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Supplementary Information

Environment-friendly nanocellulose-indigo dyeing of textiles

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[1]Materials and Methods

Materials and Reagents

Bleached, desized, un-mercerized 100% cotton print fabric (99.7 g/m^2) was purchased from Testfabrics, Inc, PA USA. The 100% cotton rotor spun yarn (unscoured, un-mercerized, and 6cc) was provided by Mount Vernon Mills, Trion, Georgia. Natural indigo (*Indigofera tinctoria*) was obtained from Dharma Trading Company, CA, USA. Carboxymethylcellulose sodium salt with a molecular mass of 90 kg/mol, chitosan with a molecular mass range of 19-375 kg/mol, and acetic acid were purchased from Sigma-Aldrich and used as received. Anhydrous sodium carbonate and triton X-100 (nonionic dispersing agent) were purchased from J.T. Baker and used as received. AATCC 1993 standard detergent WOB was received from AATCC. Formamidinesulfinic acid (thiourea dioxide) was purchased from Acros. Polystyrene latex beads suspension 2.5% in the water of a size 30 nm (L5155), 100 nm (L9902), 500 nm (L1403), and 2 μm (L4530) were purchased from Sigma-Aldrich.

Production of Nanocellulose

As per a published protocol[2], kraft pulp sheets were knife-milled three times using a mesh sieve (pore size 500 μm). Cellulose powder was mixed with hot water (1-5% cellulos powder in water) and carboxymethylcellulose sodium salt (CMC, 0.25% in water). CMC was used as a plasticizer to accelerate the halogenation process (Rebinder effect[3]). The mixture was then delaminated into nanosized fibrils during 4-5 passes in a high-pressure homogenizer (APV 1000) to produce 1-5% nanofibrillated cellulose (NFC) hydrogel[2]. The cellulose concentration was adjusted to 1% in the hydrogel by dilution with water. The presence of CMC facilitate defibrillation of pulp particles.[4] The nano-size cellulose fibers are 10 to 50 nm in diameter and up to several micrometers in length with an average aspect ratio of 1:50 (Ref.1).

Scouring of Cotton Fabric

The fabric was subjected to water at 60°C with AATCC standard reference detergent in 1:20 material liquor ratio. After 10 min, the sodium carbonate was added, and then the temperature was elevated to 80°C and maintained for another 35 minutes. After that, the samples were thoroughly rinsed in a similar amount of water twice and were dried at room temperature.

Coating of Cotton Textiles with NFC-indigo Formula

Agglomerated natural indigo of the average size of approximately 259 µm was ground using mortar and pestle to make it in powder form. The NFC-indigo formula was prepared by mixing the natural indigo powder with NFC hydrogel in amounts calculated in units of shade (pigment weight in % of the weight of the fabric for coloration). In the experiments, 1, 2, 3, and 6% shade was mixed with 1% NFC gel and 0.01% nonionic dispersing agent (Triton X-100). The mixture was stirred using a magnetic stirrer and then coated over damp, pre-scoured cotton fabric samples using a screen printer for even and thin coating. Coated samples were dried in the oven at 120°C for 60 minutes (**Supplementary Video 1**). Samples of cotton yarn were coated at the continuous passage of the yarn through the NFC-indigo formulation and dried in a tube furnace (**Supplementary Video 2**).

Post-Treatment of Coated Textiles

A chitosan solution was prepared by dissolving 1% chitosan in the water of 1:10 material to liquor ratio in the presence of 2% acetic acid (as per the volume of water) using a magnetic stirrer [5]. Each percentage shade of the sample was divided into two groups. One group was post-treated with the chitosan solution and the other group was not treated. For the post-treatment, the fabrics were dipped in chitosan solution for 15 minutes and then nipped using a manual rubber roller. The post-treated samples were dried at 150°C for 15 min. Likewise, samples of yarn were also treated in a chitosan aqueous solution and then cured.

Washing of samples

Each sample of size 5 cm x 15 cm was subjected to the colorfastness to laundering, home & commercial: accelerated, AATCC test method 61-2013-2A to perform the washing process with 25 steel balls) with Atlas Launder-Ometer (AATCC standard instrument), which is equivalent to 5 laundry cycles. For bending length and air permeability, the five home-laundering (washing/drying) procedure was performed on samples of sizes 2.5 cm x 20 cm and 20 cm x 20 cm according to AATCC Standard Method 124 using a standard reference detergent. Soluble in water CMC is rinsed out in the washing step.

Control samples

Four sets of exhaust dyed control samples were produced. The first sets of samples were dyed with indigo (1, 2, 3, and 6% shade) in the presence of thiourea dioxide (twice the amount of indigo) and 4g/l of sodium hydroxide in a material liquor ratio of 1:200. The powdered indigo and sodium hydroxide were mixed in water and heated to 50°C, thiourea dioxide was added and allowed to reduce the indigo. Then presoaked samples were dyed by dipping it for 1 minute and after taking it out, excess liquor was squeezed out. The fabric was then hanged to oxidize for 2 minutes. The second set was produced by post-treating dyed samples with chitosan, similar to NFC-indigo dyed fabrics. The third set of samples were dyed with indigo (1, 2, 3, and 6% shade) without the presence of thiourea dioxide and sodium hydroxide. Lastly, the fourth set of samples were produced by post-treatment of samples dyed with indigo (1, 2, 3, and 6% shade) without the presence of thiourea dioxide and sodium hydroxide. All samples were dried at 100°C for 20 minutes and subjected for washing as mentioned above.

Characterization

The fabric samples were conditioned overnight at 65±2% relative humidity and 20±1°C temperature for testing and characterization of color performance and comfort properties.

Dyeing performance of colored fabrics:

Dye fixation (%F) is given by

$$\%F = \frac{K/S \ \text{after Wash}}{K/S \ \text{before Wash}} \times 100$$

The color strength (K/S) of the coated samples was measured at all wavelengths (400 to 700 nm at 10 nm interval) using a Macbeth Color Eye 7000A Spectrophotometer. It was calculated using the built-in software of color matching using the Kubelka–Munk equation given by:

$$K/S = \frac{(1-R)^2}{2R}$$

where K is the absorption, S is the scattering, and R is the reflectance. The K/S value of coated samples at the maximum wavelength of absorbency (λ_{max} 630-650 nm) was reported.

The washfastness of the samples was evaluated using Colorfastness to laundering, home & commercial: accelerated, AATCC test method 61-2013-2A to perform the washing process with 25 steel balls) with Atlas Launder-Ometer (AATCC standard instrument). Colorfastness to crocking (dry and wet) was evaluated using Colorfastness to crocking crockmeter AATCC test method 8-2016 by using SDL atlas, M238BB Electronic Crockmeter. The color change for washfastness and color staining for crock fastness ratings were obtained using Macbeth Color Eye 7000A spectrometer. To evaluvate the colorfastness properties of the NFC-indigo dyed fabric, the standard minimum colorfastness requirement for denim fabrics was referred to Standard Specification for 100% cotton denim fabrics (ASTM D6554/D65554M-14)[6].

Comfort properties of colored fabrics

The samples of original and coated fabrics were initially incubated in an oven at 100°C for 20 min, and then in a desiccator for 20 min. The dry weight of coated and non-coated samples was measured to calculate the percentage weight gain:

$$\%\ \text{Weight Gain} = \frac{\text{Weight after wash} - \text{Weight before coating}}{\text{weight before coating}} \times 100$$

The thickness of NFC coatings was calculated based on weight gain as

$$\text{Thickness of coating} = \text{Initial thickness of cotton fabic} \times \%\ \text{Weight gain}$$

The stiffness test on the warp side of the samples (ASTM D1388—18 Standard Test Method for Stiffness of Fabrics) was carried out using the cantilever test with IDM Stiffness Cloth Tester S0013. Air permeability test was performed (ASTM D737—18 Standard Test Method for Air Permeability of Textile Fabrics) using Textester FX 3300 Air permeability tester.

Dynamic light scattering (DLS) measurements

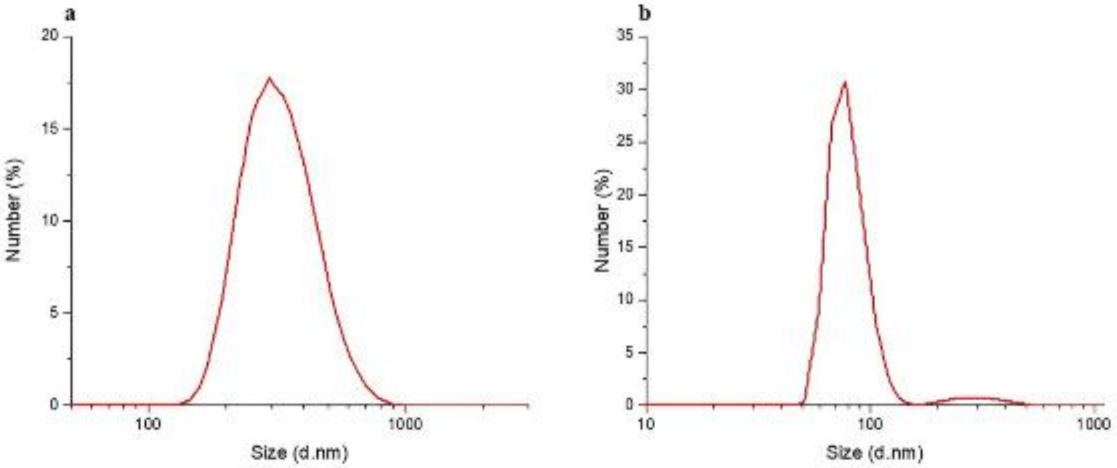
Indigo particle size was measured using the DLS Malvern Zetasizer Nano-ZS instrument. The size of ground indigo particles was estimated in a particle dispersion of 0.01% Triton X-100 aqueous solution. Samples of indigo particles extracted from the fabric, dyed by exhaustion method, were prepared by extracting the particles at 60°C at the agitation of the fabric sample in 0.01% Triton X-100 aqueous solution.

Particle retention test with NFC-based filters

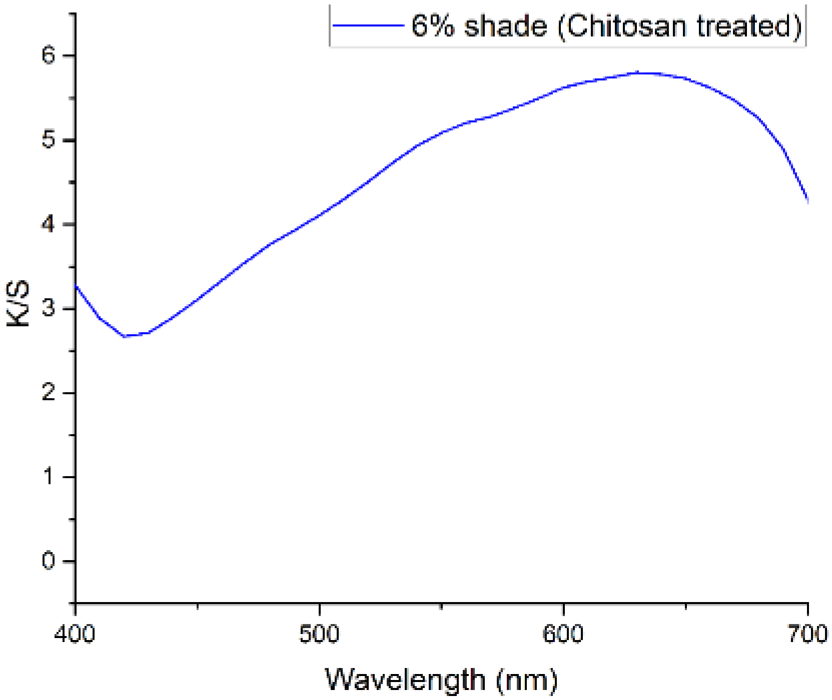
A 5 µL sample of a 2.5% polystyrene latex fluorescent-labeled beads suspension of each bead size was diluted in 20 mL of deionized water. Each diluted suspension was filtered through an NFC-coated fabric in a Büchner funnel and vacuum suction. The filtrate solution was collected, and its fluorescence intensity was measured using a spectrofluorometer (Fluorolog-3, HORIBA Scientific, USA) at the specific excitation and emission wavelengths of fluorescent particles. The calibration plot was used to estimate the fraction of the particles retained on the filter.

Supporting Figures

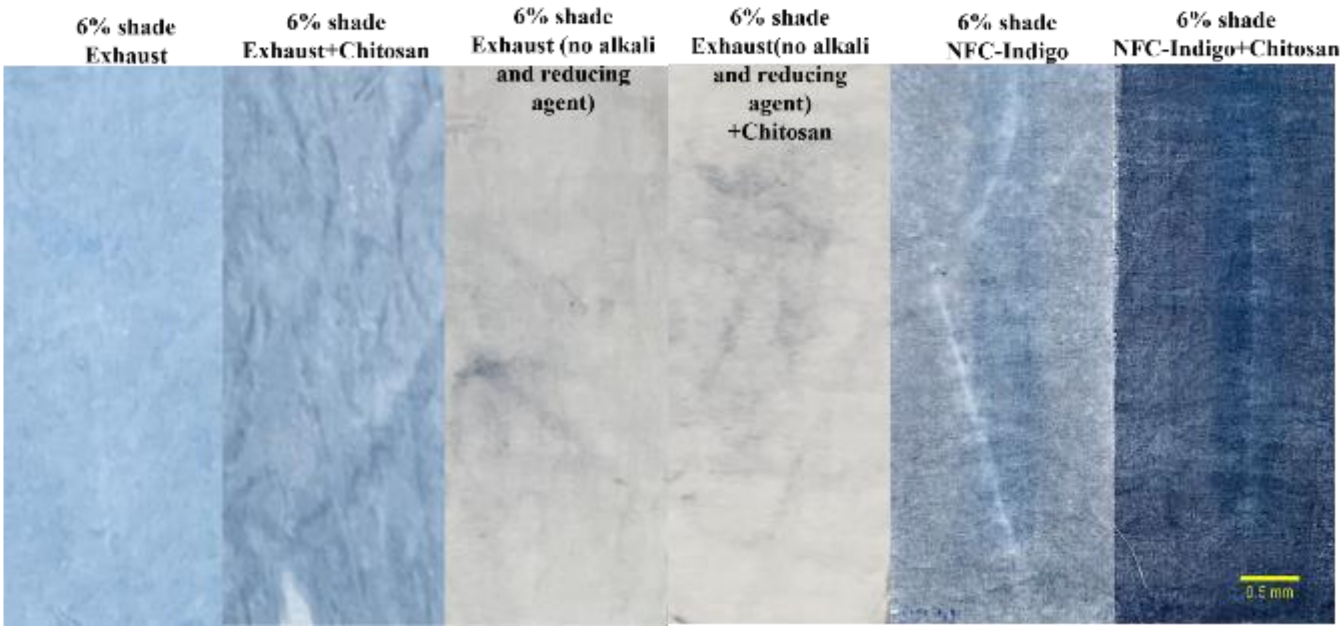
Supporting Figure S1: A Greenpeace campaigner takes a water sample from a polluted river near Dadun Village, Xintang, Zengcheng (2010). Credit: © Lu Guang / Greenpeace



Supporting Figure S2: Indigo particles size distribution by dynamic light scattering: (a) natural indigo particle dispersed in the aqueous solution of dispersing agent, an average diameter is 83 ± 14 nm; (b) reference experiment: indigo particles extracted from the denim fabric colored using traditional dyeing method by reduction of leuco-indigo; an average diameter is 331 ± 44 nm.



Supporting Figure S3: Color strength wavelength function of the chitosan post-treated 6% shade NFC-indigo dyed sample.



Supporting Figure S4: Optical images of 6% shade samples of exhuast dyed and NFC dyed samples with or without postreatment with chitosan (washed).

Supporting Tables

Supporting Table S1. Colorfastness ratings of NFC-indigo dyed fabrics

% shade of NI (wof)	**Exhaust**	**Exhaust +Chitosan**	**Exhaust (no alkali and reducing agent)**	**Exhaust(no alkali and reducing agent) +Chitosan**	**NFC-Indigo**	**NFC-Indigo +Chitosan**
1% Shade						
K/S	0.12 ± 0.02	0.18 ± 0.01	0.06 ± 0.03	0.08 ± 0.01	0.52 ± 0.16	1.31 ± 0.1
% Fixation	87.54 ± 2.33	85.54 ± 2.69			38.11 ± 5.39	91.14 ± 5.35
Washfastness	4.17 ± 0.29	4.33 ± 0.29			3.17 ± 0.5	2.78 ± 0.25
Dry Crockfastness	4.17 ± 0.29	4.17 ± 0.29			4.17 ± 0.29	3.17 ± 0.29
Wet Crockfastness	4.17 ± 0.29	4 ± 0			3.83 ± 0.29	2.83 ± 0.29
2% Shade						
K/S	0.41 ± 0.03	0.62 ± 0.08	0.04 ± 0	0.14 ± 0.05	0.77 ± 0.11	1.91 ± 0.2
% Fixation	71.52 ± 1.24	84.69 ± 3.59			37.94 ± 5.76	90.6 ± 3.29
Washfastness	4.33 ± 0.29	4.17 ± 0.29			3.33 ± 0.6	2.94 ± 0.35

Dry Crockfastness	3.5 ± 0	3.33 ± 0.58			4.17 ± 0.29	2.83 ± 0.29
Wet Crockfastness	3.5 ± 0	3.33 ± 0.58			3.5 ± 0	2.67 ± 0.29
3% Shade						
K/S	0.79 ± 0.05	0.65 ± 0.02	0.04 ± 0.01	0.09 ± 0.01	1.05 ± 0.08	2.86 ± 0.34
% Fixation	65.18 ± 1.29	81.33 ± 5.56			38.35 ± 1.23	91.97 ± 5.92
Washfastness	4.17 ± 0.29	4.5 ± 0			3.17 ± 0.33	2.5 ± 0.33
Dry Crockfastness	2.5 ± 0	3.33 ± 0.29			3.83 ± 0.29	2.33 ± 0.29
Wet Crockfastness	2.83 ± 0.29	3.33 ± 0.29			3.17 ± 0.29	2.33 ± 0.29
6% Shade						
K/S	1.00 ± 0.05	2.07 ± 0.04	0.10 ± 0.03	0.12 ± 0.05	1.96 ± 0.35	5.24 ± 0.37
% Fixation	59.5 ± 3.01	78.59 ± 3.58			36.56 ± 4.32	93.73 ± 7.33
Washfastness	4.17 ± 0.29	4.33 ± 0.29			3.28 ± 0.42	2.61 ± 0.19
Dry Crockfastness	2.67 ± 0.29	2.83 ± 0.29			3 ± 0	1.5 ± 0
Wet Crockfastness	3.17 ± 0.29	3.33 ± 0.29			2.17 ± 0.29	1.5 ± 0

Supporting Table S2. Comfort properties of NFC-dyed fabrics.

% Shade of NI (wof)	NFC-Indigo	NFC-Indigo +Chitosan
Initial measurements, Thickness of fabric 296.25 ± 3.98 µm, Bending length: 1.99 ± 0.13 cm, Air permeability:		
1% Shade		
K/S	0.52 ± 0.16	1.31 ± 0.1
% Fixation	38.11 ± 5.39	91.14 ± 5.35
Weight gain* %	-0.78 ± 0.09	1.11 ± 0.39
Thickness of coating (µm)	-	3.28 ± 1.15
Bending length (cm)	2.04 ± 0.14	2.16 ± 0.03
Air permeability (cfm)	51.9 ± 1.15	48.57 ± 0.55
2% Shade		
K/S	0.77 ± 0.11	1.91 ± 0.2
% Fixation	37.94 ± 5.76	90.6 ± 3.29
Weight gain* %	-0.31 ± 0.21	1.39 ± 0.04

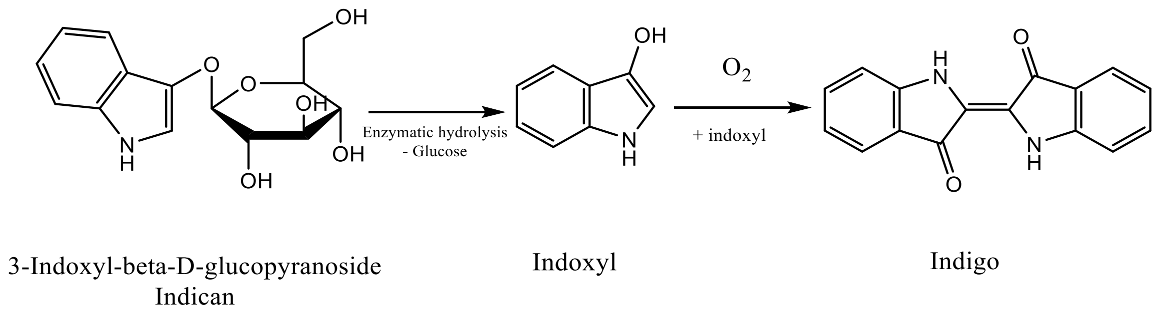
Thickness of coating (µm)	-	4.11 ± 0.11
Bending length (cm)	2.08 ± 0.09	2.16 ± 0.16
Air permeability (cfm)	50.33 ± 2.15	48.5 ± 0.61
3% Shade		
K/S	1.05 ± 0.08	2.86 ± 0.34
% Fixation	38.35 ± 1.23	91.97 ± 5.92
Weight gain* %	-0.60 ± 0.24	1.28 ± 0.22
Thickness of coating (µm)	-	3.79 ± 0.65
Bending length (cm)	2.08 ± 0.08	2.16 ± 0.11
Air permeability (cfm)	50.8 ± 0.70	47.3 ± 0.98
6% Shade		
K/S	1.96 ± 0.35	5.24 ± 0.37
% Fixation	36.56 ± 4.32	93.73 ± 7.33
Weight gain* %	-1.33 ± 0.20	2.65 ± 0.27
Thickness of coating (µm)	-	7.85 ± 0.79
Bending length (cm)	2.11 ± 0.16	2.17 ± 0.17
Air permeability (cfm)	50.57± 1.27	47.5 ± 0.85

* negative weight is due to the loss of some fibers to rinsing solutions

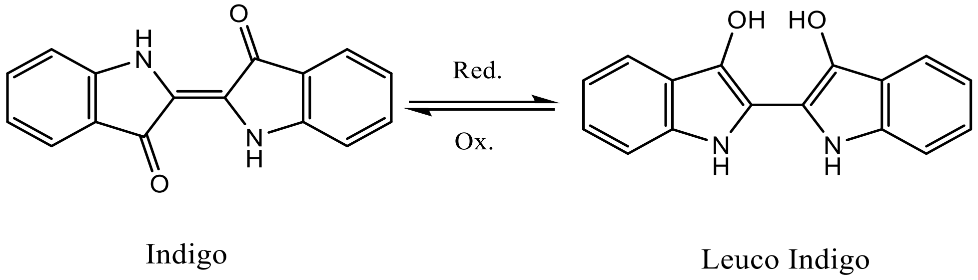
Supporting Notes

Supporting Note 1. Indigo

The uses of natural indigo go as far back as 7000 BC[7]. Recently, with an increasing consciousness of pollution control, the revival of natural dyes, including natural indigo, has occurred[8]. Natural indigo (2,2'- Bis (2,3-dihydro-3- oxoindolyliden) (I) a vat dye which is manufactured by biosynthesis of leaves and stem of indigo plants containing indican in *Indigofera. tinctorium* and *P. tinctorium*; isatan B and indican in *Is. tinctoria* to yield indoxyl, which transforms rapidly into indigo by oxidation[8, 9].



(I)



(II)

Due to the high demand for indigo, in 1925, BASF synthesized the commercially viable indigo[9]. For commercial production of synthetic indigo, crude oil (petroleum) is, first, chemically transformed in benzene, which, in turn, is converted into aniline in the presence of nitric acid, sulfuric acid, metal catalysts, and heat. Aniline is converted into the *n*-phenyglycinein by the *N*-methylation process in the presence of formaldehyde, hydrogen cyanide, and sodium hydroxide and converted into indoxyl in the presence of potassium hydroxide, sodium hydroxide, and sodium amide, which is oxidized to get indigo[9].

Dyeing with indigo is a complicated process and requires a series of parameters to be looked after. Indigo is a nonionic vat dye, which are insoluble pigments comprising of the carbonyl group(C=O) as chromophore and alkylamino group (-NHR) as auxochrome[10]. During dyeing, the aggregates of vat dyes are converted into a soluble Leuco indigo (II) anionic form of ion size 1.3 nm in the presence of reducing agent under the alkaline condition and develop substantivity towards cellulosic fibers[10, 11]. After diffusion, the dye molecules adsorbed on the cellulose via hydrogen bonds and oxidized to form submicron to micron size pigment particles in the presence of oxygen[10, 12]. Indigo is deposited over the surface of the cotton fibers with the exhaustion of only 10-20 % as compared to other vat dyes with the exhaustion of 70-95%, showing lower colorfastness properties and thus called a poor vat dye[13, 14]. To have better exhaustion and color performance, the multiple immersion and oxidation for a shorter period of 10-15 sec and 120 sec, respectively, for approximately 2% dye uptake each dip, are employed[15]. Continuous dosing of indigo and chemicals is performed to avoid shade variation. Well monitored steps lead to 70 to 80% fixation of indigo after washing[16-18]. Commercially, indigo dyeing for denim is a continuous process involves pretreating (scouring, mercerization), bottoming (sulfur dyes), dyeing, topping (sulfur, reactive, vat dyes), post-treating (washing), and drying. During dyeing, the wetted cotton yarns go through multiple dips and nips in leuco indigo vats (1-5 g/L) and oxidation by air to gain the desired percentage shade, and after dyeing, the yarns are sized before weaving[19, 20]. Bottoming or topping is a dyeing of yarns with black (or other) sulfur dyes before or after, respectively, is required to produce darker/deeper blue shade or different dyeing performance[19]. Indigo dyeing for denim is unique as it does not demand uniform dyeing through the cross-section of yarns, instead of the indigo particle aggregates over the surface of the yarns layer by layer after each dipping and does not penetrate inside[15]. This phenomenon is called the ring dyeing effect, which is desired to develop a trendy distressed look (wash down effect) in denim easily[18]. The size of the ring effect can be increased by decreasing the pH from 13 to 11[18]. The color yield of indigo on denim yarn is highest in the mono ionic form (HO-indigo-O^-) of reduced indigo within the range of 10.8 to 11.2 pH in the same alkalinity caused by a higher strike rate and poor diffusion rate[18]. Also, enough ionization of cotton fiber (cellulose-O^-) happens at pH 11 of dyebath favoring ring effect due to higher affinity, higher strike rate and lower penetration of the dye[18].

Supporting Note 2. Nanocellulose

Cellulose is an abundant biopolymer found in woods, plant fibers, marine animals, algae, fungi, and bacteria comprised of glucose monomeric units covalently bonded by β 1-4 glucosidic bond. The degree of polymerization depends on the source of cellulose (from 10 000 to 15000)[21, 22]. Cellulose in plant walls occurs in the form of elementary fibrils composed of cellulose chains. Aggregation between cellulose chains and microfibrils occurs due to van der Waals forces and hydrogen bonding[21, 23]. There are three types of nanocellulose (engineered, nano-structured cellulose[24]): nanocrystalline cellulose (NCC), nanofibrillated cellulose (NFC), and bacterial nanocellulose (BNC). BNC is secreted extracellularly by bacteria called *Gluconacetobacter*. NFC comes from many different sources, including wood pulp, bleached kraft pulp, and bleached sulfite pulp via mechanical processing, using a homogenizer or microfluidizer. NFC has both amorphous and crystalline regions and tends to form hydrogels due to the entanglement of high aspect ratio NFC fibers[22, 25, 26]. NCC is fabricated by chemical treatment of biomass with mineral acids or oxidizing agents[21]. NCC particles have a lower aspect ratio as compared to NFC and higher crystallinity. All types of nanocelluloses have a very high surface area with the surface decorated by OH functional groups[24]. In this work, we selected NFC due to the high aspect ratio of fibrils capable of generating an entangled network that cage pigment particles.

Supporting Note 3. Chitosan

Chitosan is a polysaccharide with more than 5000 glucosamine units, obtained from the deacetylation of chitin, poly-(1,4)-2-acetamido-2-deoxy-β-D-glucose[27, 28]. Chitin is the second most abundant natural polymer found in the shells of crustaceans such as crab, shrimp, and crayfish [28]. Properties such as antibacterial, antitumor, and low immunogenicity of chitosan have drawn the attention of researchers in textile, polymer, and biomedical fields[29]. FTIR spectroscopic analysis shows that chitosan is capable of forming a hydrogen bond between -NH_2 group of chitosan and -OH group of cellulose acting as a cross-linking agent[30, 31]. Chitosan introduces cationic sites on the cotton surface owing to –NH_2 functional groups in glucosamine units. Treatment of textiles with chitosan contributed to an increase in abrasion resistance, stiffness, and crease recovery properties along with antimicrobial activity[31].

Supporting Note 4. Cost-factor

We focused only on the stage of indigo-dyeing of cotton fabrics with the major goal to reduce the use of harsh chemicals. We can make only a very rough estimation of the cost factor. The combination of indigo+NFC+chitosan makes only 1-2 w% of the colored fabric. Current prices of NFC < $50/kg, chitosan about $5/kg. Adding these components to the fabric will add about $0.5/kg fabric, but we should subtract the costs of water and chemicals that are avoided by NFC dyeing technology. A typical price of indigo-colored cotton fabric is $3/kg. It is apparent that the proposed technology will have a minimal impact on the price but it provides substantial improvements of the environmental impact.

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