CELLULOSE NANOCRYSTALS FROM COTTON: EXTRACTION CHEMISTRY, SURFACE FUNCTIONALIZATION, AND STRUCTURE–PROPERTY RELATIONSHIPS — A CRITICAL REVIEW

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Cellulose nanocrystals (CNCs) are highly crystalline nanoparticles, whose properties are set chiefly by the chemistry of their isolation and surface modification. Cotton, a near-pure (>90% α-cellulose), highly crystalline, lignin-poor source of native cellulose I, is among the most attractive CNC feedstocks because isolation chemistry acts directly on an ordered lattice. This review critically synthesizes the chemistry of CNC production from cotton: the mechanism of acid hydrolysis; the comparative chemistry of mineral acids, organic/green acids, oxidative, ionic-liquid/deep-eutectic-solvent and enzymatic routes; allomorph control; and surface functionalization (sulfation, esterification, TEMPO and periodate oxidation, silylation, cationization, grafting). It links these to the characterization toolbox and to the central structure–property trade-offs – surface charge versus thermal stability, and crystallinity, dimensions and charge versus reaction parameters. Cotton emerges as both a practical feedstock and a model system, with standardized characterization the principal requirement for reproducible CNC chemistry.

Keywords: cellulose nanocrystals, cotton, acid hydrolysis, sulfate half-ester, surface functionalization, TEMPO oxidation, crystallinity index, structure–property relationships

INTRODUCTION

Cellulose nanocrystals (CNCs) are highly crystalline nanoparticles isolated from cellulosic biomass by controlled removal of the disordered (amorphous) regions.[1,2] They are most commonly rod-like (typically 3–20 nm wide and 100–500 nm long), although spherical CNCs can also be obtained under specific hydrolysis conditions.[3] Their renewable origin, high specific stiffness, large reactive surface area and tunable surface chemistry have made them one of the most studied bio-based nanomaterials.[1,4] From a chemical perspective, the properties of a CNC are not fixed by the word "cellulose": they are set by the chemistry of isolation – which acid or oxidant is used, under what conditions – and by subsequent surface modification. CNC production is therefore best understood as a problem in reaction chemistry and surface chemistry.

Among feedstocks, cotton occupies a privileged position. Cotton fibre is among the purest natural sources of cellulose, with an α-cellulose content exceeding 90%, very low contents of lignin and hemicelluloses, and a high native crystallinity in the cellulose-I allomorph.[1,5] This purity has two consequences that make cotton an ideal substrate for CNC chemistry. First, minimal pretreatment is required to remove lignin and hemicelluloses, so isolation chemistry acts almost directly on an ordered cellulose lattice, giving low-defect, high-crystallinity nanocrystals.[5,6] Second, the compositional consistency of cotton makes it an excellent model system for mechanistic and parametric studies of hydrolysis and functionalization, where confounding effects of lignin and hemicelluloses are largely absent.[7,8]

This review is deliberately narrow and chemistry-centred. Rather than surveying composite engineering or applications in breadth, it focuses on (i) the chemical structure and reactivity of cotton cellulose; (ii) the mechanism

and comparative chemistry of CNC extraction routes from cotton—mineral acids, organic/green acids, oxidative methods, ionic liquids and deep eutectic solvents, and enzymatic/mechanical assistance—including control of the crystalline allomorph; (iii) the surface functionalization chemistry that converts the native hydroxyl surface into tailored functional groups; (iv) the characterization toolbox that defines CNC quality; and (v) the structure–property relationships that connect reaction chemistry to product performance. The aim is to provide a critical, mechanistically grounded reference for the chemistry of obtaining and modifying CNC from cotton.

Despite numerous reviews devoted to cellulose nanocrystals, most publications discuss nanocellulose from multiple biomass sources or focus on engineering applications rather than reaction chemistry. Comprehensive critical analyses dedicated specifically to cotton-derived CNC remain scarce. In particular, previous reviews rarely integrate extraction mechanisms, surface functionalization chemistry, characterization methodology, and structure–property relationships within a unified chemistry-oriented framework. The present review addresses this gap by critically evaluating the chemical principles governing cotton-derived CNC production and modification.

REVIEW METHODOLOGY AND LITERATURE SELECTION

Literature search strategy

A comprehensive literature search was performed using the Scopus, Web of Science, ScienceDirect, and Google Scholar databases. The search combined the keywords “cotton cellulose nanocrystals”, “cotton CNC”, “cellulose nanocrystals”, “acid hydrolysis”, “sulfuric acid hydrolysis”, “TEMPO oxidation”, “periodate oxidation”, “surface functionalization”, “deep eutectic solvents”, “ionic liquids”, and “cotton nanocellulose”. Publications published between 2010 and 2026 were primarily considered, while earlier landmark studies were retained when they established the fundamental chemistry of cellulose nanocrystals or introduced concepts that remain central to current research.

Only peer-reviewed journal articles published in English were included in the critical analysis. Conference proceedings, patents, book chapters, and publications lacking sufficient experimental details were excluded. Duplicate records were removed before title, abstract, and full-text screening. Studies were selected according to their relevance to cotton-derived cellulose nanocrystals, extraction chemistry, surface functionalization, characterization, and structure–property relationships. The overall literature identification and selection procedure is summarized in Figure 1 (PRISMA 2020 flow diagram).

Scope of the review

This review focuses specifically on the chemistry governing the preparation and modification of cellulose nanocrystals derived from cotton. Particular attention is devoted to the mechanisms of β-(1→4)-glycosidic bond cleavage during acid hydrolysis, oxidative and solvent-assisted extraction pathways, formation of surface functional groups, and their influence on crystallinity, particle morphology, surface charge, thermal stability, and colloidal behavior.

Although the primary emphasis is placed on cotton, closely related lignocellulosic feedstocks – including wood pulp, ramie, flax, jute, dissolving pulp, and bacterial cellulose – are discussed where they provide mechanistic insight or reaction pathways that have not yet been comprehensively investigated for cotton-derived cellulose nanocrystals.

The review also critically evaluates characterization techniques, including X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), solid-state ^{13}C NMR spectroscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM), ζ-potential measurements, conductometric titration, and thermogravimetric analysis (TGA), emphasizing their complementary roles in establishing reliable structure–property relationships.

Review organization

The review is organized into nine major sections following the logical progression from cotton cellulose chemistry to cellulose nanocrystal production, surface functionalization, characterization, structure–property relationships, and practical applications. Particular emphasis is placed on reaction mechanisms (glycosidic-bond cleavage, esterification, and oxidation), processing parameters (acid identity and concentration, temperature, reaction time, and solid-to-liquid ratio), the chemical identity of introduced surface functional groups, and the characterization evidence obtained from spectroscopic, diffraction,

microscopic, electrokinetic, and thermal techniques.

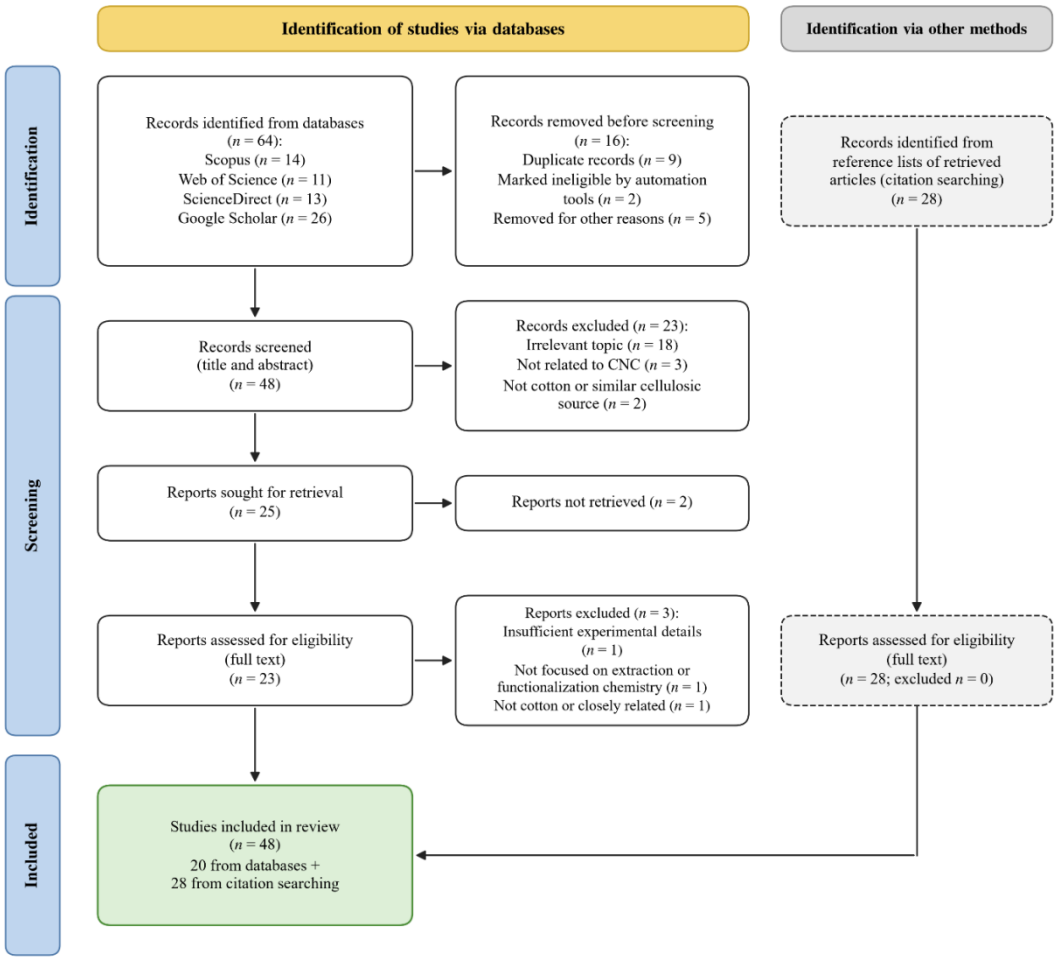


Figure 1: PRISMA 2020 flow diagram of the literature search and study selection process (20 studies identified through database searching and 28 through citation searching)

Table 1
Positioning of this review relative to representative prior reviews on cellulose nanocrystals

Review (ref.)	Year	Extraction chemistry	Surface functionalization	Structure–property	Cotton-specific focus	Quantitative literature data
Habibi *et al.*[1]	2010	✓	✓	✓	—	—
Moon *et al.*[2]	2011	◑	◑	✓	—	—
Klemm *et al.*[4]	2011	◑	◑	◑	—	—
Xie *et al.*[9]	2018	✓	—	◑	—	—
Dagnino *et al.*[10]	2025	✓	◑	—	—	—
Zhang *et al.*[11]	2024	◑	✓	◑	—	—
Rostamabadi *et al.*[12]	2024	◑	◑	✓	—	—
This review	2026	✓	✓	✓	✓	✓

✓ = covered in depth; ◑ = partial; — = not a focus

Quantitative data are reported as presented in the cited studies and should therefore be interpreted in the context of differences in feedstock origin, extraction conditions, and characterization methodology. Rather than providing a purely descriptive summary of the published literature, this review adopts a critical narrative approach by systematically comparing competing extraction and functionalization strategies, identifying unresolved scientific

challenges, and highlighting emerging trends toward sustainable, reproducible, and industrially scalable production of cotton-derived cellulose nanocrystals. The scope and distinctive features of the present review relative to representative CNC review articles are summarized in Table 1.

COTTON CELLULOSE AS A FEEDSTOCK: CHEMICAL STRUCTURE, CRYSTALLINITY AND REACTIVITY

As outlined in the Introduction, the compositional purity of cotton makes it both a practical CNC feedstock and a model substrate. This section therefore focuses on the molecular and supramolecular features of cotton cellulose that govern its reactivity during CNC isolation and subsequent chemical modification.

Cellulose is a linear homopolysaccharide of D-anhydroglucose units joined by β-(1→4)-glycosidic bonds, with three hydroxyl groups per ring at the C2, C3 (secondary) and C6 (primary) positions.[1] These hydroxyls drive an extensive network of intra- and intermolecular hydrogen bonds that packs the chains into highly ordered crystalline domains interspersed with disordered amorphous regions.[1,2] The crystalline–amorphous architecture is the chemical basis of all CNC isolation: the amorphous regions are kinetically and sterically more accessible to reagents, so controlled chemistry can remove them selectively while preserving the crystalline core.[1,11]

Native cotton cellulose adopts the cellulose-I allomorph (parallel chains), which is thermodynamically metastable relative to cellulose-II (antiparallel chains) formed upon dissolution and regeneration or under harsh treatment; this allomorphic identity governs crystallinity, reactivity and thermal behaviour and can shift during aggressive hydrolysis.[9,13] Cotton's high α-cellulose content and crystallinity make its accessible-surface hydroxyl chemistry comparatively well defined, which is advantageous both for reproducible hydrolysis and for subsequent functionalization. The same hydroxyl-driven hydrogen bonding, however, is the principal obstacle to chemical modification: it restricts solvent access and reagent diffusion and promotes aggregation, so most surface chemistry on cotton CNC requires either an activating pretreatment (*e.g.*, TEMPO oxidation, sulfate half-ester formation) or reaction media that disrupt hydrogen bonding.[11,14] The reactivity of the three hydroxyls is not equivalent: the primary C6–OH is the most accessible and reactive (the selective site of TEMPO oxidation), while the secondary C2/C3 hydroxyls are targeted by periodate oxidation, a distinction central to controlled functionalization.[15,16]

These structural and chemical characteristics explain why cotton has become one of the most frequently investigated model substrates for cellulose nanocrystal production. Nevertheless, although cotton offers excellent reproducibility and high product quality, it is not universally superior to other cellulose sources. The advantages and limitations of cotton relative to alternative feedstocks are summarized in Table 2.

Table 2
Cotton relative to other cellulose feedstocks for CNC production

Feedstock	Cellulose content / purity	Native crystallinity	Lignin + hemicelluloses	Pre-treatment before hydrolysis	Ref.
Cotton (fibre / linter)	>90% α-cellulose	high (cellulose I)	very low	minimal (scour/bleach)	[1,5]
Cotton stalk (residue)	up to ~98.6% α-cellulose (after purification)	high	moderate	acetic-acid/alkali + bleach	[17]
Wood pulp	~40–45% cellulose in wood	moderate–high	high (lignin-rich)	delignification + bleaching	[2]
Bast fibres (ramie, jute)	high	high (CrI up to ~90% after hydrolysis)	moderate	alkali + bleach	[18,19]
Microcrystalline cellulose	high (commercial)	high	low	none (pre-purified)	[20]

EXTRACTION CHEMISTRY OF CELLULOSE NANOCRYSTALS FROM COTTON

Reaction principle

CNC isolation from cotton exploits the differential reactivity of the amorphous and crystalline domains. Under acidic conditions, hydronium ions diffuse preferentially into the disordered regions and protonate the glycosidic oxygen, promoting hydrolytic cleavage of the β-(1→4) bonds far faster than in the densely hydrogen-bonded crystallites; the crystalline domains survive, and the fibre is cut down to rod-like (or, under specific conditions, spherical) nanocrystals.[1,11]

Because cotton carries little lignin or hemicelluloses, this selectivity is unusually clean, which is why cotton yields well-defined, high-crystallinity CNCs.[5,6]

Figure 2 highlights that cellulose nanocrystal formation is governed by selective chemical degradation rather than complete cellulose depolymerization. The preservation of crystalline domains explains why reaction severity must be carefully balanced. Excessively mild hydrolysis results in incomplete removal of amorphous cellulose, whereas excessive reaction conditions reduce nanocrystal dimensions and lower overall yield.

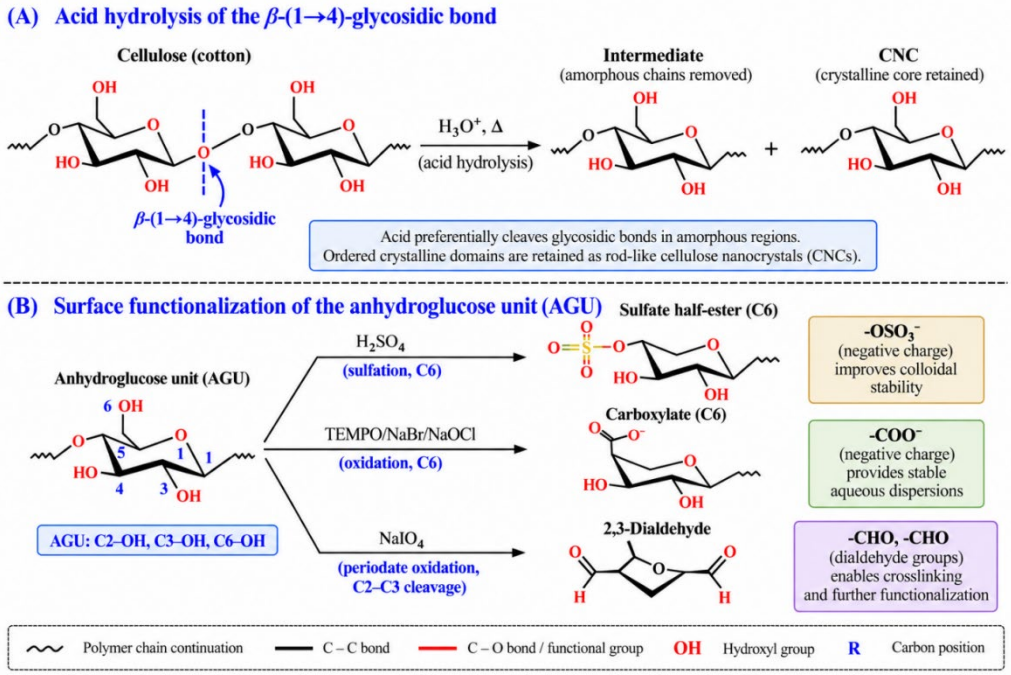


Figure 2: Key reaction chemistry of CNC from cotton: (A) acid hydrolysis of β-(1→4)-glycosidic bonds, which removes accessible amorphous chains and leaves the crystalline core; (B) surface functionalization of the anhydroglucose unit – sulfation (C6 → –OSO_3^-), TEMPO oxidation (C6 → –COO^-) and periodate oxidation (C2–C3 cleavage → 2,3-dialdehyde)

Mineral-acid hydrolysis and sulfate half-ester chemistry

Sulfuric acid (typically ~64 wt%, 45–50 °C, 30–90 min) is the benchmark route and is itself a two-fold reaction: it both hydrolyses glycosidic bonds and partially esterifies surface hydroxyls (chiefly C6–OH) to anionic sulfate half-esters (cellulose–O–SO_3^-).[1,11] These groups are decisive for product behaviour. They impart a strong negative surface charge that stabilizes aqueous suspensions through electrostatic repulsion – well-prepared CNC reach ζ-potentials of roughly −30 to −50 mV with sulfate half-ester contents on the order of 200–250 μmol g^{-1} – but they simultaneously lower thermal stability by catalysing dehydration during heating.[11,21] The reaction parameters set the outcome: increasing hydrolysis time raises surface sulfation, drives crystallinity index upward (e.g., from ~80% to ~90% as amorphous material is removed) and makes the ζ-potential more negative (*e.g.*, −1 → −30 mV), at the cost of reduced onset decomposition temperature and eventual over-digestion of the crystallites.[18] Factorial-design and parametric studies on cotton pulp and fibres show that higher acid concentration and solid/liquid

ratio, with milder temperature and shorter time, maximize NCC yield, while excessive severity lowers it through complete hydrolysis.[5,7] Ultrasound assistance accelerates acid diffusion into the cotton fibre and the mechanical separation of crystalline from amorphous domains, improving structural and thermal characteristics of cotton CNCs.[6] Hydrochloric acid yields CNCs with very low surface charge (poor colloidal stability), and mixed-acid systems (H_2SO_4/HCl, HCl/HNO_3) are used to access spherical or carboxylated morphologies, though typically within a narrower operating window.[9]

The hydrolysis follows pseudo-first-order kinetics: the accessible amorphous chains are cleaved rapidly, while the degree of polymerization decreases toward a level-off value (LODP) characteristic of the crystalline domains. For cotton, this LODP and the associated plateau in surface charge are reached within roughly one hour, after which prolonged reaction mainly erodes the crystallites and lowers yield.[5,7]

Organic and "green" acid hydrolysis

Mono- and poly-carboxylic acids – formic, acetic, oxalic, maleic and *p*-toluenesulfonic (*p*-TsOH) – address the central drawback of sulfuric acid (the sulfate–thermal-stability penalty) while offering recyclability.[10] Because of their higher pK_a (weaker acidity), organic acids hydrolyse more gently, producing longer, more thermally stable, higher-crystallinity CNC. Formic acid (HCOOH, pK_a 3.74) yields CNC with crystallinity index ~79% and a decomposition temperature near 375 °C, and is readily recovered by distillation.[10,22] *p*-TsOH affords CNCs with crystallinity index up to ~90% and high aspect ratio (~33) without introducing surface esters, with ~72% acid recovery by crystallization – an attractive "green" alternative.[10] Importantly, dicarboxylic acids such as oxalic and citric carboxylate the surface during hydrolysis, introducing –COOH groups (carboxyl content ~0.2–0.3 mmol g^{-1} in DES-mediated routes) that improve dispersibility, so the isolation step simultaneously functionalizes the surface.[10] The fibrous cellulosic residue from organic-acid hydrolysis is also an excellent low-energy feedstock for subsequent mechanical fibrillation to CNF.[10]

Oxidative routes

Oxidation introduces charged surface groups that both isolate and pre-activate the nanocrystals. TEMPO-mediated oxidation (TEMPO/NaBr/NaOCl, pH ~10) selectively converts the primary C6 hydroxyls to carboxylate groups, introducing electrostatic charge that eases fibrillation and provides a reactive –COOH handle for downstream chemistry; catalyst and oxidant concentrations govern carboxyl content and yield.[15,16] Periodate oxidation ($NaIO_4$) cleaves the C2–C3 bond to generate surface dialdehyde groups, a versatile platform for subsequent silylation, secondary TEMPO oxidation or cationization.[15] A third oxidative option, ammonium persulfate (APS) oxidation, simultaneously removes amorphous and non-cellulosic material and installs surface carboxyls, yielding carboxylated CNC with high crystallinity and strong colloidal stability (*e.g.*, crystallinity index ~87%, ζ-potential ~ −49 mV) in a single, low-cost step.[23] These oxidative routes are central to CNC chemistry because they define the reactive functional group (–COOH or –CHO) used in later modification.

Ionic-liquid and deep-eutectic-solvent routes

Ionic liquids (ILs) dissolve or swell cellulose by disrupting its hydrogen-bond network; under mildly acidic or dilute conditions they yield CNCs with crystallinity comparable to conventional acid routes, but low intrinsic surface functionalization and excellent colloidal stability (>90 days) – a desirable starting point for clean post-functionalization.[24,25] It should be noted that acidic ILs such as [BMIM][HSO4] have so far been optimized mainly for non-cotton feedstocks (*e.g.*, corncob),[24] and their transfer to cotton remains to be demonstrated. Deep eutectic solvents (DES), such as choline chloride/oxalic acid, combine fractionation with partial esterification of the surface (carboxylation), again merging isolation and modification, and can give high yields with high crystallinity.[10] These solvent routes are attractive on toxicity and recyclability grounds but require closed-loop solvent recovery to be genuinely green.

Enzymatic and mechanical assistance

Enzymatic hydrolysis uses cellulases to cleave accessible chains selectively, and enzymatic pretreatment of cotton linters combined with controlled-temperature refining isolates nanocellulose at very low energy (~9.96 kWh kg^{-1}) and high purity.[26] Enzymatic routes avoid surface sulfation entirely, preserving thermal stability, but are kinetically limited by the high crystallinity of cotton, so they are often paired with mild acid or

mechanical (ultrasound, homogenization) steps.[8,26] The bleaching method applied before hydrolysis markedly affects the hydrodynamic size and crystallinity of cotton-origin CNCs obtained by acid versus enzymatic routes, underscoring that upstream chemistry propagates into product quality.[8]

Despite their distinct reaction mechanisms and processing conditions, all extraction routes share the common objective of selectively removing amorphous cellulose while preserving the crystalline domains. The principal pathways and their relationship to subsequent surface functionalization are summarized in Figure 3.

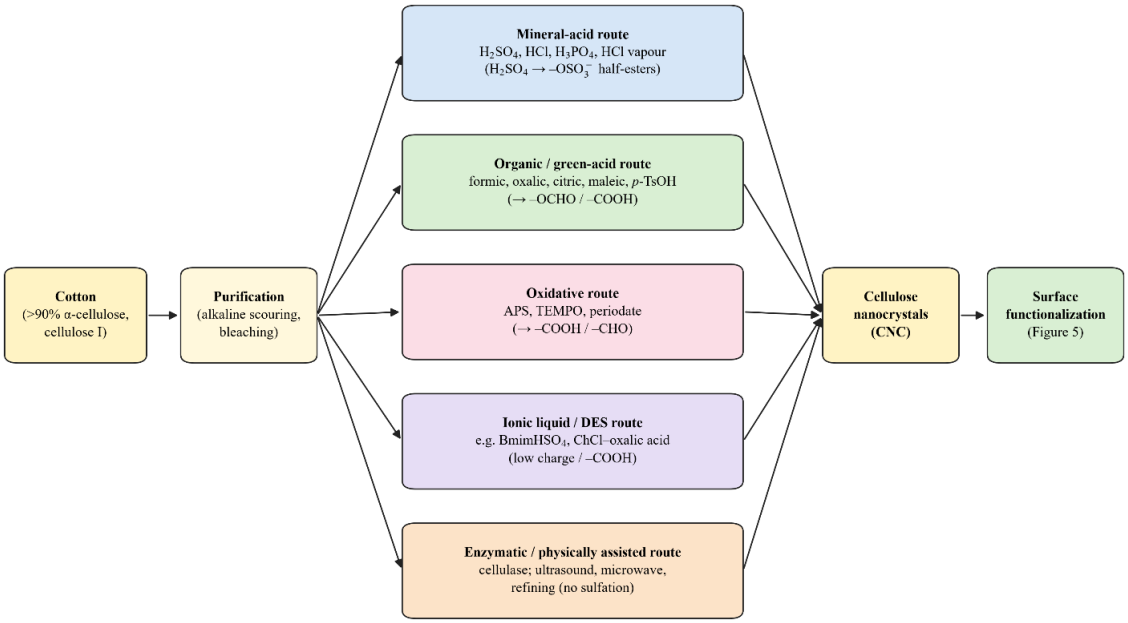


Figure 3: Extraction routes of cellulose nanocrystals from cotton: mineral-acid, organic/green-acid, oxidative, ionic-liquid/DES and enzymatic/physically assisted (ultrasound, microwave, refining) pathways, leading to CNCs and onward surface functionalization

Control of crystalline allomorph

Hydrolysis severity can change the crystalline allomorph and therefore the product's properties. Aggressive treatment can drive a partial cellulose-I → cellulose-II transformation accompanied by a fall in crystallinity index (*e.g.*, 66 → 60%) and lower thermal stability, whereas controlled one-pot acid hydrolysis can target a near-pure allomorph by tuning acid identity, concentration, temperature and time.[9,13] For a synthesis-oriented programme, recognizing and controlling allomorph is essential, because allomorph dictates crystallinity, surface reactivity and thermal behaviour of the resulting CNCs.

The principal extraction routes discussed above are compared in terms of representative reaction conditions, surface chemistry, crystallinity, colloidal stability, and thermal behavior in Table 3.

Critical comparison of extraction routes

The extraction methods summarized in Table 3 demonstrate that no single approach simultaneously maximizes yield, crystallinity, thermal stability, colloidal stability, environmental sustainability, and process economy. Instead, each route represents a different balance between these competing performance parameters.

Sulfuric acid hydrolysis remains the benchmark method because it consistently produces highly crystalline cellulose nanocrystals with excellent colloidal stability resulting from the introduction of sulfate half-ester groups. However, these same sulfate groups reduce thermal stability by promoting dehydration during heating, thereby limiting applications involving elevated processing temperatures.

Hydrochloric acid avoids surface sulfation and therefore provides thermally more stable nanocrystals, although their low surface charge frequently results in poor dispersion stability unless additional surface modification is performed.

Organic acids, including formic acid, oxalic acid, and p-toluenesulfonic acid, have emerged as attractive alternatives because they combine improved thermal stability with lower

environmental impact and the possibility of solvent recovery. Nevertheless, slower reaction kinetics and lower overall productivity currently limit their industrial competitiveness.

Oxidative methods, particularly TEMPO-mediated oxidation and ammonium persulfate oxidation, simultaneously isolate cellulose nanocrystals and introduce reactive functional groups, thereby reducing the need for subsequent surface modification. These methods are especially attractive when further chemical functionalization is required.

Table 3
Extraction chemistry of CNCs from cotton (and closely comparable feedstocks): route, representative conditions and resulting properties

Route	Representative conditions	Surface group	Crystallinity index	Charge / stability	Thermal stability	Ref.
H_2SO_4 hydrolysis	~64 wt%, 45–50 °C, 30–90 min	$–OSO_3^-$ (sulfate half-ester)	up to ~90%	ζ −30 to −50 mV; ~200–250 μmol g^{-1} sulfate	Reduced (sulfate-catalysed)	7,11,18,21
H_2SO_4 + ultrasound	as above + sonication	$–OSO_3^-$	enhanced	improved dispersion	enhanced vs conventional	6
Formic acid	HCOOH, recoverable by distillation	–OCHO (formate)	~79%	moderate	high (T_d ~375 °C)	10,22
p-TsOH	recoverable (~72%) by crystallization	none added	~90% (aspect ratio ~33)	low surface charge	high	10
Oxalic/citric (incl. DES)	dicarboxylic acid / choline chloride–oxalic	–COOH (~0.2–0.3 mmol g^{-1})	high	good (carboxylate)	high	10
TEMPO oxidation	TEMPO/NaBr/NaOCl, pH ~10	–COOH (C6)	preserved	high (carboxylate)	moderate	15,16
Ionic liquid (dilute/acidic; non-cotton data included)	mildly acidic IL	low/none	comparable	stable >90 d	superior for sulfated CNC	24,25
Enzymatic (cotton linters)	cellulase + controlled refining	none	high	low charge	high (no sulfation)	26

Ionic liquids and deep eutectic solvents represent one of the most promising directions for sustainable cellulose processing owing to their tunable solvent properties and potential recyclability. However, large-scale implementation remains constrained by solvent cost, purification, and recovery efficiency.

Enzymatic hydrolysis provides the most environmentally benign extraction strategy and completely avoids sulfate-induced thermal degradation. However, relatively slow reaction rates and limited productivity currently restrict its application to specialized or hybrid processing routes.

Overall, the optimal extraction strategy depends on the intended application rather than on a single performance parameter. Applications requiring excellent aqueous dispersibility generally favor sulfuric acid hydrolysis, whereas thermally demanding applications benefit from organic-acid, oxidative, or enzymatic approaches. Consequently, extraction chemistry should be selected by balancing crystallinity, surface chemistry, thermal stability, sustainability, and process feasibility rather than maximizing a single material property.

Reported characteristics of cotton-derived CNC (literature survey)

The isolation chemistry above translates into a characteristic range of properties for cotton CNCs. Table 4 summarizes representative literature values for yield, dimensions, crystallinity index and ζ-potential across cotton feedstocks and routes. Several patterns recur. Cotton's high native crystallinity gives CNC with crystallinity indices typically in the ~54–95% range, the spread

reflecting route and, importantly, the crystallinity-index calculation method.[3,8,27] Sulfuric-acid CNC from cotton are short rods (length ~50–360 nm, width ~4–16 nm) with strongly negative ζ-potential (commonly −30 to −47 mV), but modest mass yields (~30%).[3,27,28] Phosphoric acid affords tunable, longer crystals (~238–475 nm) with higher thermal stability than sulfuric acid;[29] an acidic ionic-liquid route, so far reported for corncob rather than cotton, gives low-charge CNC (CrI ~62%, diameter ~52 nm);[24] spherical CNCs of very high crystallinity (~95%) and excellent stability (ζ −46.8 mV) can be obtained from cotton cloth waste;[3] and denim- and blend-fabric wastes yield CNC with high crystallinity (~88%) comparable to bleached cotton, supporting textile-waste valorization.[28,30] The picture is consistent across less-refined cotton by-products: needle-shaped CNC from cotton balls (diameter ~6.4 nm, length ~109 nm),[31] and rod-like CNCs from cotton stalk waste and cotton gin motes/waste, confirm that even agro-industrial cotton residues yield well-defined nanocrystals, although their ζ-potential is somewhat lower (cotton ≈ −27.5 mV vs cotton stalk ≈ −21.8 mV) and pulp yields differ markedly (cotton ~77% vs cotton stalk ~23%), reflecting feedstock purity.[17,32] Because reported values depend on feedstock purity, acid identity, concentration, time and temperature, and on the crystallinity-index method and drying history, cross-study comparison must remain cautious; the table therefore reports values as given by the cited studies, with "n.r." where a parameter was not reported in the retrieved text.

Green and alternative isolation routes broaden this range further. Gaseous (HCl-vapor) hydrolysis of cotton cellulose is notable for very high yield (97–99%) and a clean solid product, but the resulting CNC are essentially uncharged and therefore difficult to disperse without further treatment.[33-35] Microwave-assisted hydrolysis affords rapid (~10 min), tunable production,[36] and heat–moisture-assisted acidolysis reaches yields above 93% at greatly reduced acid dosage.[20] Organic-acid routes (acetic, citric, malic, tartaric, oxalic, maleic) simultaneously esterify/carboxylate the surface and deliver markedly higher thermal stability (T_d ~290–375 °C) than sulfuric-acid CNC, at the cost of lower yields.[37,38] An important transparency caveat applies: whereas mineral-acid and several waste-cotton studies are cotton-specific, the maleic-acid, organic-acid, acidic ionic-liquid and HCl-hydrothermal routes have so far been reported mainly on closely related lignocellulosic feedstocks (agromass, bamboo, corncob, eucalyptus) rather than on cotton itself; these entries are italicized in Table 4 and included to indicate the green-chemistry options transferable to cotton, which remain an open opportunity for future research.

Table 4

Characteristics of cotton-derived cellulose nanocrystals reported in the literature (yield, dimensions, crystallinity index, ζ-potential), with green/organic-acid, gaseous-HCl and microwave routes; entries on closely related feedstocks (not yet widely reported for cotton) are italicized

Feedstock	Route / conditions	Yield	Dimensions (L × W; aspect ratio)	Crystallinity index (T_d where noted)	ζ-potential	Ref.
Cotton cloth waste (rod-like)	H_2SO_4 55 wt%	~31%	L 49–53 nm, W 4.3–6.6 nm	n.r.	n.r.	3
Cotton cloth waste (spherical)	H_2SO_4 55 wt%	~31%	spherical	94.6%	−46.8 mV	3
Industrial cotton waste (unwoven)	H_2SO_4 50–64 wt%, 60–75 min	n.r.	rod-like (TEM)	75–81%	negative (reported)	27
Postconsumer cotton / denim fabric	H_2SO_4 + TEMPO	≈ bleached cotton	≈ bleached cotton	~88%	n.r.	30
Cotton balls	H_2SO_4 64 wt%, 50 °C, 60 min	n.r.	L ~108.8 nm, ⌀ ~6.35 nm	reported	n.r.	31
Cotton (bleached pulp)	H_2SO_4 hydrolysis	pulp ~77%	rod-like (TEM)	reported	−27.5 mV	17
Cotton stalk waste	H_2SO_4 hydrolysis	pulp ~23%	L ~90.5 nm, W ~7.0 nm	reported	−21.8 mV	17
Cotton gin motes / gin waste	H_2SO_4 hydrolysis	n.r.	rod-like (TEM)	reported	reported	32

Feedstock	Route / conditions	Yield	Dimensions (L × W; aspect ratio)	Crystallinity index (T_d where noted)	ζ-potential	Ref.
Cotton	H_3PO_4 (design of experiments)	n.r.	length tunable 238–475 nm	high	trend with phosphate content	29
Polyester/cotton-blend fabric waste	H_2SO_4	n.r.	L 78–358 nm, W 5–16 nm	reported	reported	28
Cotton	Ultrasound-assisted H_2SO_4 (30–50%)	n.r.	rod-like (acid-dependent)	increased vs cotton	n.r.	6
Corncob (related feedstock)	Ionic liquid ([BMIM][HSO4]) hydrolysis	n.r.	diameter ~52 nm	62.5%	low-charge, stable	24
Cotton-origin NCC	acid vs enzymatic; bleaching variants	n.r.	DLS hydrodynamic size	54.1–63.2%	reported	8
Cotton	HCl vapor (gaseous, ~8.19 kPa)	97–99%	L 100–300 nm, W 7–8 nm	high (↑ with vapor pressure)	low / uncharged	33-35
MCC (cotton/wood-derived)	microwave-assisted H_2SO_4, 10 min	16–82%	⌀ 126–1310 nm (DLS)	n.r.	n.r.	36
MCC (cotton/wood-derived)	H_2SO_4 + heat–moisture, 2 h	93.7%	rod ~100 nm / spherical ~10 nm	70.9–81.1%	−19.6 to −22.8 mV	20
Agromass (related feedstock)	organic acids (acetic, citric, malic, tartaric, oxalic) + steam explosion	59–62%	aspect ratio ~20.7	77–81% (T_d 290–343 °C)	−16 to −34 mV	37
Bamboo (related feedstock)	maleic acid + ball-mill pretreatment	10.6–24.5%	carboxylated rods	improved (carboxylated)	reported	38
Eucalyptus / cellulose (related)	HCl hydrothermal	~93%	rod-like	high (T_d thermally stable)	reported	39

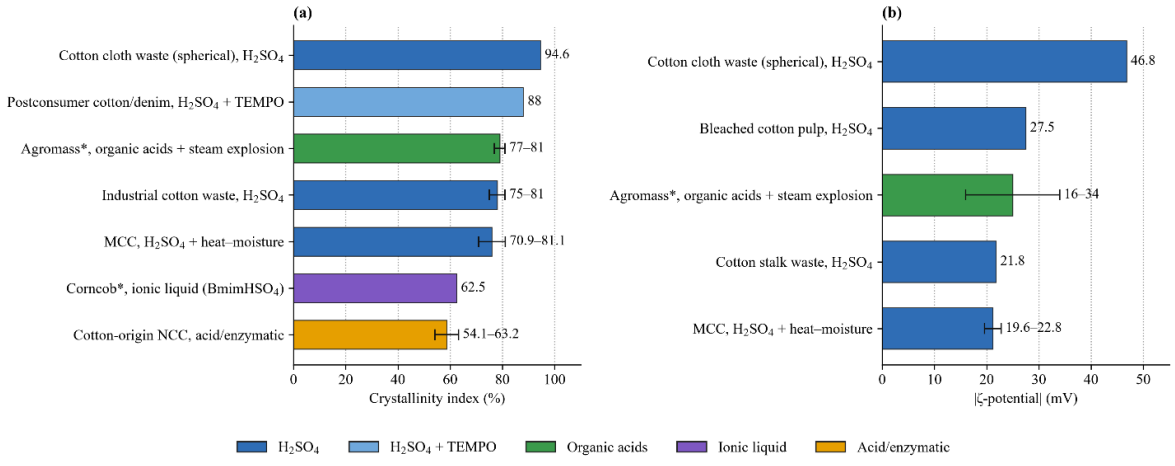


Figure 4: Literature-reported crystallinity index (a) and magnitude of the ζ-potential (b) of CNCs from cotton and closely related feedstocks, grouped by isolation route (data from Table 4). Bars show single reported values or range midpoints, and whiskers indicate the reported ranges; * denotes a closely related (non-cotton) feedstock. The gaseous-HCl route gives essentially uncharged CNCs for which no ζ-potential value was reported, and it is therefore not shown in (b)

SURFACE CHEMISTRY AND FUNCTIONALIZATION OF COTTON-DERIVED CNCs

Origin of surface reactivity

The functional behaviour of a CNC is dominated by its surface. The native surface presents C2, C3 and C6 hydroxyls; the sulfuric-acid route adds anionic sulfate half-esters; and oxidative routes add carboxyl or aldehyde groups (see the section on extraction chemistry).[1,11] Surface modification is generally a prerequisite for using CNCs in non-aqueous media or hydrophobic matrices, because the strong inter-fibril hydrogen bonding promotes aggregation and limits compatibility.[11,14] The central challenge of CNC surface chemistry is to react the accessible surface hydroxyls heterogeneously, without dissolving or degrading the crystalline core, so most strategies either activate the surface first (TEMPO/periodate oxidation, sulfation) or use reagents and media that tolerate the hydrogen-bonded substrate.[14,15]

Esterification and acetylation

Esterification of surface hydroxyls with acid anhydrides or acyl chlorides installs ester groups (–OCOR) that lower surface energy and improve compatibility with hydrophobic media.[15,40] Acetylation is the simplest case; longer-chain acylation increases hydrophobicity further. Esterification is among the most patented CNC modifications because it is operationally simple and tunable, but heterogeneous esterification must be controlled to avoid eroding crystallinity.[11,40]

Oxidation: TEMPO and periodate

Oxidative modification is the most versatile route because it installs defined, reactive handles. TEMPO oxidation converts C6–OH to carboxylate ($–COO^-$) selectively, raising surface charge and enabling carbodiimide coupling, amidation or grafting.[16,41] Periodate oxidation opens the C2–C3 ring bond to dialdehyde (–CHO), which can be reductively aminated, used for Schiff-base crosslinking, or combined with secondary oxidation/silylation/cationization to build dual-functional surfaces; periodate-oxidized CNC films, for example, crosslink to strengths around 66 MPa.[15] The choice between TEMPO (C6, carboxyl) and periodate (C2/C3, aldehyde) is a deliberate selection of reactive site and functional group.

Silylation

Reaction of surface hydroxyls with organosilanes installs siloxane linkages and pendant organic groups, the standard route to hydrophobization and matrix coupling. Aminosilanes such as 3-aminopropyltriethoxysilane (APTES) graft amino-functional silane to the surface (confirmed by EDX/XPS) without significantly altering CNC dimensions or crystalline structure, and improve thermal stability and char yield.[42] Aqueous bifunctional silylation with amino- and alkylsilanes allows simultaneous tuning of surface charge and hydrophobicity, as demonstrated for CNCs applied as collectors in quartz microflotation.[43] Silylation is favoured industrially for its robustness and the breadth of accessible chemistries.

Cationization and other charge modifications

Where a positive surface is required (*e.g.*, for antimicrobial action or interaction with anionic substrates), cationization with reagents such as glycidyltrimethylammonium chloride installs quaternary ammonium ($–N^+R_3$) groups, reversing the native anionic charge.[15] Charge can also be tuned reversibly: metal–phenolic-network coatings on TEMPO-oxidized CNCs, followed by covalent attachment of long-chain amines, provide a facile, reversible hydrophobization without harsh chemistry.[41]

Polymer grafting

Covalent attachment of polymer chains gives the greatest control over interfacial properties. Grafting-to couples preformed chains to surface –COOH/–OH, while grafting-from grows chains from surface-immobilized initiators; for example, polycaprolactone has been grafted onto TEMPO-oxidized nanocellulose both by esterification and by click chemistry, and the grafting method was shown to govern the resulting surface polarity.[40] Mechanochemical activation (*e.g.*, tosylation to install a –OTs leaving group, followed by nucleophilic substitution) extends grafting to solvent-minimized, scalable conditions.[14] Grafting is chemically the most demanding but the most powerful tool for engineering CNC interfaces.

The principal surface functionalization strategies discussed above are compared in terms of representative reagents, installed functional groups, reactive sites, and resulting chemical effects in Table 5. While Table 5 summarizes the

individual chemical reactions, the overall relationship between the native hydroxyl surface and the major functionalization pathways is illustrated schematically in Figure 5.

Table 5
Surface-modification methods for cotton CNC: reagent, installed functional group and chemical effect

Modification	Typical reagent	Functional group installed	Reactive site	Chemical effect	Ref.
Sulfation	H_2SO_4 (during hydrolysis)	$–O–SO_3^-$ (sulfate half-ester)	C6 (mainly)	Anionic charge; colloidal stability; ↓ thermal stability	11,21
Esterification / acetylation	Anhydride / acyl chloride	–OCOR (ester)	C2,C3,C6	Hydrophobization; matrix compatibility	15,40
TEMPO oxidation	TEMPO/NaBr/NaOCl, pH 10	$–COO^-$ (carboxylate)	C6	Anionic charge; reactive handle for coupling/grafting	16,41
Periodate oxidation	$NaIO_4$	–CHO (dialdehyde)	C2–C3	Platform for amination, crosslinking, dual functionalization	15
Silylation	APTES / alkylsilanes	$–Si–O–$ / $–NH_2$ / alkyl	surface –OH	Hydrophobization; coupling; thermal stability	42,43
Cationization	Glycidyltrimethyl ammonium chloride	$–N^+R_3$ (quaternary ammonium)	surface –OH	Cationic charge; antimicrobial/anionic binding	15
Tosylation + substitution	TsCl, then nucleophile	–OTs → –Nu	surface –OH	Leaving group for nucleophilic substitution/grafting	14
Polymer grafting (grafting-to / grafting-from)	Preformed polymer (*e.g.*, PCL) or initiator + monomer	Grafted polymer chains	–COOH/–OH	Tunable interfacial polarity	40

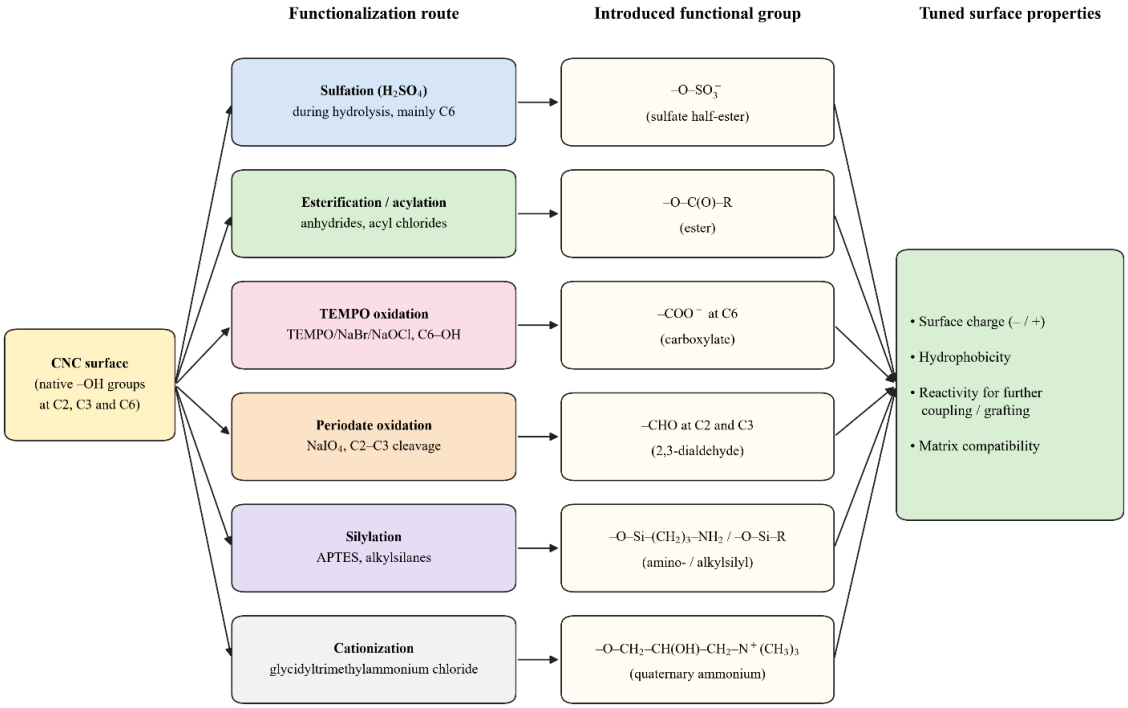


Figure 5: Surface functionalization of cotton-derived CNCs: the native hydroxyl surface is converted by sulfation, esterification, TEMPO/periodate oxidation, silylation or cationization into defined functional groups that tune charge, hydrophobicity, reactivity and matrix compatibility

Figure 5 demonstrates that the hydroxyl groups located at the C2, C3, and particularly the C6 positions constitute the central reactive platform for chemical modification of cotton-derived cellulose nanocrystals. Depending on the selected reaction pathway, surface functionalization can independently tailor surface charge, hydrophobicity, chemical reactivity, interfacial compatibility, and colloidal behavior without substantially altering the crystalline cellulose core.

Comparative evaluation of functionalization methods

The functionalization strategies summarized in Table 5 and Figure 5 demonstrate that no universal surface modification exists for cellulose nanocrystals. Instead, each reaction pathway is designed to tailor a specific combination of surface charge, chemical reactivity, hydrophobicity, and compatibility with polymer matrices.

Sulfation primarily improves colloidal stability through electrostatic repulsion, but reduces thermal stability. TEMPO oxidation introduces highly reactive carboxyl groups suitable for subsequent coupling reactions, whereas periodate oxidation provides aldehyde functionalities for crosslinking and dual functionalization. Silylation significantly improves compatibility with hydrophobic polymers, while cationization enables electrostatic interaction with negatively charged biomolecules and inorganic surfaces.

Therefore, surface functionalization should always be selected according to the desired application rather than considered as an independent post-treatment process. The close relationship between extraction chemistry, surface chemistry, and resulting physicochemical properties forms the basis of rational CNC design.

CHARACTERIZATION TOOLBOX

Reproducible CNC chemistry depends on a defined set of analyses, each probing a specific structural attribute. X-ray diffraction (XRD) identifies the cellulose-I (or II) allomorph from its characteristic (1−10), (110), (200) and (004) reflections and quantifies the crystallinity index (CrI), most commonly by the Segal empirical method (from the (200) maximum and the amorphous minimum) and, more rigorously, by amorphous-subtraction/peak-deconvolution; the two methods give systematically different values, so the method must always be stated.[44-46] Fourier-transform infrared (FTIR) spectroscopy confirms cellulose identity and the success of modification (*e.g.*, loss of the ~1738 cm^{-1} hemicellulose band on purification; appearance of carbonyl/ester/silane bands on functionalization).[18,42] Solid-state ^{13}C NMR resolves allomorph and surface chemistry, and is the definitive probe of supramolecular structure.[7] Electron and force microscopy (TEM, SEM, AFM) give morphology and dimensions, while dynamic light scattering (DLS) gives hydrodynamic size; together they define length, width and aspect ratio (typically aspect ratio >5 to <50 for CNC).[3,21,47] Conductometric titration quantifies surface acidic groups – sulfate half-esters or carboxyls (*e.g.*, ~239 μmol g^{-1} sulfate) – and ζ-potential measures colloidal stability, with elemental analysis or XPS/ICP quantifying sulfur or grafted heteroatoms.[21,48] Thermogravimetric analysis (TGA) measures thermal stability, which is acutely sensitive to surface sulfation. Small-angle X-ray scattering (SAXS) and rheology/polarized-optical microscopy further characterize suspension structure and the chiral-nematic ordering of CNC.[21] A recurring methodological point is that drying method (freeze- vs spray-drying) alters size, aspect ratio and sulfur content – and therefore measured properties – so sample history must be reported alongside the data.[48]

Quantitatively, the surface sulfate half-ester content is determined by conductometric titration (commonly ~150–300 μmol g^{-1}, corresponding to roughly 0.5–1.0% sulfur by elemental analysis), and the carboxyl content of oxidized CNC is obtained by the same method; these charge densities correlate directly with ζ-potential and colloidal stability.[21,48]

STRUCTURE–PROPERTY RELATIONSHIPS

The extraction and surface chemistry discussed above maps onto product properties through a small set of coupled relationships. Crystallinity rises as hydrolysis removes amorphous cellulose, increasing stiffness and (for non-sulfating routes) thermal stability; cotton's high native crystallinity gives it a head start.[6,18] Surface charge and colloidal stability are governed by the density of ionizable groups: sulfate half-esters or carboxyls raise the magnitude of the ζ-potential (commonly −28 to −58 mV) and confer electrostatic stabilization, with the chiral-nematic self-assembly of CNC suspensions depending on this charge and on aspect ratio.[21,47] The defining trade-off of CNC

chemistry is sulfation versus thermal stability: the sulfate groups that stabilize aqueous suspensions also catalyse dehydration and lower the decomposition temperature, which is precisely why organic-acid, oxidative and enzymatic routes – producing carboxylated or unsulfated CNC – are pursued when thermal robustness is required.[10,11] Dimensions and aspect ratio depend on source and reaction severity: milder/organic-acid hydrolysis yields longer crystals, harsher conditions shorter ones, and aspect ratio in turn governs reinforcing efficiency, rheology and self-assembly.[10,47] Finally, allomorph (cellulose I vs II) underlies crystallinity, reactivity and thermal behaviour, and can be deliberately controlled through reaction conditions.[13] For cotton specifically, the combination of high purity and high native crystallinity means product quality is governed primarily by the isolation chemistry rather than by feedstock variability—an advantage for systematic structure–property study.

A direct manifestation of these structural variables is liquid-crystalline self-assembly: above a critical concentration, charge-stabilized cotton CNC suspensions organize into a chiral-nematic (cholesteric) phase whose helical pitch – and the structural colour of the dried films – is governed by aspect ratio, surface-charge density and ionic strength.[1,21] This charge- and shape-dependent ordering links the isolation chemistry directly to optical function and is a sensitive probe of CNC quality.

APPLICATIONS OF COTTON-DERIVED CNCs

Although this review is chemistry-centred, the purpose of CNC chemistry is ultimately functional: the surface groups installed during or after isolation dictate the accessible applications. The main application areas of cotton-derived CNCs are outlined below, with emphasis on the link between surface chemistry and performance.

Polymer nanocomposites and films. The high axial stiffness, large specific surface area and high aspect ratio of CNCs make them efficient reinforcing fillers at low loadings, provided that they are well dispersed in the matrix.[1,2] Anionic (sulfated or carboxylated) cotton CNCs disperse readily in water-soluble polymers; for example, CNCs extracted from post-consumer polyester/cotton-blended fabrics have been incorporated into poly(vinyl alcohol) composite films, illustrating a direct route from textile waste to value-added materials.[28] Films of chemically crosslinked, periodate-oxidized CNCs reach tensile strengths of about 66 MPa,[15] whereas hydrophobized (esterified, silylated or polymer-grafted) CNCs are required for non-polar matrices, in which interfacial compatibility controls stress transfer.[40,42]

Colloidal, rheological and food-related applications. Charge-stabilized CNCs act as rheology modifiers and thickeners in water-borne formulations, and partially hydrophobized CNCs adsorb at oil–water interfaces, stabilizing Pickering emulsions without molecular surfactants.[1,12] In food systems, CNCs are being explored as emulsion stabilizers, fat replacers, and components of edible coatings and packaging, where drying history and surface chemistry strongly affect redispersibility and functionality.[12,48]

Photonic and optical materials. Above a critical concentration, sulfated CNCs self-assemble into a chiral-nematic phase that is retained on drying, yielding iridescent films with tunable structural colour.[1,21] Because the helical pitch depends on surface-charge density, aspect ratio and ionic strength, the isolation chemistry directly determines optical performance, which makes cotton CNCs with well-defined dimensions attractive for decorative and security coatings and for colorimetric sensors.

Biomedical and hydrogel applications. Carboxylated (TEMPO-oxidized) and aldehyde-functional (periodate-oxidized) CNCs act as crosslinkers and reinforcing phases in hydrogels and as carriers of drugs and bioactive molecules, since –COOH and –CHO groups permit covalent coupling and Schiff-base chemistry;[15,41] cationized CNCs provide antimicrobial surfaces.[15] At the same time, the crystallinity and aspect ratio of cellulose nanomaterials have been shown to govern their pro-inflammatory and immune-adjuvant effects, so dimensional and surface control is also a safety requirement.[47]

Environmental and separation applications. Charged and functionalized CNCs are investigated as adsorbents for metal ions and dyes, as membrane components, and as bio-based reagents in mineral processing; amino/alkyl bifunctionally silylated CNCs, for example, act as collectors in quartz microflotation.[4,11,43] The conversion of cotton-textile and agro-industrial wastes into CNCs[3,17,28,30,32] further links these applications to circular-economy strategies for the cotton value chain.

Across all of these application areas, industrial implementation of cotton-derived CNCs remains limited by solvent recovery, drying costs, particle aggregation, and process reproducibility. Continuous-flow hydrolysis, recyclable solvent systems, and standardized characterization protocols are expected to become key enabling technologies for commercial-scale production.

CHALLENGES AND FUTURE PERSPECTIVES

Several chemistry-centred challenges define the field's forward agenda. First, the sulfate–thermal-stability trade-off remains the core problem of the dominant sulfuric-acid route; recyclable organic acids (formic, oxalic, *p*-TsOH) and oxidative or enzymatic routes that yield thermally robust, carboxylated or unsulfated CNC are the most promising resolution, provided acid/solvent recovery is closed-loop.[10,26] Second, green-solvent routes (ionic liquids, deep eutectic solvents) offer mild, tunable chemistry but require demonstrated recovery and reuse to be genuinely sustainable.[24,25,43] Third, selective and scalable surface chemistry – heterogeneous reactions that modify the surface without degrading the crystalline core, ideally solvent-minimized (*e.g.*, mechanochemical, aqueous) and regioselective (C6 vs C2/C3) – is needed to translate laboratory functionalization to manufacture.[14,41] Fourth, allomorph and dimension control through reaction engineering would allow CNC properties to be specified by design rather than discovered empirically.[13] Underpinning all of these is the need for standardized characterization: because CrI depends on the calculation method, and because surface-group content, ζ-potential and thermal stability depend on sample history (including drying), harmonized reporting is essential for reproducible CNC chemistry and for building reliable structure–property datasets.[45,48] For cotton specifically, its purity and consistency make it the ideal substrate on which to develop and standardize these chemistries.

Accordingly, future research should prioritize four interconnected directions: (i) the development of recyclable green extraction systems; (ii) one-step extraction and surface functionalization; (iii) standardized characterization protocols; and (iv) pilot-scale industrial validation.

CONCLUSION

Cellulose nanocrystals from cotton are, above all, products of chemistry: their crystallinity, dimensions, surface charge, thermal stability and reactivity are determined by the isolation route and by subsequent surface modification, not by the feedstock alone. Cotton's near-pure, highly crystalline cellulose-I structure makes it both an excellent practical feedstock and an ideal model system, because isolation chemistry acts directly on an ordered lattice with minimal interference from lignin or hemicelluloses. Acid hydrolysis remains the central reaction, with sulfuric acid delivering colloidally stable but thermally limited sulfated CNCs, while organic/green acids, oxidative (TEMPO, periodate), ionic-liquid/DES and enzymatic routes increasingly resolve the sulfate–thermal-stability trade-off and, in several cases, functionalize the surface in a single step. Surface chemistry – esterification, oxidation, silylation, cationization and grafting – converts the native hydroxyl surface into defined functional groups that set colloidal behaviour, hydrophobicity and application scope, and is enabled by a characterization toolbox in which XRD crystallinity, FTIR, NMR, microscopy, conductometric titration, ζ-potential and thermogravimetry each probe a specific structural attribute. The decisive structure–property relationships – crystallinity, the sulfation–thermal-stability trade-off, charge-governed colloidal stability and self-assembly, and allomorph control – together define a coherent design space.

From a critical perspective, no currently available extraction strategy simultaneously maximizes cellulose nanocrystal yield, crystallinity, colloidal stability, thermal resistance, environmental sustainability, and process economy. Consequently, future progress is unlikely to arise from replacing one extraction chemistry with another, but rather from integrating sustainable extraction routes with rational surface functionalization and standardized characterization protocols. Such integration will enable the reproducible production of application-specific cellulose nanocrystals while supporting the transition from laboratory-scale synthesis to industrial manufacturing.

Overall, cotton remains not only an outstanding renewable feedstock, but also an indispensable model substrate for advancing cellulose nanocrystal chemistry. Its reproducible reactivity provides an ideal platform for investigating extraction mechanisms, surface engineering, and structure–property relationships that are directly transferable to other lignocellulosic resources. Continued progress in green chemistry, scalable

processing, and internationally standardized characterization will be essential for realizing the full technological potential of cotton-derived cellulose nanocrystals in advanced materials, sustainable composites, biomedical systems, and next-generation bio-based products.

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