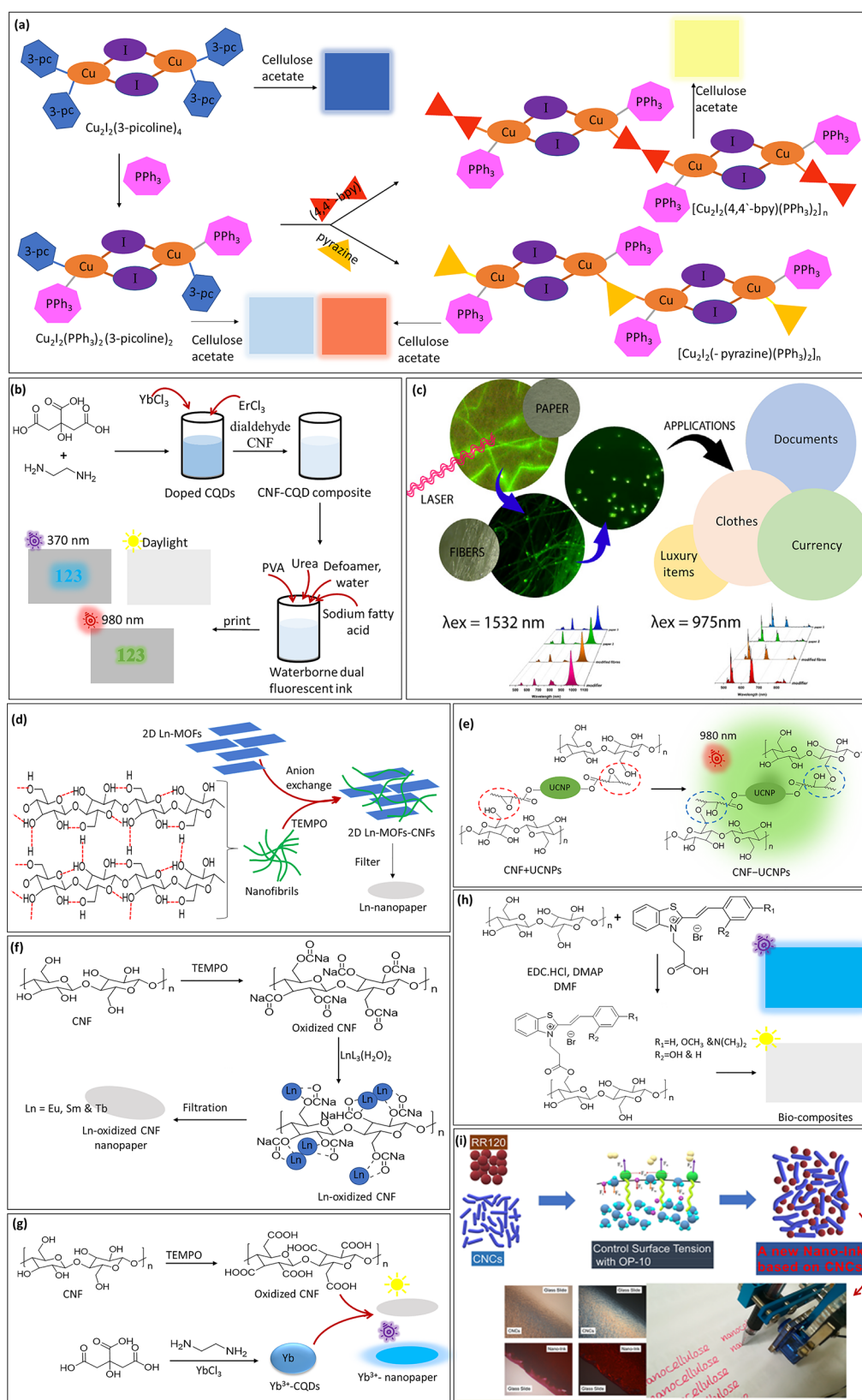


Figure 3. (a) Luminescent materials with wide-spectrum emissions based on cellulose acetate–CuI complex nanofibers. (b) Yb/Er CQD–dialdehyde CNF composites with UV luminescence and UCPL for waterborne dual fluorescent security ink. (c) Functionalized cellulose fibers and papers based on La nanoparticles for advanced anticounterfeiting. Reprinted with permission from ref 85. Copyright 2022 Elsevier. (d) 2D Ln-MOF-grafted CNF fluorescent nanopaper with good transparency, haze, and flexibility, (e) luminescent nanopaper based on garlic skin cellulose–UCNPs, (f) Eu, Sm, and Tb complex-functionalized oxidized CNF hybrid nanopaper and (g) Yb³⁺ nanopaper and water-based ink with NIR and visible emission. (h) Biocomposite film based on chitosan-reinforced styrylbenzothiazolium-g-CNC and (i) RR120-CNC nanoink with unique polarization properties for anticounterfeiting. Reprinted from ref 106. Copyright 2019 American Chemical Society.

textiles/fabrics, as shown in Figure 2h, can also be prepared using these composites to serve as efficient protection systems against counterfeiting including security labels for clothing.

5. NANOCELLULOSE IN ANTICOUNTERFEITING

Nanocellulose, developed from cellulose, has gained growing interest as a prominent green material of the modern era.⁷⁵ The negative surface charge, electric double layers, and steric effects account for the stability of nanocellulose.⁷⁶ These nanosized cellulose materials are attractive due to their abundant availability, superior mechanical properties, and renewable and biocompatible features. Nanostructures of cellulose include CNFs and CNCs that are generally obtained through mechanical processing, and acid hydrolysis, respectively. Smart luminescent materials with tunable properties can be realized through a wide range of chemical reactions involving the abundant surface hydroxyl functional groups, while the internal structure is barely altered.

5.1. Nanofibers. CNFs are several microns long with a diameter of tens of nanometers. They are ideal building blocks to host a wide variety of guest materials for developing CNF-based flexible matrices. These rod-shaped nanomaterials are becoming popular in the anticounterfeiting arena due to large surface area, plentiful hydroxyl groups, easy modification prospects, distinct rheological properties, low thermal expansion coefficient, high mechanical modulus and strength, good biocompatibility, and renewability.^{77–80} These CNFs are explored to design and construct advanced materials through surface modification by doping with organic/inorganic small molecules/materials, either by physical or chemical modifications.^{81,82} Various luminescent materials, including up-conversion nanoparticles (UCNPs), dyes, CdS quantum dots, and La-based complexes, have been effectively used to modify nanocellulose for diverse antiforgery applications.

5.1.1. Coordination Complex–Cellulose Acetate Composite Fibers. Coordination complexes based on Copper(I) iodide (CuI) are renowned for their strongly emissive optical features due to the Cu₂I₂ dimer retained in a ligand-exchange process. Therefore, Chen et al. combined this optical material and cellulose acetate nanofibers through a simple top-down electrospinning process to obtain four types of one-dimensional (1D) luminescent inorganic–organic hybrid nanofibers.⁶⁹ The emission color of the prepared CuI-organic ligand–cellulose acetate nanofibers was tunable through modification of the ligands: purple for (3-picoline)₄, blue for triphenyl phosphine (PPh₃)₂(3-picoline)₂, orange for (pyrazine)(PPh₃)₂, and yellow for (4,4'-bipyridine)(PPh₃)₂ (Figure 3a). The bonding sites of the polymer, conformation of polymer chains, density of the electrospun solutions, the distance between the needle and collector, feeding rate, and the applied voltage decide the surface morphology of the fibers. These unique CuI–organic ligand–cellulose acetate nanofibers with 300–600 nm diameter showed excellent thermal stability until 280 °C and photostability with >80% intensity retained after UV lighting for 48 h. These 1D composites could serve as materials in trademarking and anticounterfeiting.

5.1.2. La–Cellulose Nanofiber Composites. Luminescent fibers and papers that can be excited using a single wavelength of light are prone to easy forgery because of the rapid developments in science and technology. Hence, it is increasingly essential to implement innovative and complex strategies to protect genuine goods, security documents, and currency notes.⁸³ In this context, cellulose can be modified

using two distinct, noninterfering molecules that can be excited using different wavelengths to achieve dual-excited fibers and papers.⁸⁴ However, the main drawback associated with this strategy is the need to use two different materials in sufficient and optimum quantities to ensure bright and visible luminescence perceivable by the naked eye. Unfortunately, the functional properties of cellulose deteriorate significantly in the presence of large amounts of additives in the matrix, which can affect further processing of the composite material.^{85,86}

Compared to UV-excited ones, up-converting materials are more sophisticated as they require advanced and expensive IR sources to excite them. Anticounterfeiting performance through double excitation by UV and NIR light sources can be realized using rare-earth elements.^{87,88} Large Stokes shift and narrow emission in the NIR region with absorption near 980 nm lead to up-conversion photoluminescence (UCPL) performance of Er³⁺ and Yb³⁺ ions. This strategy that assists in higher energy transfer probability to enhance UCPL was well-utilized by Li et al.⁸⁹ He blended Yb and Er to carbon quantum dots (CQDs) that were obtained hydrothermally from citric acid and ethylenediamine. Further, the doped CQDs were grafted through reductive amination reaction onto dialdehyde CNF prepared by cellulose endonuclease-mediated hydrolysis and subsequent periodate oxidation. The composite obtained was mixed with poly(vinyl alcohol) (PVA) and additives to prepare a waterborne dual fluorescent ink for industrial use in printing and packaging. The CQDs exhibited blue fluorescence and green UCPL upon UV and NIR excitation at 370 and 980 nm, respectively, to achieve a dual anticounterfeiting effect, as presented in Figure 3b. The composite ink can be used to generate QR or bar codes to store information and also to obtain invisible letters, 2D code patterns, and art pictures on paper. This invisible ink performs remarkably well on several substrates, including cotton and linen clothes, cardboard, polystyrene plastic boards, and packaging wood boards for security purposes, attributed to good thixotropy and yield stress of CNF.

Yet another choice was to incorporate a solo material that could be excited using two different wavelengths into the CNF. Though this strategy demands more complex luminescent structures, these modifiers are required only in less quantity and are homogeneously dispersed in the cellulose fiber–matrix, which preserves the mechanical properties of the fibers. Hence, Szczszak and co-workers fabricated lyocell fibers by introducing β-NaYF₄:Yb³⁺,Er³⁺ into the cellulose matrix.⁸⁵ The luminescent fibers were spinned using the environmental friendly NMMO method to form a luminescent up-converting paper that could offer multimodal protection to documents. The paper exhibited bright green or yellowish up-conversion emission upon either 975 or 1532 nm NIR laser excitation (Figure 3c). This feature of the modified paper is very challenging to imitate or forge and can provide a high level of security. A potential counterfeiter can probably reproduce and mimic the visual protection enabled by paper through green luminescence of the fibers using some commonly available fluorophores that are excited with UV light. However, the up-converting fibers/paper have substantial potential as antiforgery composites with exceptional performance as they display advanced “three-level” safety: (i) green-yellow luminescence upon NIR laser excitation (975 or 1532 nm), (ii) unique “fingerprint” spectral pattern ascribed to the narrow emission bands of Er³⁺, and (iii) long UCNP emission lifetimes depending on Ln³⁺ ions in the host matrix and the spectral

region monitored. The genuine item can be distinguished from its fake replica by observing the delayed fluorescence to avoid the short-lived background fluorescence.

The security levels in anticounterfeiting technology can be further improved by introducing materials with superior bifunctional properties. In addition to fluorescence measurements, genuine articles can be identified by checking their magnetic properties, which makes them more difficult to counterfeit. Magnetic core/luminescent shell-type nanostructures that offer simultaneous luminescent–magnetic or luminescent–plasmonic activity through the combination of two dopant Ln ions (Tb^{3+} and Eu^{3+} with intense green and red luminescence) and magnetite (biocompatible and highly magnetic) have been reported.⁹⁰ Therefore, Skwierczyńska and group fabricated fluorescent–magnetic cellulose fiber ($\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{NH}_2/\text{PAA}/\text{LnF}_3$) based on the Ln-doped fluorides.⁹¹ The inner silica layer coating over iron (II,III) magnetic core in the magnetic core/shell nanostructures helped to avoid the possible explosive redox reactions between iron ions and NMMO during cellulose dissolution and dry-wet fiber spinning process. The composite fiber with good mechanical features exhibited a strong magnetic response, in addition to the superior and uniform bright multicolor emission under UV light. These luminescent–magnetic fibers offer advanced, multimodal protection, which could be used in document and clothing security systems to prevent fake documents and textiles. The pattern sewn on fabric using these unique, multifunctional threads is almost impossible to counterfeit. Their authenticity can be proven by observing a glow under UV light and magnetization using a magnetometer.

Advancement in processing more sophisticated up-converting materials that use expensive equipment with an IR excitation source makes it more difficult to counterfeit than the UV-excited ones. Therefore, the same research group reported yet another multifunctional magnetic upconverting fibers using core/shell type nanostructured magnetite nanoparticles and Ln-doped fluorides that could find possible applications in smart textiles and security documents.⁹² They modified cellulose fibers by introducing Fe@Yb,Er NPs that contain upconverting $\text{YOF:Yb}^{3+},\text{Er}^{3+}$ nanocrystalline fluorescent shell, which not only displayed a magnetic response, but also showed bright red emission under NIR laser irradiation at 975 nm. The presence of a surfactant improved the dispersion and stability of the magnetic-luminescent modifier NPs in the fiber structures. The superior mechanical properties of these bifunctional fibers allow their processing to knitted fabrics and documents to enable advanced and multimodal protection against counterfeiting.

5.1.3. Ln-Based Cellulose Nanopaper. Cellulose nanopapers are widely used for packaging and labeling applications and need anticounterfeit methods for tracking the production as well as distribution chain.⁹³ Nanopaper with CNF as a polymer matrix with good mechanical features, high optical transparency, low coefficient of thermal expansion, good biodegradability, high stability and strength can be modified by combining the luminescent materials/fluorophores into the cellulose matrix.^{94,95}

Chang et al. reported cellulose nanopapers using 2D Ln (Nd, Yb, or Er) molecular organic framework (MOF)-grafted TEMPO-oxidized CNFs.⁸⁰ These composite nanosheets prepared using an ultrasonic peeling method from 3D supramolecular H-bonded single crystals revealed characteristic ligand-field-splitting emissions of Yb^{3+} (975 nm) and Nd^{3+}

ions (888, 1062, and 1337 nm) upon 250–400 nm excitation. The efficient NIR luminescence, high optical haze and >90% transparency offer an opportunity to utilize these flexible Ln nanopapers in paper-based anticounterfeiting (Figure 3d).

Zhao et al. prepared luminescent CNF nanopaper from garlic skin by grafting activated rare-earth UCNP for elongating the fibrous network using a pressure-controllable extrusion paper-making technique (Figure 3e).⁹⁶ The UCNP ($\text{NaYF}_4:\text{Yb,Er}$) were activated with oleic acid ligand capped on the surface through epoxidation treatment. The heterogeneous network of CNF forms the backbone in the nanopaper and the UCNP are chemically incorporated into the spaces of CNF to restrict the light scattering. This assembled structure holds high transparency, strong UCPL upon 980 nm excitation, and good flexibility that can offer diversified multimodal anticounterfeiting facilities.

Miao et al. used a simple solvent exchange and subsequent fast press-controlled extrusion paper-making process via the TEMPO method for three kinds of Ln (Eu, Sm, Tb) complex-functionalized oxidized CNF hybrid nanopapers with heterogeneous network architectures (Figure 3f).⁹⁷ The surface carboxyl groups of oxidized CNF undergo covalent coupling with Ln ions. All three Ln-based nanopapers showed good thermal stability, unique optical transparency, good flexibility and multiluminescence upon ligand-mediated excitation of the corresponding Ln ions (Eu: red, Sm: orange, and Tb: green) through the intramolecular energy transfer from the ligands to the Ln ions. These features of the nanopapers can be potentially utilized in security applications, especially for credit and ID card protection.

Zhang and co-workers reported highly transparent and flexible Yb^{3+} nanopaper with NIR and visible emissions.⁹⁸ Yb^{3+} -CDs synthesized through the hydrothermal method from citric acid, ethylenediamine, and ytterbium(III) chloride (YbCl_3) was grafted onto TEMPO-mediated oxidized CNF matrix using a press-controllable extrusion film-making process. High-level triple-model security using Yb^{3+} nanopaper in terms of blue to yellow color tuning, NIR/visible spectra, and nanosecond/microsecond lifetime was accomplished. Moreover, the colorless and transparent aqueous solution of Yb^{3+} -CQDs-CNF can be used as a water-based security ink on paper, and the patterns are stable under moist or aqueous environment (Figure 3g). In yet another study, Chen et al. fabricated (Nd-MOFs)-grafted TEMPO-oxidized CNFs using with down-conversion NIR (1080 nm under 311 nm excitation) and up-conversion visible (450 at 580 nm excitation) emissions through solvothermal approach.⁹⁹ These Nd nanopapers with switchable up- and down-conversion fluorescence (visible and NIR dual emissions) could be used in anticounterfeiting applications. Further, Zhang and co-workers demonstrated the preparation of transparent nanopapers using Ln-MOF (Ln = Eu and/or Tb)-modified TEMPO-oxidized CNFs. The luminescence of these nanopapers could be modulated to achieve green, yellow, and red emission colors upon 365 nm illumination, while only a pink colored emission was observed when excited with 254 nm light source.¹⁰⁰ The combination of color-tuning and photoswitching features that can be controlled by adjusting $\text{Eu}^{3+}/\text{Tb}^{3+}$ molar ratio and excitation wavelength, respectively could be exploited in anticounterfeiting.

5.1.4. Plasmonic Nanopapers. Cheng et al. fabricated stable and flexible plasmonic nanopapers with good mechanical properties using CNFs and silver nanocubes by vacuum

filtration method.¹⁰¹ The nanopapers could serve as a nonforgeable anticounterfeiting system, as the information from any optically active molecule can be encoded in the nanopaper. The nanopapers were coded with multiple optical signals incorporating various layers of security features: (i) surface plasmon resonance and fluorescence information that can be easily verified by naked eye and (ii) difficult to replicate SERS mapping with random Raman intensity distribution that can be readily authenticated by Raman spectroscopy using a computer vision technique.

5.2. Nanocrystals. CNCs are crystalline, lightweight, less dense and demonstrate a unique combination of large surface area, superior rheological properties, high mechanical strength, eco-friendly, biocompatibility, biodegradability, and a wide range of aspect ratios (1 to >100).^{102–104} In recent years, the low-cost commercial production from natural sources, including wood pulp, has prompted the manipulation of CNCs to develop new products at the nanolevel. The presence of abundant surface hydroxyl groups and negative surface charges allow surface modifications through easy conjugation of small fluorescent molecules to introduce unique properties and features.^{89–92} The following section focuses on the use of CNCs for security or anticounterfeiting applications.

5.2.1. CNC Ink. Fardioui et al. reported a multicolor luminescent biocomposite film based on chitosan-reinforced styrylbenzothiazolium-g-CNC.¹⁹ The invisible/photoluminescent film was obtained by combining CNC, highly transparent and flexible biopolymer chitosan, and donor- π -acceptor benzothiazole dye with excellent fluorescence. The styrylbenzothiazolium derivatives synthesized using Knoevenagel condensation were chemically functionalized onto CNC through trans-esterification and covalent coupling. Further, these photonic materials were integrated into chitosan by solvent casting method. The biocomposite exhibited increased film resistance, stiffness, and ductility. The solution of biocomposites can be used as an ink to make a colorless design under visible light, which produces a fluorescence response under 365 nm UV light for anticounterfeiting application (Figure 3h). The fluorescent biocomposite can be used for drawing or printing to impart security features on fabric or other products.

Wang et al. successfully prepared a nanoink based on reactive red 120 dye (RR120)-grafted CNCs for antiforgery in security applications.⁷⁶ CNCs obtained in high yield through acid hydrolysis of cellulose materials were purified by adding ammonium bicarbonate. The nanoink from dyed CNCs displayed good writing performance using a gel pen with no ink congregation and breakage, when the optimum proportion of RR120 was 1.67%. However, the nanoink was lighter in shade than the routine ink in gel pens, which affected the readability. In order to improvise the writing quality, the same team made another attempt wherein CNCs were directly mixed with RR120 (instead of grafting) and surfactant (OP-10).¹⁰⁶ They succeeded in preparing a new nanoink with deep-red color, which displayed the best writing performance with 2.5% of RR120 and 0.04% of OP-10 (Figure 3i). The cost-effective ink met the requirements of the commercial inks, and also inherited the unique polarization properties that is beneficial for its use in anticounterfeiting.

Chirality can be useful in realizing security inks for anticounterfeit applications. The plane of polarization of the incident light will be rotated if a linearly polarized light passes through a chiral media; this phenomenon is called circular

birefringence or optical rotation. Birefringence produces various fascinating optical effects when transmission is observed after placing the object of interest between crossed polarizers. All effects of polarization can be easily masked by diffused and depolarized reflection from a white background, though specular reflection may be of use in security printing. This problem can be evaded by using CNC-based birefringent ink on dark paper to avoid multiple scattering and attenuate diffuse reflectance under crossed polarizers. Chindawong et al. worked on the nematic order of the CNC-latex blend for use as a birefringent ink in security printing.¹⁰ The chiral-nematic fraction of phase-separated dispersions (15% solid content) of CNC was blended with latex 3:4 weight ratio to prepare security ink that showed good adhesion onto paper. This CNC-based special ink exhibited diffuse reflection when the polarizers were inserted between the paper and the incident light or the observer. Moreover, the ink was peculiar as it scrambled the background polarization without being a strong scatterer. When printed onto dark paper and viewed without polarizers, the letters appeared darker than the background. On viewing with crossed polarizers, the letters appeared brighter than the background. This contrast inversion style holds excellent potential utility in security printing and subsequent optical authentication.

5.2.2. CNC-Photonic Films and Papers with Chiral Nematic Coatings. Artificial structural colors have fascinated researchers for their plausible application in anticounterfeiting because they offer superior properties compared to organic dyes and pigments in terms of durability, nontoxicity, resistibility to photo or chemical bleaching, iridescence that cannot be mimicked, and flexible tunability, as long as the constructed structures remain undamaged.¹⁰⁷ In this context, it is worth mentioning that the aqueous dispersions of CNCs can arrange themselves (evaporation-induced self-assembly (EISA)) above a critical concentration into an ordered chiral nematic structure with periodic spiral structures along a given axis.^{108–110} The phase is retained even in dried films with photonic properties. This layered chiral nematic organization rotates through the stack selectively, and reflects circularly polarized light (CPL) to display vivid iridescent structural colors. These colors derived from interference, diffraction, or light scattering depend on the refractive index and the pitch of the helical structure.^{111,112} The color arising from the periodically layered CNC photonic crystals is entirely different from the emission mechanisms based on specific energy consumption of light across the visible range of conventional dyes and pigments.

Security features that use polarization-dependent structural colors and selective swelling patterns based on chiral nematic or cholesteric CNCs have gained immense research attention. The application of chiral coatings on smart materials can trigger stimuli-responsive behavior. Environmental factors, including pH, electric current, magnetic field, pressure, stress, humidity and heat can influence selective reflection and diffraction of these chiral materials. Besides, the abundant surface hydroxyl groups on CNCs assist in the formation of aligned mesoporous structures with adjustable channels and binding sites, depending on the chiral nematic structure.¹⁰ Photonic crystals with multiple and complex stimuli-responsive strategies offer great design possibilities for optical data encryption. Phenol formaldehyde (PF) resins as well as CDs and zinc oxide quantum dots are reported as admirable substrate materials to fabricate CNC-based photonic compo-

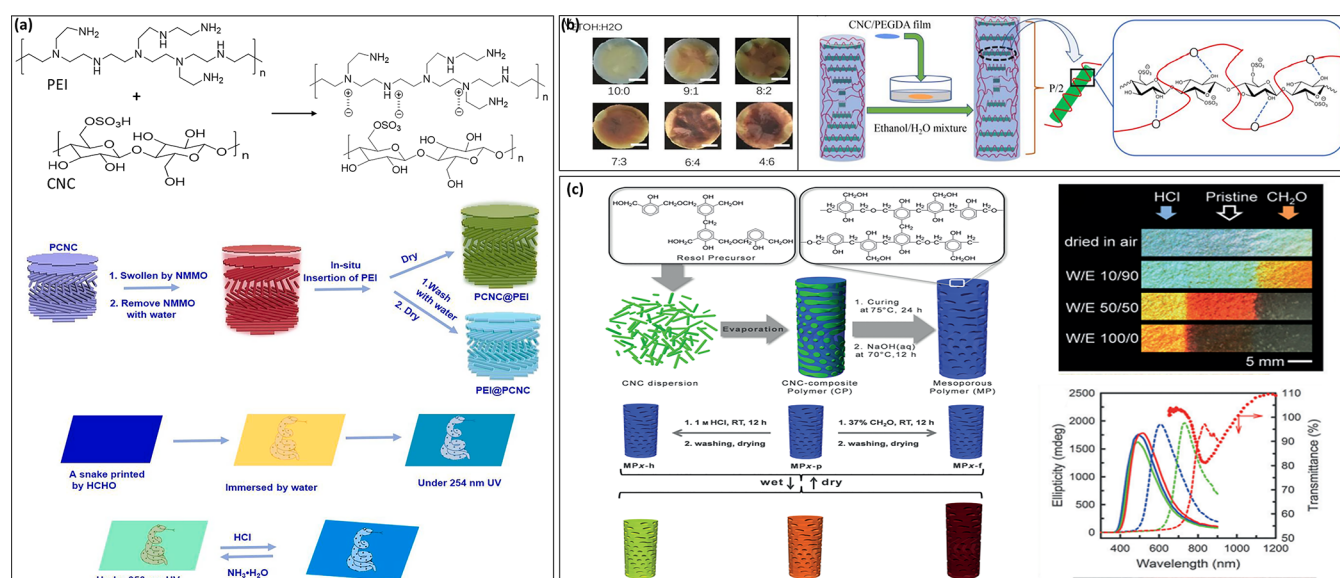


Figure 4. (a) CNC–PEI composites based iridescent patterned photonic film with multiresponsive features for anticounterfeiting. Reprinted with permission from ref 105. Copyright 2022 Elsevier. (b) Optical images of CNC/PEGDA composite film immersed in ethanol/water mixture and swelling mechanism for red-shift of the multifunctional film. Reprinted with permission from ref 122. Copyright 2020 Elsevier. (c) Chiral nematic mesoporous iridescent CNC-PF resins with solvent swelling/drying-based reflected colors. Reprinted with permission from ref 113. Copyright 2015 John Wiley and Sons.

sites with stimuli-responsive color tuning.^{113,114} Yet another effective stimulation strategy of photonic crystals is their wettability response. Infiltration and subsequent swelling can increase the period of the photonic crystals and construct invisible red-shifted structural color codes that are revealed upon stimulation with liquids.¹¹⁵ Surface modifications of CNC materials and dynamic humid flow can create invisible patterns that could appear by wetting.¹¹⁶

It is well-known that electrostatic interactions can play a vital role in chiral systems and their response to external stimuli.¹¹⁷ In this context, the development of intelligent coatings through the introduction of ionizable polymers or polyelectrolytes that possess cationic or anionic charges to form electrostatic interactions with chiral nematic CNCs are worth mentioning. The self-assembly of polymers into the chiral nematic CNCs can efficiently increase mechanical flexibility. Moreover, the interactions during the assembly process can enable conformational changes to regulate the helical pitch finely and thereby the iridescent colors based on the charge density of both the species, polymer conformation and network formation.^{118–120} When CNC is combined with neutral polymers, the helical pitch is controlled by means of H-bonding associations between similar mesogenic units that carry hydroxyl groups. Moreover, these invisible/photoluminescent films whose properties can be tuned using external stimuli can provide next-generation functional materials for advanced anticounterfeiting applications.^{121–123}

Jiang et al. developed chiral nematic composite films through in situ incorporation of poly(ethylene imine) (PEI: a weakly basic polyelectrolyte) into the swollen matrix of poly(ethylene glycol) (PEG)–CNC films (Figure 4a).¹⁰⁵ PEG coassembled with CNCs derived from wood obtained through acid hydrolysis to improve the homogeneous distribution of PEI into the PEG–CNC matrix. The ionic interaction and H-bonding between the cationic PEI and negatively charged pulp fibers in the well-assembled structures increased the reinforcement and high folding endurance properties of the prepared

film. The intercalation of PEI into CNC resulted in CPL with controllable handedness and dissymmetry factors and displayed optical responsiveness in terms of structure color and fluorescence intensity to various stimuli for manufacturing foldable encryption composite films. The blue fluorescence of the film changes to yellow-green when immersed in a water–ethanol mixture due to the water-induced increase in helical pitch, as depicted in Figure 4a. However, the fluorescence intensity decreased with an increase in water content due to swelling-induced softer and looser conformation. Further, upon immersing these films in formaldehyde, the Schiff base bond formed between formaldehyde and PEI resulted in red-shifted emission color. The patterns encrypted on the composite films using formaldehyde solution can be decrypted by immersing the films in water to display the patterns. Besides, the cyan fluorescence that was quenched when the patterns were dipped into acidic aqueous solutions could be restored later upon treating with a basic solution (Figure 4a). These beneficial multiple responsive natures of the films offer excellent features for data encryption-decryption process.

A multifunctional 3D-cross-linked composite film was constructed by Huang et al. through the coassembly of CNC and poly(ethylene glycol) diacrylate (PEGDA) precursor, subsequent UV curing, and final masking with poly(ethylene glycol) methacrylate (PEGMA).¹²² The PEGDA matrix encapsulated CNC to provide good water-resistant properties and flexibility to the film through H-bonding interactions. Upon immersing the CNC/PEGDA anticounterfeiting film in ethanol/water mixture (Figure 4b), the region with higher and lower degrees of cross-linking exhibited different redshift degrees and turned into green and orange, respectively, which was distinguishable with naked eyes. These color changes are attributed to the corresponding lower and greater degrees of expansion, which decreases and increases the helical pitch of the chiral nematic structure. The original blue color of the film was restored upon drying, and the patterns disappeared in the reusable film. Environmentally friendly LiCl inks can be used

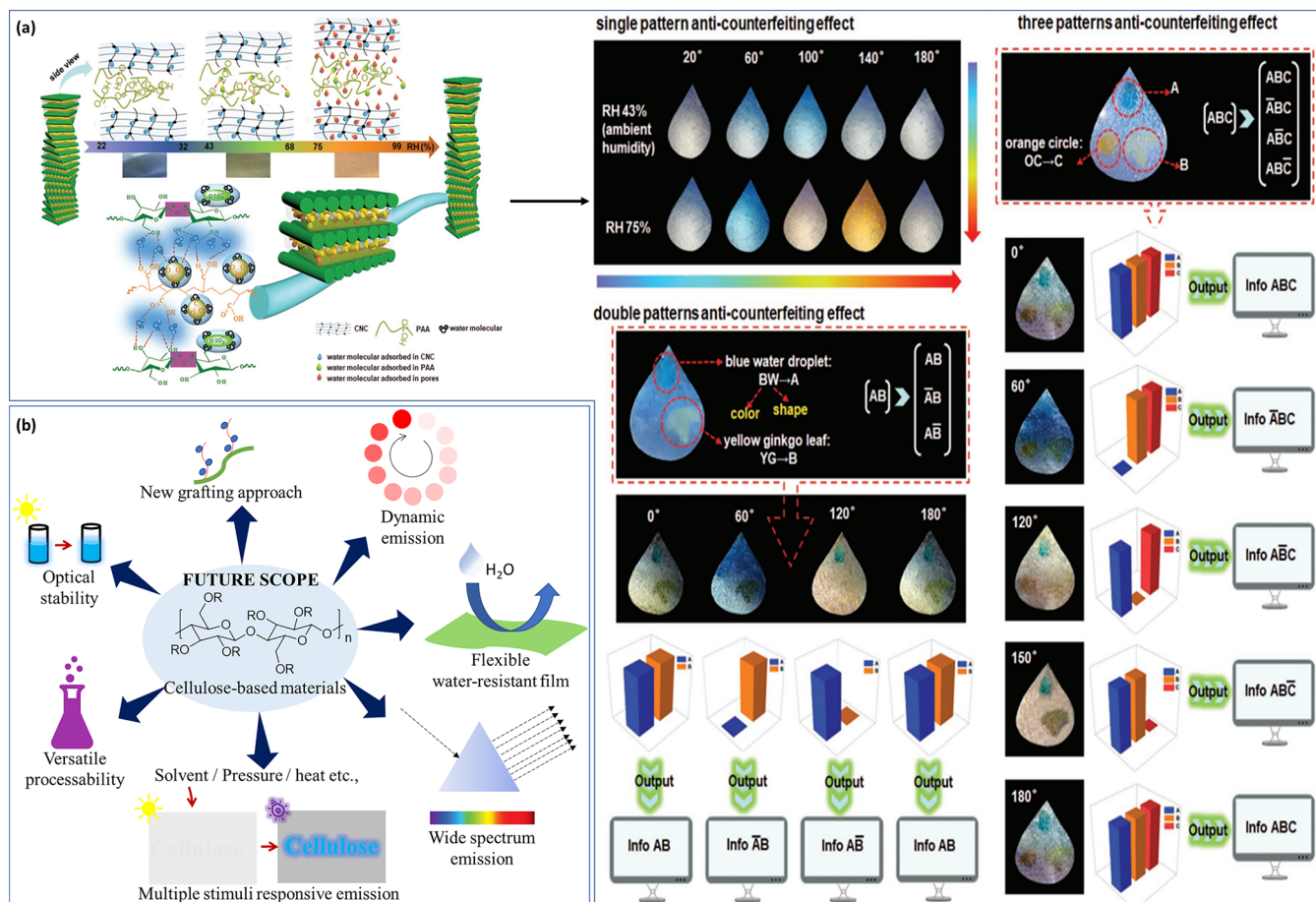


Figure 5. (a) Humidity-responsive chiral nematic coatings as a multiplexing platform for dual anticounterfeiting. Reprinted with permission from ref 118. Copyright 2021 John Wiley and Sons. (b) Schematic representation introducing the future scope of research work on cellulose-based materials for optical anticounterfeit application.

to make colorful patterns as it absorbs water in air, resulting in the swelling of PEGDA matrix and thereby increases the helical pitch. Moreover, the photonic paper made of CNC/PEGDA displayed color change from green to yellow, orange, and red spanning the entire visible spectral region with corresponding reflectance peaks at 550, 598, 634, and 716 nm, respectively, upon varying the mass concentrations (10% to 40%) of the LiCl inks.

Khan and group mixed CNC dispersion with PF resin in water/ethanol mixture, and dried to prepare chiral nematic iridescent composite films.¹¹³ Acid or formaldehyde can be used as chemical inks to write on these photonic mesoporous film. The density of methylol groups in the resin is changed, and the latent colored images were subsequently presented only upon swelling. The extent of film swelling in polar solvents can vary the pitch, and consequently the reflected color of the chiral nematic assembly (Figure 4c). Moreover, the helical pitch and thereby the colors of the patterns or the matrix can be tuned during the synthesis of original resin films by either adding salts or altering the CNC to resin precursor ratio. High resolution invisible texts and images can be obtained using inkjet printing on these films, which can be visualized only upon swelling and erased by drying. This reversible visualization process may be applied to visual graphic signage and anticounterfeit tags.

Chen et al. chemically cross-linked methacryloxyethyl trimethylammonium chloride with cholesteric CNCs to

achieve a rewritable/reprintable chiral photonic paper with reprogrammable wettability.¹⁰⁹ The nanocomposite film could effectively swell in ethanol without affecting the cholesteric structural organization. The film exhibited triple encoding: (i) polarization-dependent structural colors attributed to cholesteric alignment, (ii) invisible patterns triggered by reversible counterion-controlled wettability, and (iii) fluorescent counterions based on permanent fluorescent labels. Moreover, complex, multidimensional and independent responsive systems can be created based on various encodings: wetting responsive fluorescence patterns and bilayer photonic paper. The invisible patterns are revealed upon wetting and hiding the bottom layer by polarization-dependent transparency of the top layer under CPL. High resolution full-color patterns of invisible complex information can be reversibly constructed via inkjet printing to realize a wetting/polarization double-key decryption. Rewritable chiral photonic paper with invisible printing, tunable wettability, tunable colors, and fast response can offer pronounced opportunities in security printing to combat counterfeiting. This simple and programmable technique can encode complex data based on fluorescence, polarization and chemical responses on a single material platform.

CNC films and coatings can serve as beneficial scaffolds to construct humidity-responsive materials. Based on this background, Zhao et al. fabricated self-assembled, humidity-responsive iridescent chiral coatings based on ionic inter-

Table 1. Pros and Cons of Cellulose Based Materials for Anticounterfeiting Application

pros	cons
cellulose is abundantly available, environment-friendly, and biocompatible	polymer composites using hydrophilic cellulose fillers is difficult due to less dispersion and compatibility issues with many hydrophobic polymers
large surface area and plentiful hydroxyl groups on cellulose provide easy surface modifications to realize unique properties	poor solubility in water and some common organic solvents makes chemical modification of cellulose difficult
cellulose can be used both as a recyclable reinforcement fiber and a matrix material with good mechanical performance	a large amount of additives used along with cellulose reduces its functional properties and processability
easy preparation of fluorescent inks from conventional ACQ fluorophores as the cellulose chains hinder aggregation and self-quenching of fluorescence	use of different fluorescent materials along with cellulose is necessary to obtain dual or good emission properties
modified cellulose-based inks can be easily processed into different printing patterns, coatings, films, and fibers	use of up-converting materials require advanced, sophisticated, and expensive IR sources to excite them
CNFs display exceptional film-forming ability and compatibility with different substrates including glass, plastics, metals, and ceramics	pure CNC films are brittle in nature
FRET can be realized through simple blending process for screening/detection devices used in security applications	multifunctional CNC films are not always water-resistant
owing to chain stiffness, cellulose and derivatives form cholesteric structures, offering stimuli-responsive chiral behavior for different security features	short-lived covert data storage using external stimuli-responsive materials with reversible properties may affect the cellulose paper

actions between CNCs and PAA (Figure 5a).¹¹⁸ The mechanically robust CNC–PAA smart film with chiral nematic CNC structure displayed high anisotropic dissymmetry and sensitivity to environmental humidity. The shifts in selective light (green to orange) reflection and polarization of the chiral helix structure enable iridescent CNC/PAA coating to achieve tunable transmitted colors (blue to orange) at given rotation angles. These properties are integrated conveniently into a “relative humidity-rotation angle-color” ternary code anti-counterfeiting technology, taking advantage of dynamic appearance and disappearance of varying multicolor patterns depending on the relative humidity and rotation angle.

Chen et al. demonstrated the construction of CdS quantum dot (QD)-functionalized (CNCs) thin-film system through layer-by-layer self-assembly.¹⁰⁷ The QDs were anchored on the surface carboxyl groups formed through TEMPO-assisted oxidation of CNC. Further, uniform coating of PEI on the CNC surface was achieved by partial desulfation. The composite material interestingly combined the iridescent structural colors from thin-film interference for colorimetry based security identification, and photoluminescence from the embedded QDs for UV-emission-based secondary authentication. A realistic application was demonstrated for the protection of Canadian currencies using the prepared composite. Furthermore, an affordable multilayer security film with different emission colors for anticounterfeiting applications was achieved by constructing negatively charged CNC/QDs with red emission QDs, and positively charged CNC/QDs with green emission QDs, and carefully regulating the amounts of the two building blocks. These nanocomposite films on PET substrates were stable in the presence of water/ethanol and displayed high transmittance over the entire range of visible light, structural colors, and photoluminescence and could be used in anticounterfeiting applications.

6. SUMMARY

Cellulose is a biomass material abundantly available in nature and has been extensively used in our daily life due to its attractive properties. In recent years, the structural modification and functionalization of cellulose fibers have garnered immense research attention because of great bonding sites in the polymer and large surface area of the nanopolymer. Therefore, cellulose fibers can be explored as an ideal organic polymer matrix to design and fabricate smart and intelligent

composite materials for security printing and anticounterfeit applications.

Cellulose can be used as it is or modified structurally through chemical/physical processes, grafting or by simply mixing the cellulose with suitable material for anticounterfeiting application. The construction of high-resolution printed patterns and independent encoding/decoding of complex information using cellulose-based biomaterials can lead to promising applications for optical encryption. Fluorescent composite inks can be prepared easily through fluorophore grafting, ascribed to the excellent processability innate to cellulose materials. The exceptional ability to form films endows the compatibility of cellulose-based fluorescent inks with various substrate surfaces, including glass, plastics, ceramics, and even metals. Further, the ACQ property, which is detrimental to the application of certain fluorescent materials for anticounterfeit applications can be avoided by incorporating them into the cellulose matrix to obtain good fluorescence emission. The anchoring and diluting effects of biopolymer chains in combination with ionic repulsion can efficiently transform ACQ luminogens into materials with good fluorescence emission that might be more valuable in practice. CDs and PF resins are excellent substrates for developing stimuli-responsive CNC-based photonic composites, wherein CNC serves as either a matrix or a template. Ln–metal complexes, UCNPs, organic dyes, CQDs, and other fluorophores can be combined with cellulose to obtain composite inks, films and papers for anticounterfeiting applications. Besides, cellulose-based composites exhibit phototunable reversibility, dynamic fluorescence in full-color space as well as noncontact and nondestructive authentication, which are advantageous in anticounterfeiting and security printing. The advantages and limitations of the cellulose-based materials in optical anticounterfeiting applications are listed in Table 1.

Some of the current fluorescence-based anticounterfeiting systems are associated with a possibility of migration and leakage of the fluorophore, which is harmful to the detection stability and protection of these materials during their usage. In this regard, nanocellulose-based environmentally friendly iridescent coatings offer a stable alternative, creating a more reliable and safer choice for multimodal encryption. These iridescent functional coatings allow information storage and encoding capabilities that span a wide color range. Thus, modified cellulose and nanocellulose-based materials that can

be fabricated into diverse forms, including composite inks, films and papers can offer versatile performance to facilitate novel anticounterfeiting applications. Besides, using cellulose as an abundantly available and renewable biopolymer can also endorse sustainable development.

7. FUTURE SCOPE

Cellulose-based functional materials are in high demand due to their eco-friendly and sustainable nature. They can be drawn into different shapes and sizes and offer superior properties suitable for security and anticounterfeit applications. To prevent and identify falsification of currency notes, branded goods, pharmaceuticals, valuable documents etc., continuous improvement of anticounterfeiting technology is particularly essential. A schematic representation introducing the future scope of research work on cellulose-based materials for optical anticounterfeit application is presented in Figure 5b.

Though technology has seen rapid advancements, it is still highly challenging to fabricate renewable materials with tunable fluorescence from sustainable sources. Renewable and biocompatible fluorescent composites that can simultaneously meet all desired features, including (i) full-color, wide-spectrum emission, (ii) distinct fluorescence responses to multiple stimuli, (iii) stimuli-responsive tuning of dynamic color and intensity, (iv) excellent stability and reversibility, and (v) versatile processability of the material that can provide multilevel security features are always sought after. Also, combining fiber properties with multiple functional features of nanomaterials can offer new opportunities for diverse anticounterfeiting applications. The security levels in counterfeiting or reverse engineering can be enhanced if several stimuli-responsive properties such as thermochromism, halochromism, ionochromism, etc. can be introduced into product authentication in combination with photochromism.

CNC is a renewable biopolymer that has been continuously used as a natural template for the fabrication of mesoporous chiral nematic materials. Charge-driven assemblies can open new avenues for chiral nematic CNCs that support precise information encryption. However, the construction of stimuli-responsive, chiral nematic photonic multifunctional materials with a complete-visible range display for security applications is still demanding and needs to be explored more. Though humidity-responsive hygroscopic CNC films have been realized, the brittleness of pure CNC film seriously hinders its real-life applications. Hence, to address this issue, few commonly used water-soluble polymers such as PEG, PVA, and small additive molecules such as glycerol, glucose, zwitterionic surfactants, and ionic liquids are incorporated into the CNC matrix. However, poor water-resistance or a single function limits the utility of these films.^{124,125} Therefore, the fabrication of water-resistant as well as multifunctional, flexible CNC films is an extremely daunting task.

Though functionalization through chemical reactions of organic compounds with primary hydroxyl functional groups of CNCs has been reported to offer distinctive properties to the resulting composites, these chemical reactions generally offer low grafting ratios.¹²⁶ Therefore, new approaches to improve the incorporation of dopants must still be worked upon. The utilization and disposal of toxic chemicals and solvents during the modification of cellulose are of high cost, adds complexity to manufacturing operations, have potential negative effects on the environment, and increases the burden of waste discharge treatment. Hence, developing eco-friendly, simple, and efficient

preparation methods with minimal use of toxic chemicals and solvents are highly desirable during the chemical modification procedures of cellulosic materials.

Through this appraisal, we attempt to provide comprehensive insights on the plausible candidature of cellulose and nanocellulose composites as sustainable and environment-friendly smart anticounterfeit materials. We anticipate that this appraisal would aid further advancements in the highly expanding but challenging arena of biocompatible and sustainable materials for intelligent anticounterfeiting technology.

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Notes

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LIST OF ACRONYMS

7-AC	7-Acryloxycoumarin
ACQ	Aggregation caused quenching
ATRP	Atom transfer radical polymerization
CD	Carbon dot
CdS	Cadmium Sulfide
Ce	Cerium
CNC	Cellulose nanocrystals
CNF	Cellulose nanofibers
CPL	Circularly polarized light
CQD	Carbon quantum dot
CuI	Copper Iodide
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
DMAC	<i>N,N</i> -Dimethylacetamide
EISA	Evaporation-induced self-assembly
Er	Erbium
Eu	Europium
Fe	Iron
Fe ₃ O ₄	Iron(II,III) oxide
FRET	Förster resonance energy transfer
Gd	Gadolinium
H-bonds	Hydrogen bonds
La	Lanthanum
LiCl	Lithium chloride
Ln	Lanthanide
LnF ₃	Lanthanide fluoride
MDI	Methylene diphenyl diisocyanate
MFC	Microfibrillated cellulose
MOF	Molecular organic framework
NaYF ₄	Sodium yttrium fluoride
Nd	Neodymium
NIR	Near-infrared
NMMO	<i>N</i> -Methylmorpholine- <i>N</i> -oxide

PAA	Poly(acrylic acid)
PEI	Poly(ethylene imine)
PEG	Polyethylene glycol
PF	Phenol-formaldehyde
PEGDA	Poly(ethylene glycol) diacrylate
PEGMA	Poly(ethylene glycol) methacrylate
PET	Polyethylene terephthalate
PLA	Poly(lactic acid)
PPh ₃	Triphenyl phosphine
PVA	Poly(vinyl alcohol)
PVP	Polyvinylpyrrolidone
QD	Quantum dot
RAFT	Reversible addition–fragmentation chain transfer polymerization
RFID	Radio frequency identification
ROP	Ring-opening polymerization
RR120	Reactive red 120 dye
SiO ₂	Silicon dioxide
Sm	Samarium
TABF	Tetrabutylammonium fluoride trihydrate
Tb	Terbium
TEMPO	2,2,6,6-Tetramethylpiperidinyloxy radical
TPA	Thiazolopyridine carboxylic acid
UCNPs	Up-conversion nanoparticles
UCPL	Up-conversion photoluminescence
UV	Ultraviolet
Yb	Ytterbium
YbCl ₃	Ytterbium(III) chloride
YOF	Yttrium oxyfluoride

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