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Highly stable, antiviral, antibacterial cotton textiles via molecular engineering

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This supplementary information file includes:

Supplementary Notes 1–4

Supplementary Figures 1–22

Supplementary Tables 1-3

Supplementary References 1–16

Supplementary Note 1: Comparison of the Cu-IT with pristine cotton textiles and other surface-modified cotton textiles.

In Fig. 1b, we compare the Cu-IT with unmodified cotton textiles and other surface-modified cotton textiles in terms of cost, scalability, mechanical performances, and antiviral and antibacterial activity:

Scalability:

The Cu-IT is fabricated using a three-step approach, including preparation of the Cu(II)-saturated NaOH solution, diffusion and coordination of Cu ions with the cellulose molecules, and washing and drying; all the three steps in the procedure are highly scalable. However, the preparation of surface-modified cotton textiles, such as those involving using Cu/CuO_x nanoparticles,[1,2] requires the use of complex chemical reaction[1-4] or other high-cost techniques[5] such as chemical vapor deposition, physical vapor deposition, evaporation, sputtering, and thermal/plasma spraying to form the nanoparticles. The complexity and/or high cost make these methods difficult to scale up.

Cost:

The cost can be divided into two parts, namely, materials and manufacturing costs. For the Cu-ITs, metal Cu is the major consumed raw material, with a price of ~$7/kg (all the prices are based on the listed prices on www.alibaba.com); and the manufacturing is based on the low-cost soaking and drying processes. For surface-modified cotton textiles, such as those deposited/plated with Cu/CuO_x nanoparticles,[1,2] the raw materials include Cu salts (*e.g.*, $15/kg for $Cu(CH_3COO)_2$, ~$2/kg for $CuSO_4$), reducing agents (e.g., ~$20/kg for $NaBH_4$, ~$7/kg for ascorbic acid) and solvents (e.g., water, ethanol, etc.), which make the materials cost much higher than that of the Cu-ITs. Moreover, the manufacturing costs of the surface-modified cotton

textiles are also higher due to the complex chemical reactions and other high-cost techniques involved (as described in the prior Scalability section), compared with the simple fabrication process of the Cu-ITs.

Mechanical stability

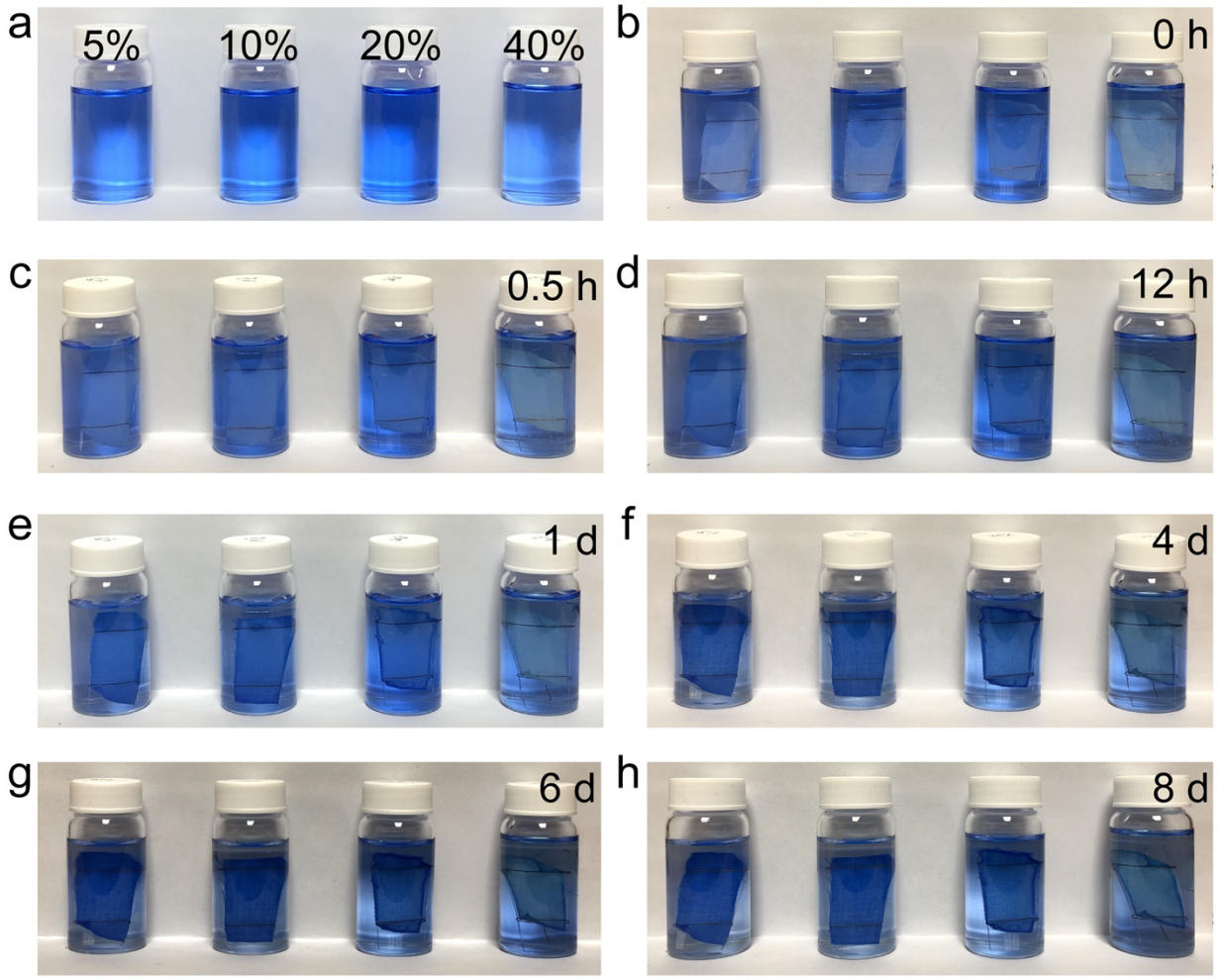
For the Cu-ITs, the hierarchical structures of the cotton textiles are preserved during the processing, and the Cu ions are coordinated with O atoms of the hydroxyl groups on the cellulose chains, producing highly stable material able to sustain repeated washing in water. Moreover, the Cu coordination makes the tensile strength of the Cu-IT higher than that of the unmodified textile. The results are described in Fig. 3. For the surface-modified cotton textiles, the mechanical properties of the additive coating layer may differ greatly from that of the cotton substrate. As a result, the deformation, fracture, and delamination of the coating layer often occur during use, due to its low mechanical strength, poor adhesion, and limited bonding strength.[6,7]

Antiviral and antibacterial activity

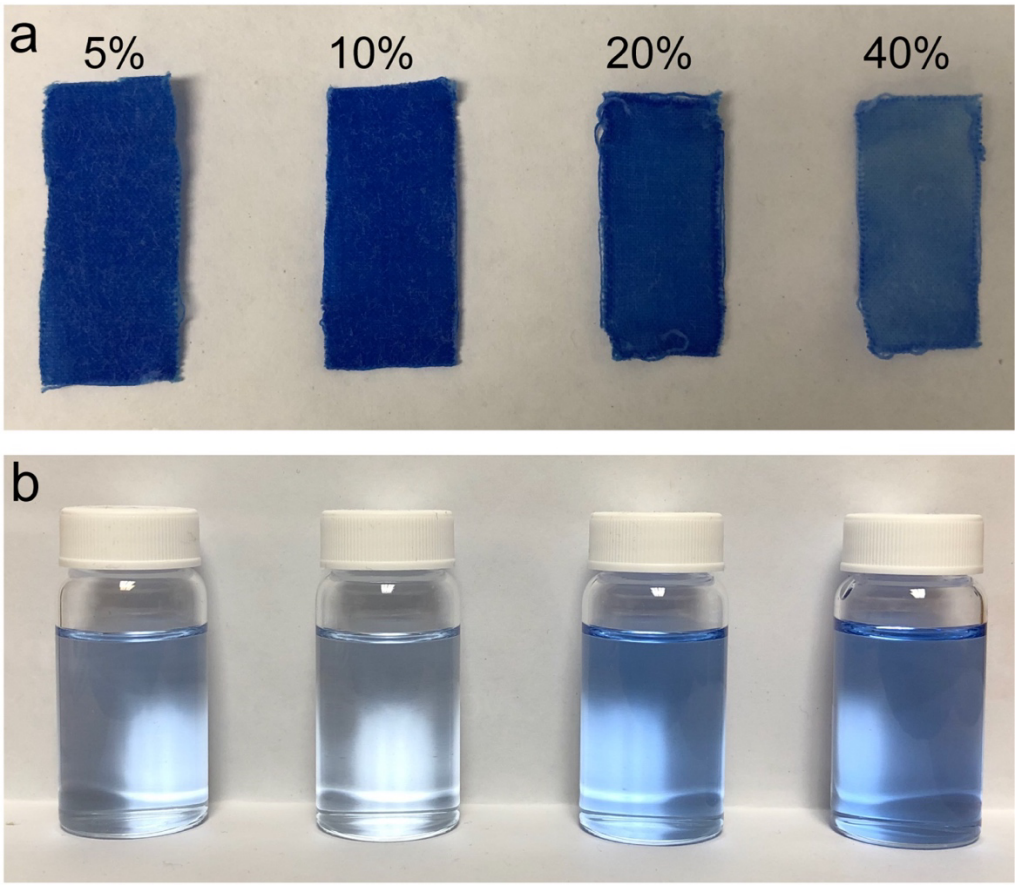
The antiviral and antibacterial activities of the Cu-ITs are attributed to the Cu ions in the cotton textile, based on the same working mechanisms as that of surface-modified cotton textile with Cu species additives; and their efficacies of virus and bacteria-killing are verified (discussed in detail in the main texts).

Supplementary Note 2: Optimization of the NaOH concentration for the fabrication of the Cu-ITs

We prepared four Cu(II)-saturated NaOH aqueous solutions of equal volume but of different NaOH concentrations (5%, 10%, 20% and 40% by weight), in which we soaked four pieces of cotton textile strips of the same size. Photographs of the solutions containing the cotton textiles were taken at different times, as shown in Supplementary Fig. 1. For the samples soaked in the 5% and 10% NaOH solutions, the color of the textiles completely changed to dark blue within one day, while the sample soaked in the 40% NaOH solution still exhibited uneven blue color even after eight days (Supplementary Fig. 2). It is hypothesized that the high concentration of NaOH may overly swell the cellulose matrix, failed in providing the ideal chemical environment for Cu ion coordination. In addition, at lower concentrations (<10%), the NaOH solutions have a viscosity close to that of water (*e.g.*, 1.31 mPa·s and 1.86 mPa·s for the 5% and 10% NaOH solutions, respectively, compared to 1.0 mPa·s for water at 20 ℃); the viscosity is subject to a dramatic increase once the NaOH concentration exceeds ~10%, *e.g.*, for 20 % and 40 % NaOH solutions, the viscosities are 4.4 mPa·s and 38.1 mPa·s, respectively.[8] As a result, the high viscosity may also hamper diffusion of Cu ions. According to thermogravimetric analysis (TGA; Supplementary Fig. 3 and Supplementary Note 3), the sample treated with the 10% NaOH solution has the highest Cu content of ~8.43 wt.%. Therefore, we used the 10% NaOH solution to fabricate the Cu-IT samples.



Supplementary Fig. 1: Visual Inspection on the influence of NaOH concentration and soaking time on the infiltration of Cu(II) ions into the cotton textiles. **(a)** Cu(II)-saturated NaOH aqueous solutions at a NaOH concentration of 5%, 10%, 20% and 40% by weight (from left to right). **(b-h)** cotton textile samples immersed in the solutions over a period of 8 days. For the samples soaked in the 5% and 10% NaOH solutions, the color of the textiles completely changed to dark blue within one day, while the color changes were much slower for the samples soaked in the 20% and 40% NaOH solutions.



Supplementary Fig. 2: Visual inspections on the final results of Cu(II)-saturated NaOH solution treatment (after 8 days of soaking) of cotton textiles. **(a)** cotton textile samples treated using Cu(II)-saturated NaOH solutions at a NaOH concentration of 5%, 10%, 20%, and 40% by weight (from left to right). **(b)** the corresponding residual soaking solutions. The color of the textiles soaked in the 5%, 10%, and 20% NaOH solutions changed to dark blue, while the textile soaked in the 40% NaOH solution exhibited only uneven blue color after eight days. The lighter color of the residual NaOH solutions also indicates that more Cu ions are diffused into the cotton textile in the 5% and 10% solutions.

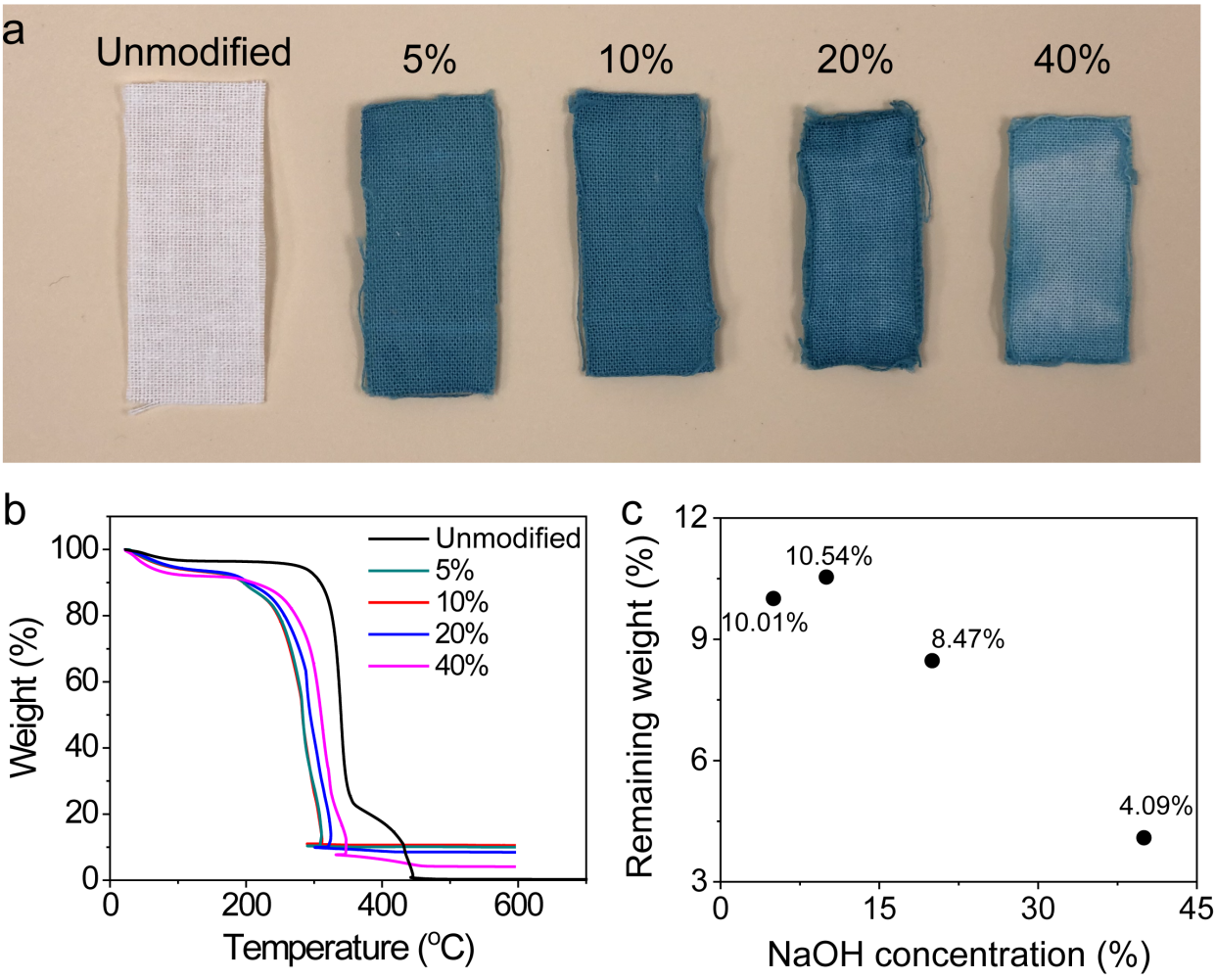
Supplementary Note 3: Cu content determination of the Cu-IT samples based on the thermogravimetric analysis (TGA) results

The TGA tests of the cotton textile samples were performed at a heating rate of 5 °C min^{-1} in air.

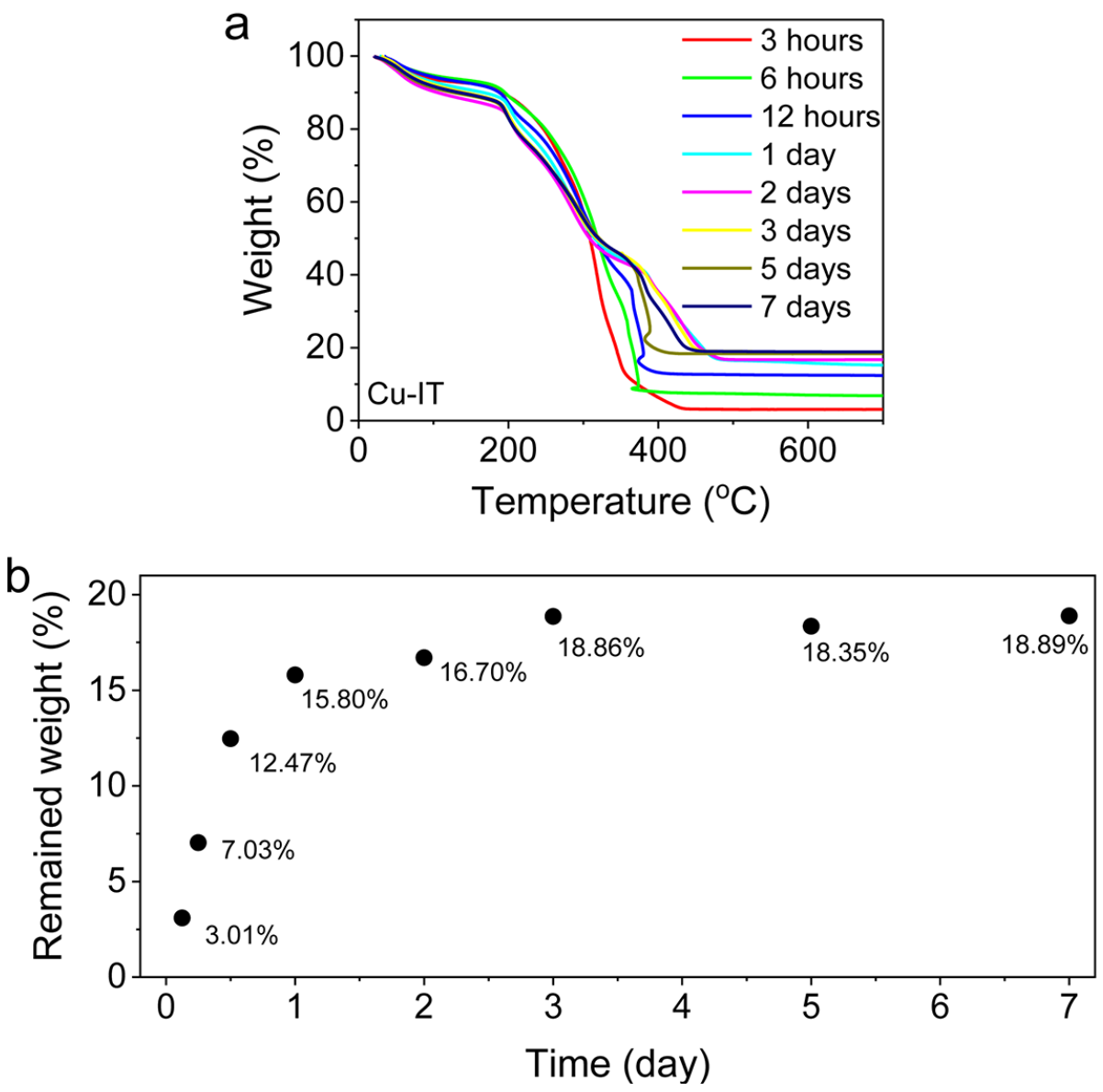
The cellulose molecules are completely decomposed at 450 °C, seen from the TGA trace of the unmodified cotton textile in Supplementary Fig. 3b. For the Cu-IT samples, assuming that the cellulose is completely decomposed and the remaining weight is attributed to the formed CuO, the Cu content can be calculated using the following equation:

$$Copper\ content\ (\%) = \frac{w \times M(Cu)}{M\ (CuO)} = 0.8w,$$

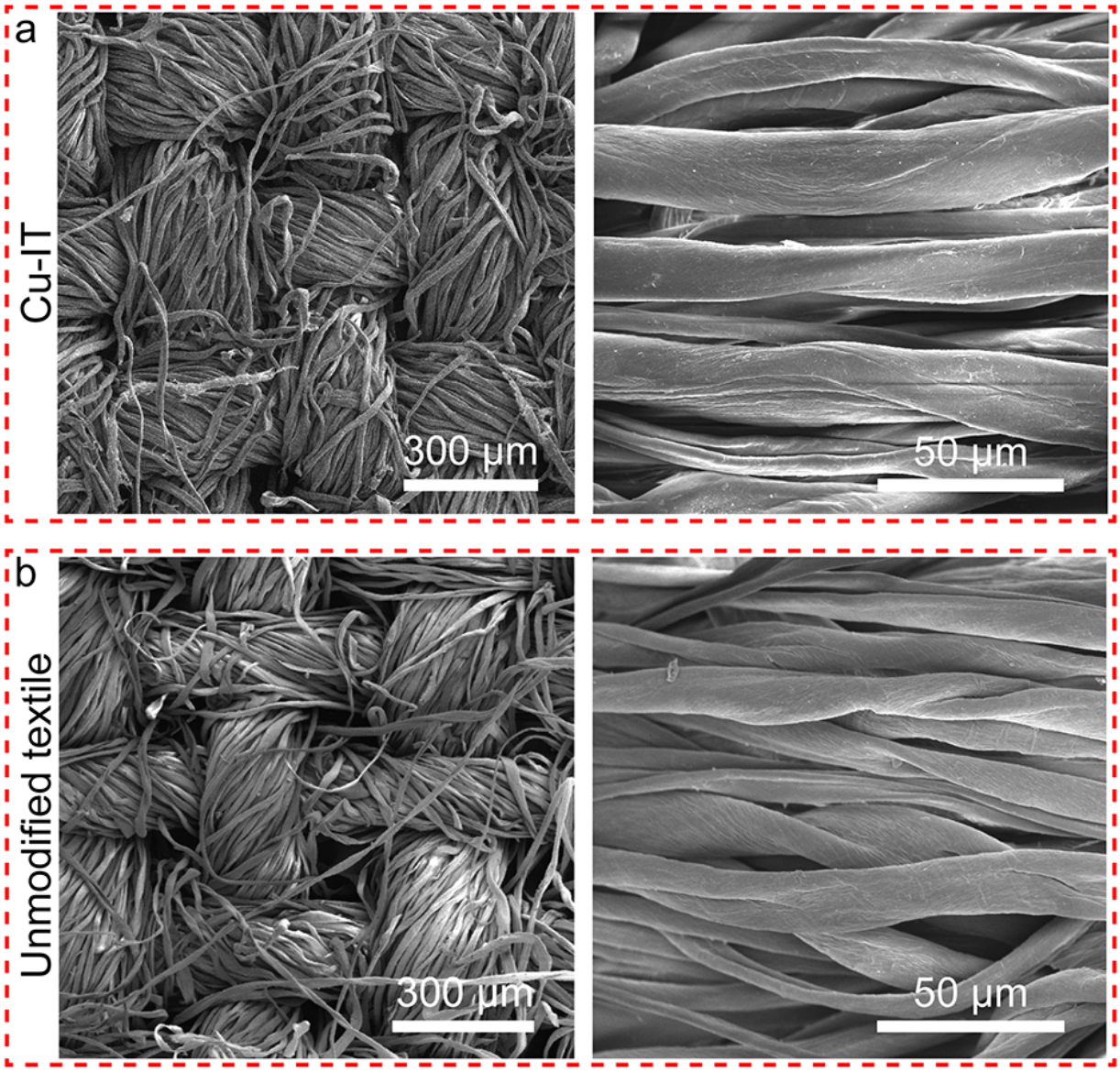
where *w* is the remaining weight percentage (%) after the TGA test, and *M(Cu)* and *M(CuO)* are the molecular weights of Cu and CuO, respectively.



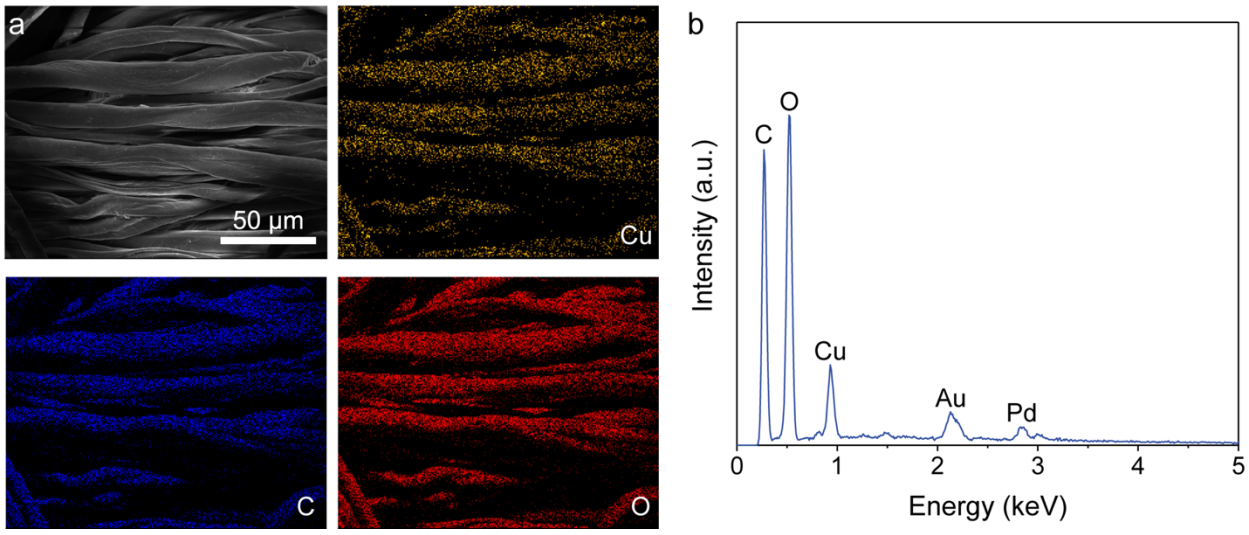
Supplementary Fig. 3: (a) Photographs of the unmodified cotton textile and the Cu-IT samples treated using Cu(II)-saturated NaOH solutions at a NaOH concentration of 5%, 10%, 20% and 40% by weight (from left to right). **(b)** The corresponding TGA traces (at a heating rate of 5 °C min^{-1}). **(c)** The remaining weight of the different Cu-IT samples after the TGA measurements. The cotton textile treated with 10% NaOH solution showed the highest Cu content of ~8.43 wt% (see Supplementary Note 3 for the details of calculating the Cu content).



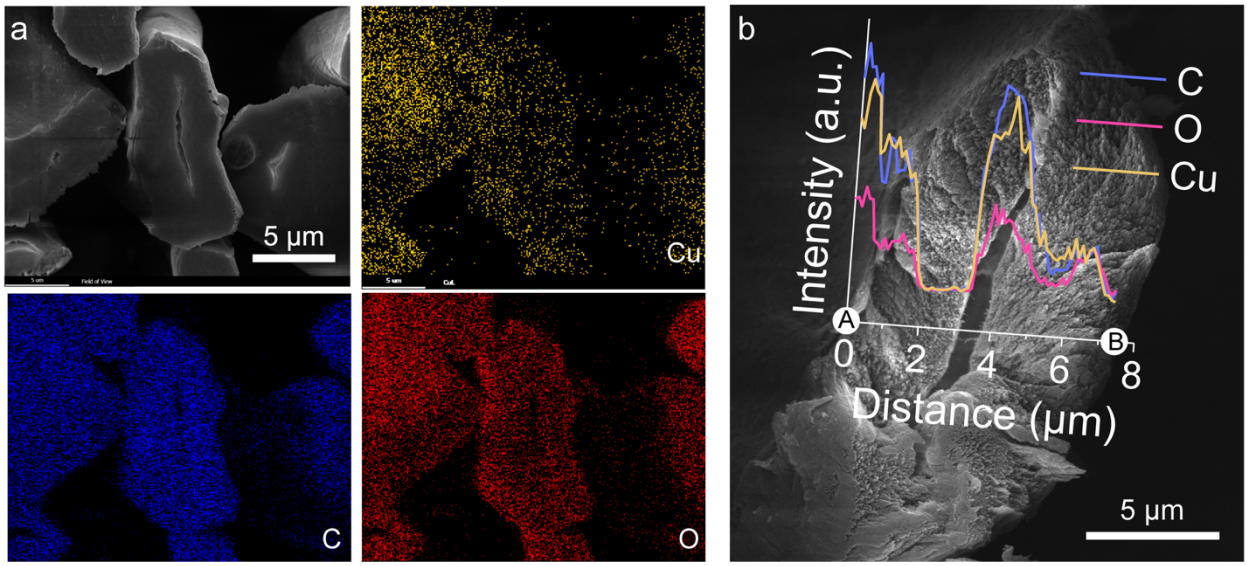
Supplementary Fig. 4: Influence of soaking time on the Cu content of the Cu-IT. **(a)** The TGA traces of the Cu-ITs obtained after being soaked in Cu(II)-saturated NaOH solution for different times (NaOH concentration is 10% by weight). **(b)** the remaining weights in the TGA measurements for the Cu-ITs being soaked for different times. The TGA measurements were performed with an air environment at a heating rate of 5 °C min^{-1}. The Cu content can be calculated after different reaction times (see Supplementary Note 3).



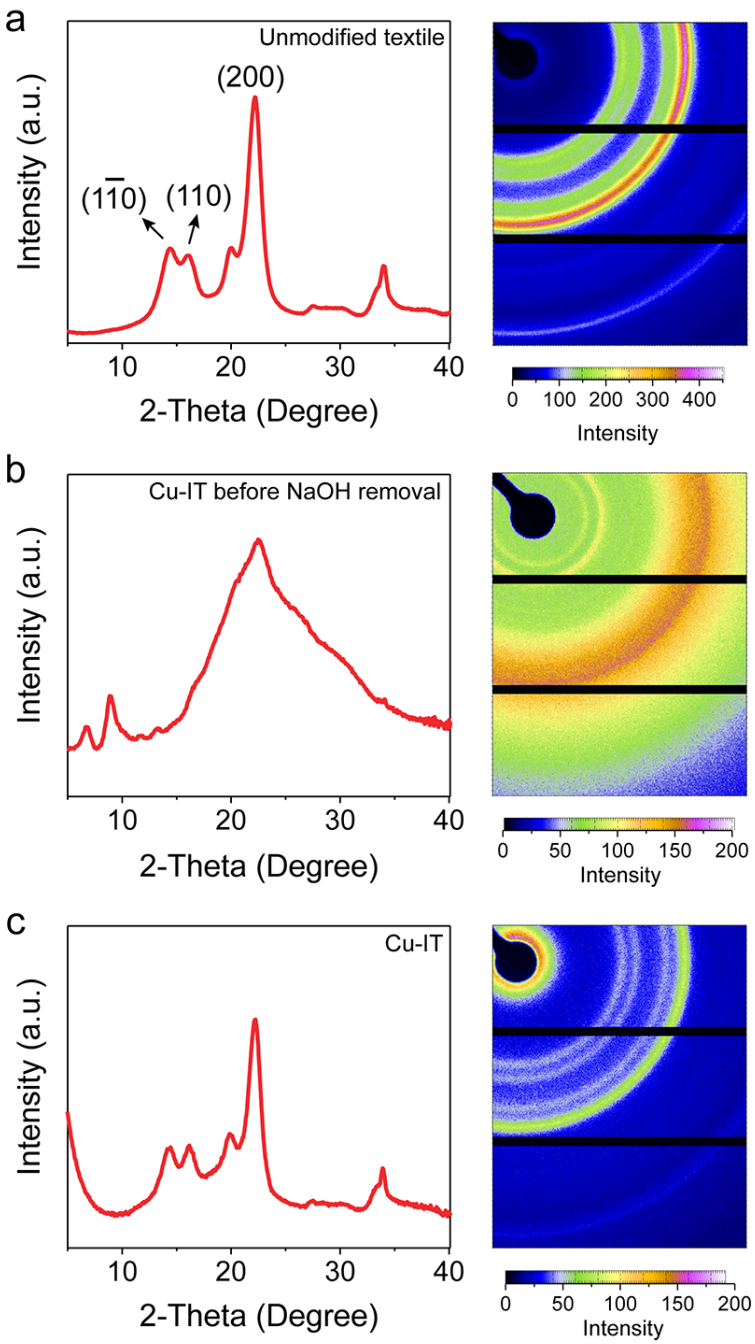
Supplementary Fig. 5: Low and high magnification SEM micrographs of **(a)** Cu-IT and **(b)** unmodified cotton textile.



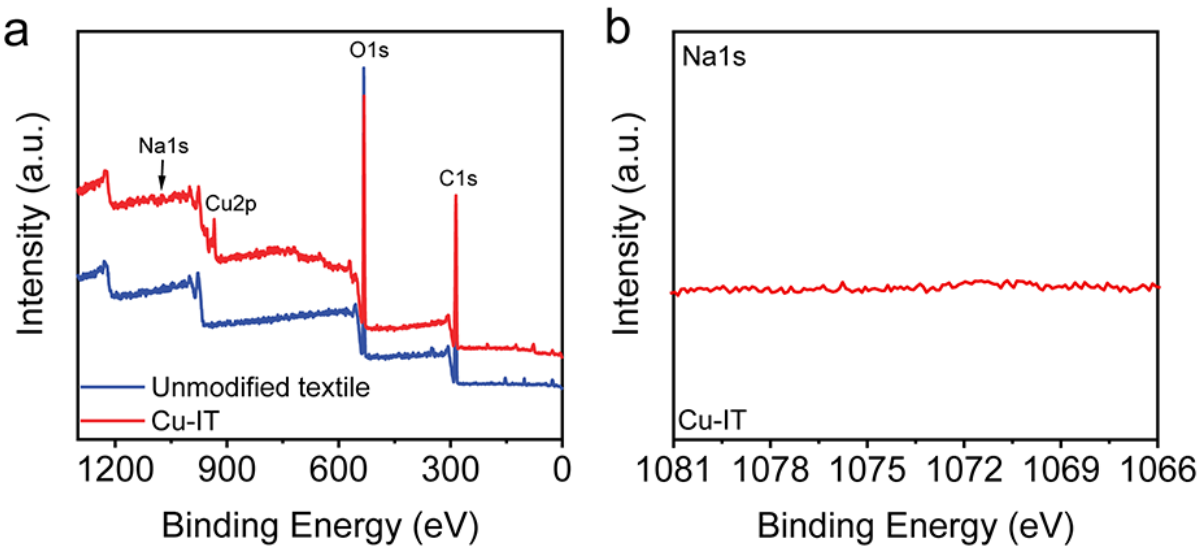
Supplementary Fig. 6: (a) Top-view SEM micrograph of the Cu-IT and the elemental mapping of Cu, C, and O. **(b)** The corresponding EDS spectrum. The EDS elemental mapping confirms the uniform distribution of Cu throughout the cellulose microfibers. Additionally, no Na signal was detected in the EDS spectrum, suggesting that the NaOH was completely removed after washing the textile in water.



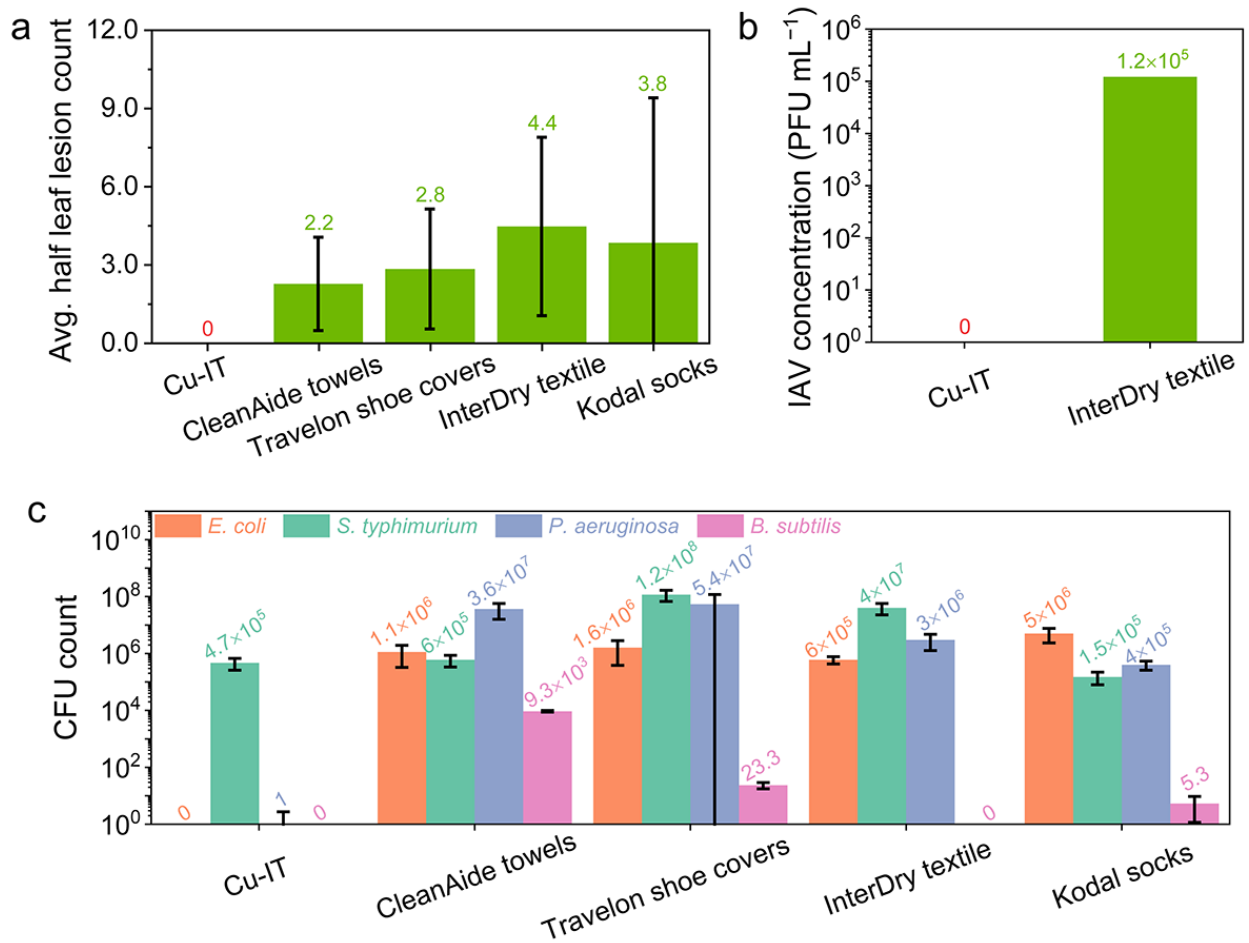
Supplementary Fig. 7: (a) The cross-sectional SEM micrograph of the Cu-IT and the corresponding elemental mapping. **(b)** line scan analysis of the elemental distribution across the Cu-IT fiber. The intensity change of Cu is in accordance with that of C and O, which characterizes an even distribution of Cu throughout the fibers.



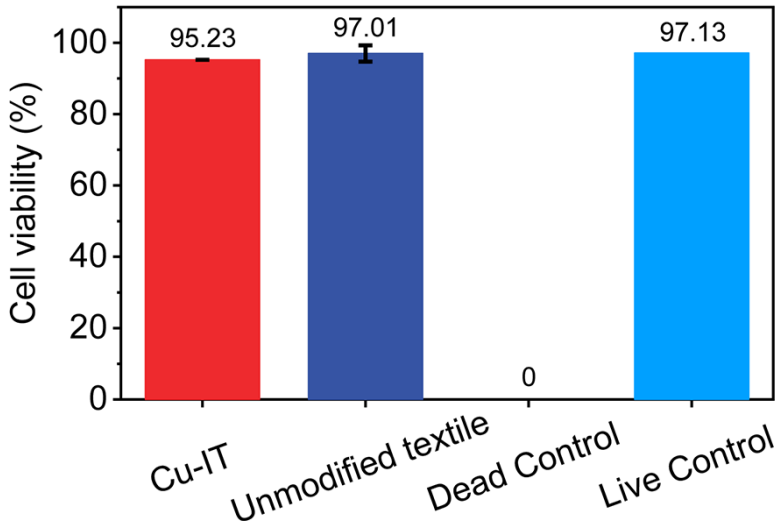
Supplementary Fig. 8: XRD data (left, 1D traces; right, 2D diffraction patterns) of **(a)** unmodified cotton textile, **(b)** cotton textile treated with Cu(II)-saturated 10% NaOH before NaOH removal, and **(c)** Cu-IT. The cotton textile being treated with Cu(II)-saturated 10% NaOH shows the Na-cellulose II(Cu) structure, confirming the formation of cellulose-Cu-NaOH in crystals.[9]



Supplementary Fig. 9: (a) XPS wide scan spectra of unmodified textile and Cu-IT. **(b)** XPS Na1s spectrum region of the Cu-IT. The absence of Na 1s peak confirms that NaOH has been completely removed from the Cu-IT.



Supplementary Fig. 10: Antiviral performance against **(a)** TMV (with an initial concentration of 500 ng mL^{-1} and the treating time of 3 hours) and **(b)** IAV (with an initial concentration of ~3×10^6 PFU mL^{-1}). **(c)** Antibacterial performance against *E. coli*, *S. typhimurium*, *P. aeruginosa*, and *B. subtilis* bacteria of Cu-IT compared to various commercial antimicrobial materials, including the *DSS Coloplast InterDry Textile with Antimicrobial Silver Complex*, *CleanAide Silver Embedded Cleaning Microfiber Towels*, *Travelon Clean-Antimicrobial 4 Shoe Covers-SILVADUR Treated-Gray Heather*, and *Kodal Copper Infused Ankle Socks*. For comparison, the commercial materials were cut to the same size as Cu-IT (16 mm in diameter).



Supplementary Fig. 11: Cell viability of human dermal fibroblasts after incubation with Cu-IT and unmodified textile samples.

We performed a cytotoxicity assessment using artificial perspiration on human dermal fibroblasts to study the biocompatibility of Cu-IT with human skin (Supplementary Fig. 11). We incubated the Cu-IT in artificial perspiration at 37 °C for three hours, then collected the artificial perspiration and applied it to human dermal fibroblasts for an additional three hours. The resulting cell viability of the fibroblasts was 95.23%, which not significantly different than tests using the unmodified textile (97.01%). These results suggest the Cu-IT does elevate cytotoxicity due to ions produced by the textile's contact with human perspiration,

Although these results cannot clearly demonstrate skin biocompatibility of the Cu-IT (i.e., animal studies would be more relevant), we can suggest that the material may have relevance beyond that as a wearable fabric (e.g., wipes, protective devices, etc.).

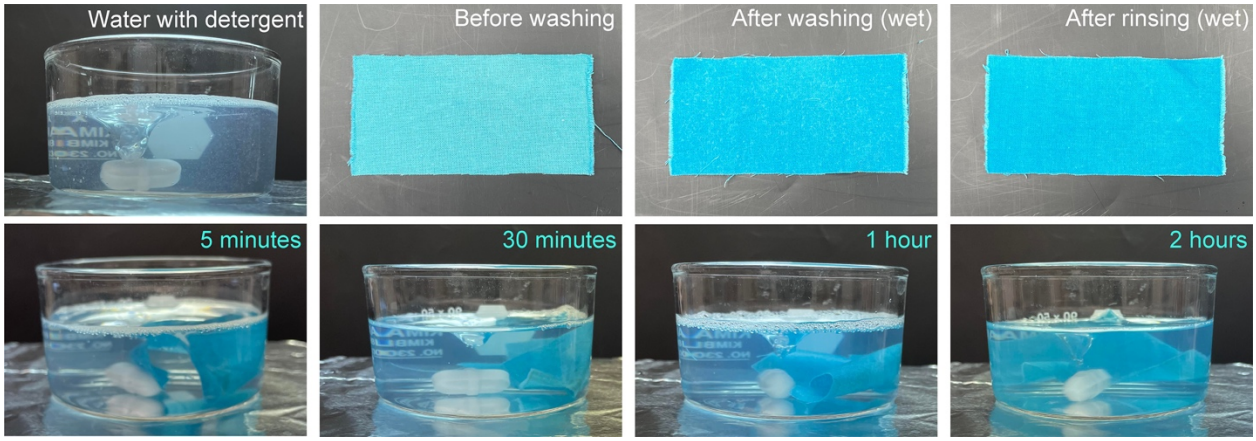
Supplementary Note 4: Measurement of the Cu content during the washing test.

Ironically, it is difficult to collect the wash wastewater from a front-loading, horizontal drum type washing machine. So, we used a modified method instead of the ISO standard for the post-wash Cu content. That is, we simplified the washing tests by extensively "washing" the Cu-IT samples in a vigorously stirred (1000 rpm) water bath, this time with detergent added (Supplementary Fig. 12). Specifically, a piece of Cu-IT with a size of 9 cm × 4.5 cm was immersed into ~200 mL of water with 1 g of detergent. After different washing times, the wastewater was collected and the Cu concentration was measured by ICP-OES (Agilent 725ES) to determine whether the Cu ions migrate from the Cu-IT (Supplementary Fig. 13).

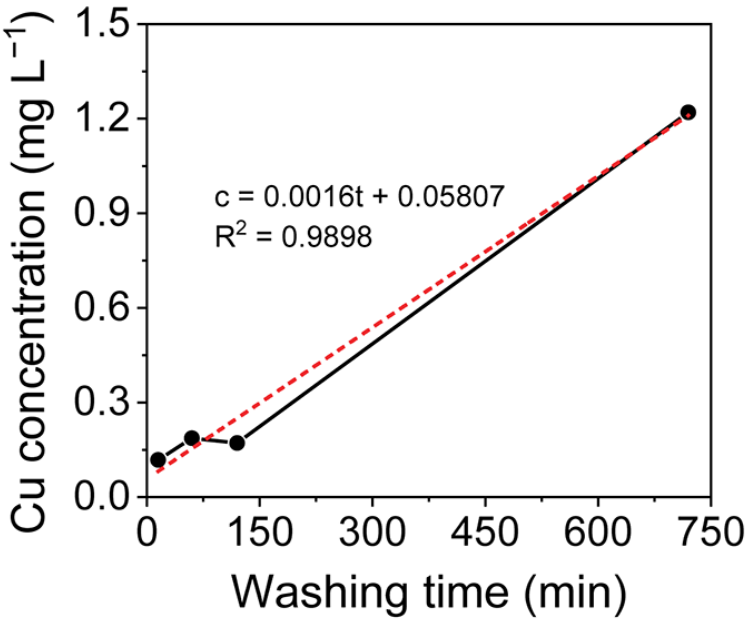
The Cu concentrations (c) in the washing wastewater at different washing times (t = 15, 60, 120, and 720 minutes) are shown in Supplementary Fig. 13, demonstrating a linear (zeroth-order) relationship. We performed a linear fit between the Cu concentration and the washing time to obtain the equation: c (mg/L) = 0.0016t (minute) + 0.05807 (R^2 = 0.9898, Supplementary Fig. 13). With this equation, we decided to "predict" a Cu half-life time ($t_{1/2}$), i.e., the washing time at which the Cu content in Cu-IT decreases to half of its original value, to determine the durability of Cu-IT during washing.

The areal mass density of Cu-IT is weighed and calculated to be ~0.015 g/cm^2 and the Cu content in Cu-IT is ~12.5 wt% according to the TGA measurements, therefore the areal loading of Cu in the Cu-IT sample is ~0.001875 g/cm^2, and the total amount of Cu in the pre-washed Cu-IT sample (size of 9 cm × 4.5 cm) was calculated to be 0.076 g. If the Cu ions were completely leached into the 200 mL of wastewater, the Cu concentration would be 380 mg/L and the concentration at the half-life time ($t_{1/2}$) would be 190 mg/L, then $t_{1/2}$ could be calculated to be ~120,000 minutes based on the above equation. Typically, a wash time for cotton fabrics is 15

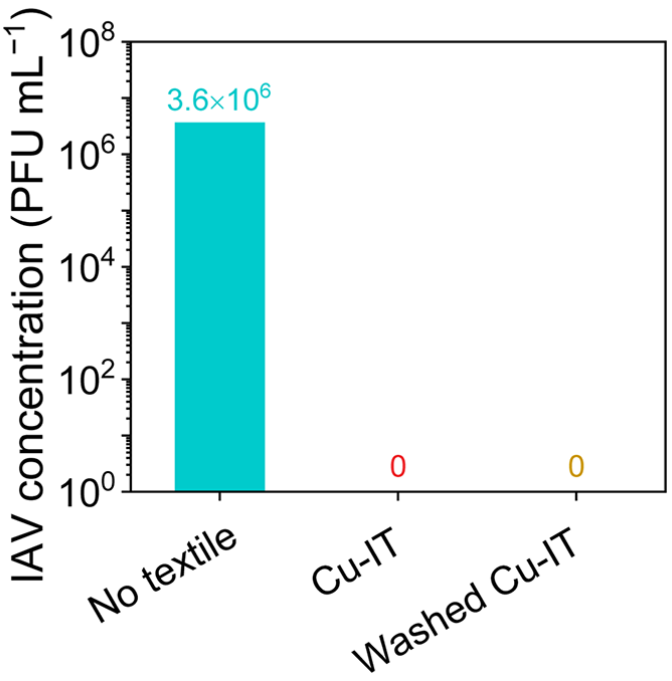
minutes to 1 hour,[10] so we calculated a pseudo longevity for the Cu-IT. That is, we estimated that the Cu-IT should be able to undergo 1,978 to 7,914 wash cycles before reaching the Cu half-life time. We note that this is longer than the typical lifespan for cotton fabric (200 wash and use cycles[11])!



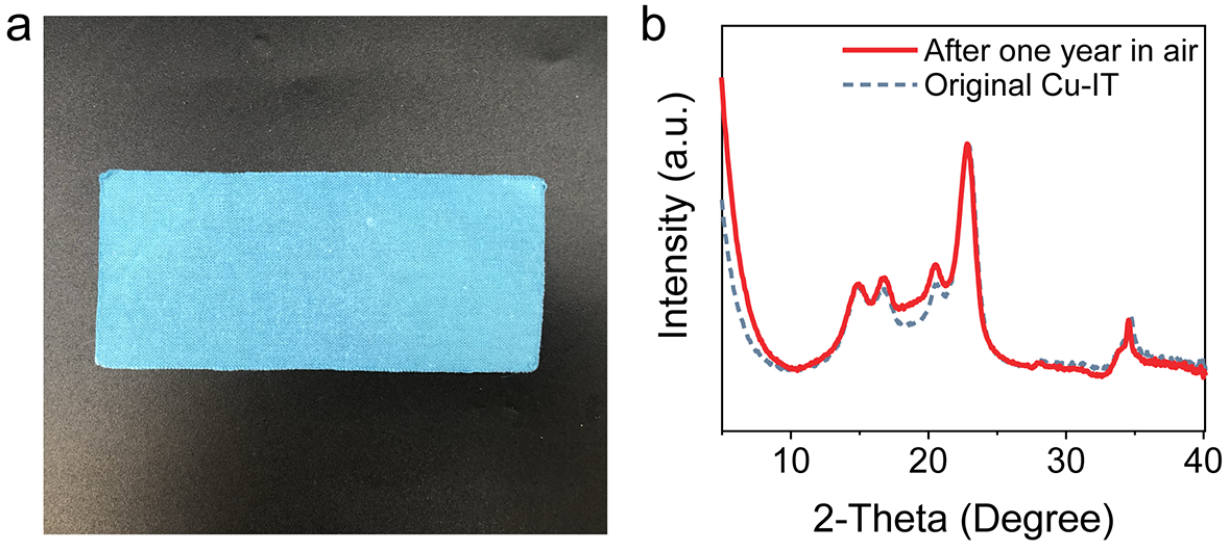
Supplementary Fig. 12: Digital images of the Cu-IT before and after being immersed in water with detergent under vigorous stirring for 2 hours.



Supplementary Fig. 13: ICP-measured Cu concentrations in the wastewater after washing with Cu-IT.

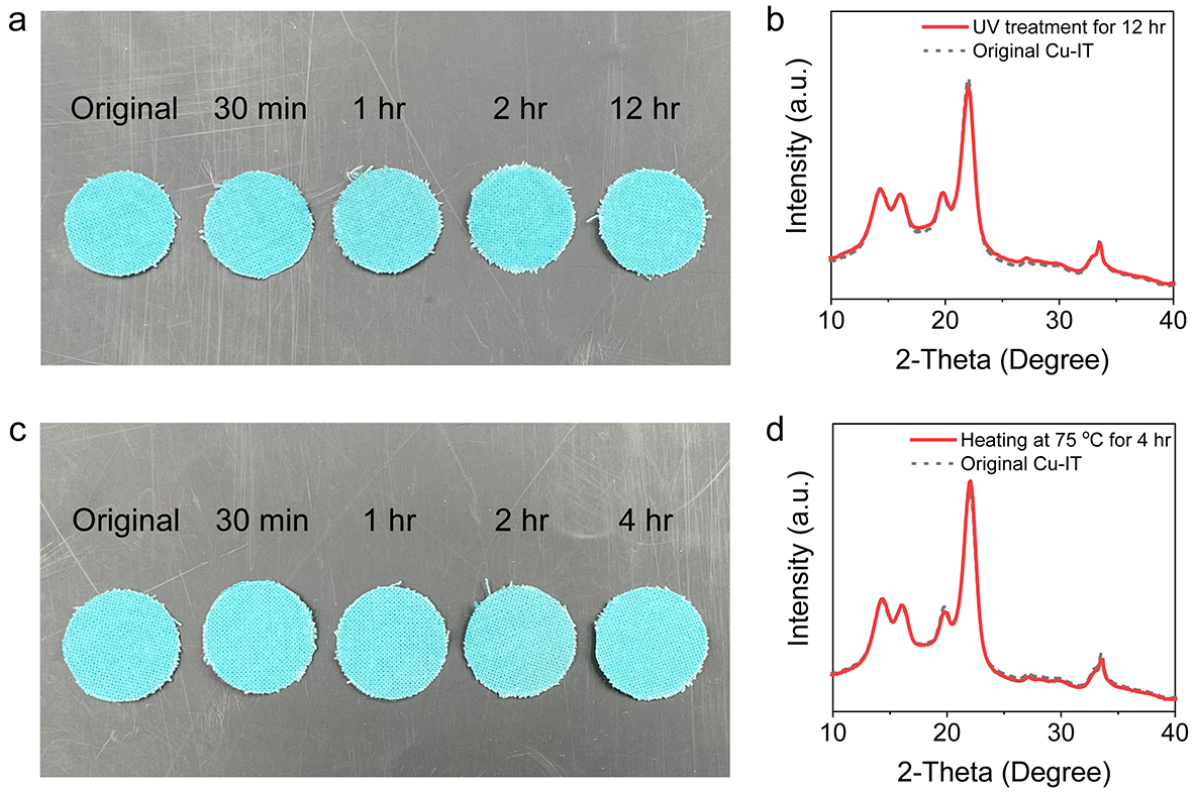


Supplementary Fig. 14: Infectivity of high concentration IAV (3×10^6 PFU mL^{-1}) after incubation with the Cu-IT, before and after 10 washing cycles.



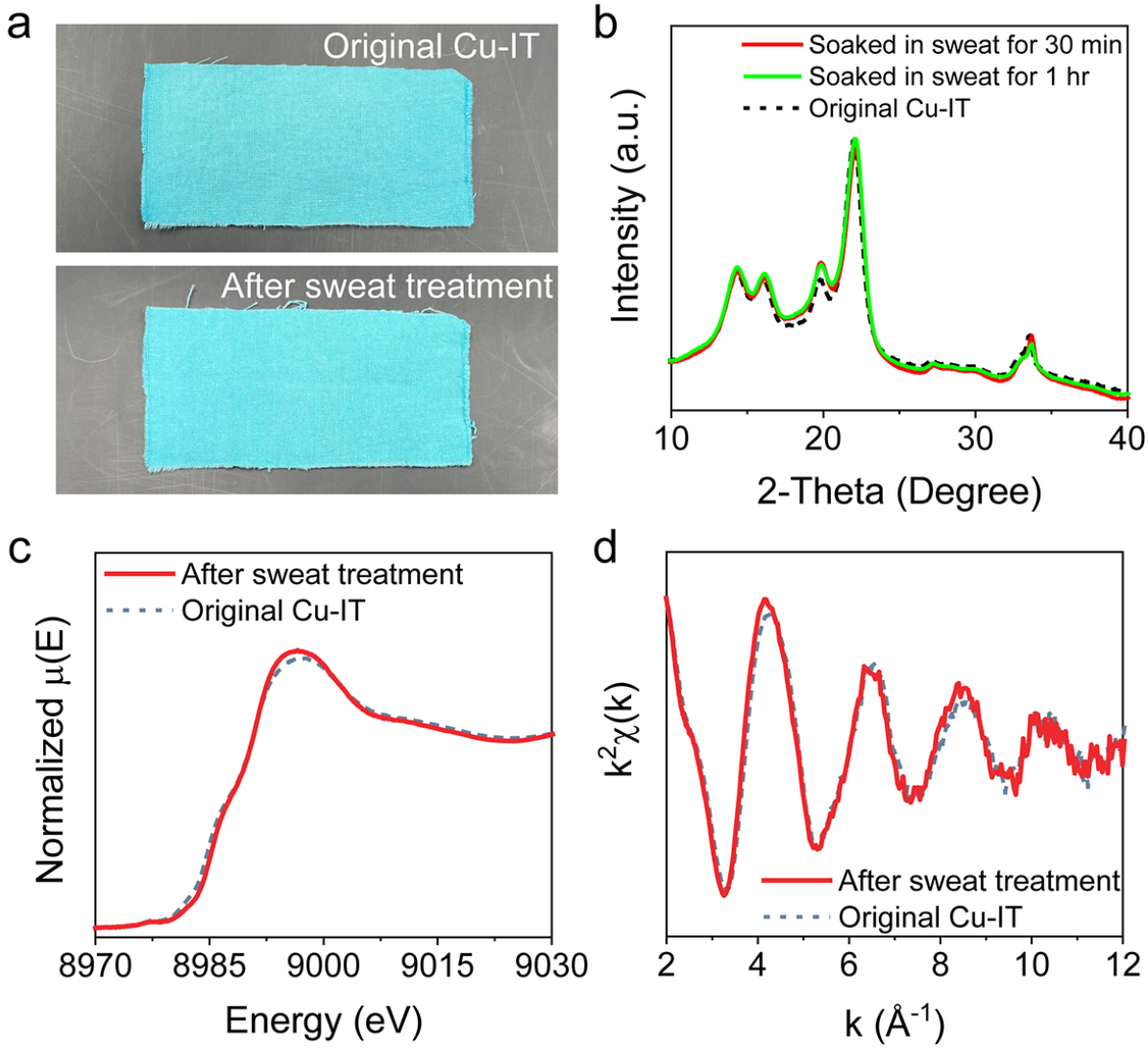
Supplementary Fig. 15: (a) Photograph and **(b)** XRD pattern of the Cu-IT sample being stored in air for over one year.

No apparent changes in the color were observed for the Cu-IT sample being stored in air for over one year. Additionally, the XRD profile of Cu-IT sample being stored in air for over one year is almost identical with that of the original Cu-IT, indicating the excellent stability of Cu-IT under ambient conditions.



Supplementary Fig. 16: (a) Photographs of the Cu-IT samples before and after the UV treatment for different times. **(b)** XRD patterns of the Cu-IT sample after UV treatment for 12 hours. **(c)** Photographs of the Cu-IT samples after heating at 75 °C for different times. **(d)** XRD patterns of the Cu-IT sample after heating at 75 °C for 4 hours.

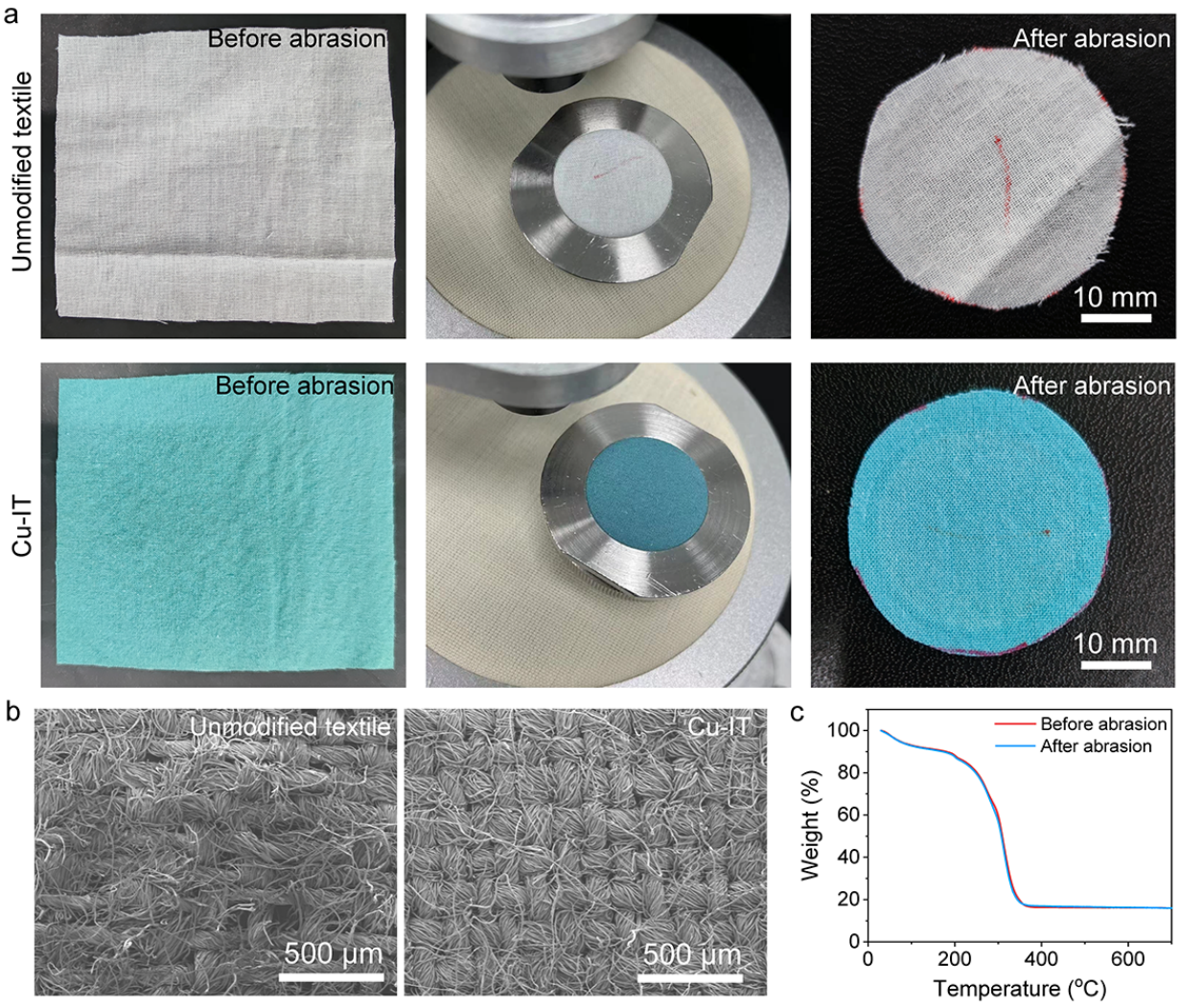
To confirm the UV and thermal stability of the Cu-IT, we placed pieces of Cu-IT under a ultraviolet (UV) lamp and in an oven at 75 °C for different times (the set temperature was higher than the normal temperature of 55 °C used for drying cloth[12]). No apparent changes in the color were observed during the experiments (Supplementary Fig. 16a, c). The X-ray diffraction (XRD) patterns (Supplementary Fig. 16b, d) of the samples after the UV and thermal treatments were also consistent and showed no changes, indicative of no structural changes. These analyses demonstrate the excellent UV and thermal stability of the Cu-IT material.



Supplementary Fig. 17: (a) Photographs of the Cu-IT samples before and after treatment with artificial sweat for 1 hour. **(b)** XRD patterns of the Cu-IT samples after being soaked in sweat for 30 minutes and 1 hour. **(c)** The Cu K-edge XANES and **(d)** EXAFS spectrum of the Cu-IT samples after being soaked in sweat for 1 hour.

We observed no apparent changes in color of the Cu-IT samples after the sweat treatment (Supplementary Fig. 17a). The XRD patterns of the samples after the sweat treatments were also consistent and showed no changes (Supplementary Fig. 17b), indicative of no structural changes.

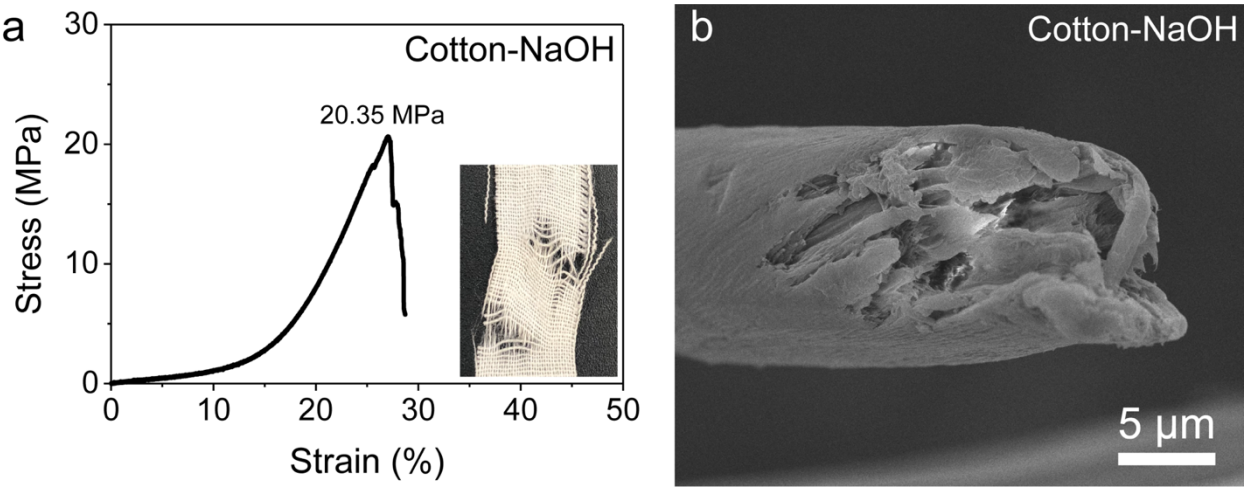
To study the effects of the sweat treatment on the Cu coordination structure of Cu-IT, we performed X-ray absorption spectroscopy (XAS) measurements on the Cu-IT samples after treatment (Supplementary Fig. 17c, d and Supplementary Table 2). The Cu K-edge X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra of the Cu-IT before and after the treatment were almost identical, verifying the stable Cu coordination structure in Cu-IT against sweat.



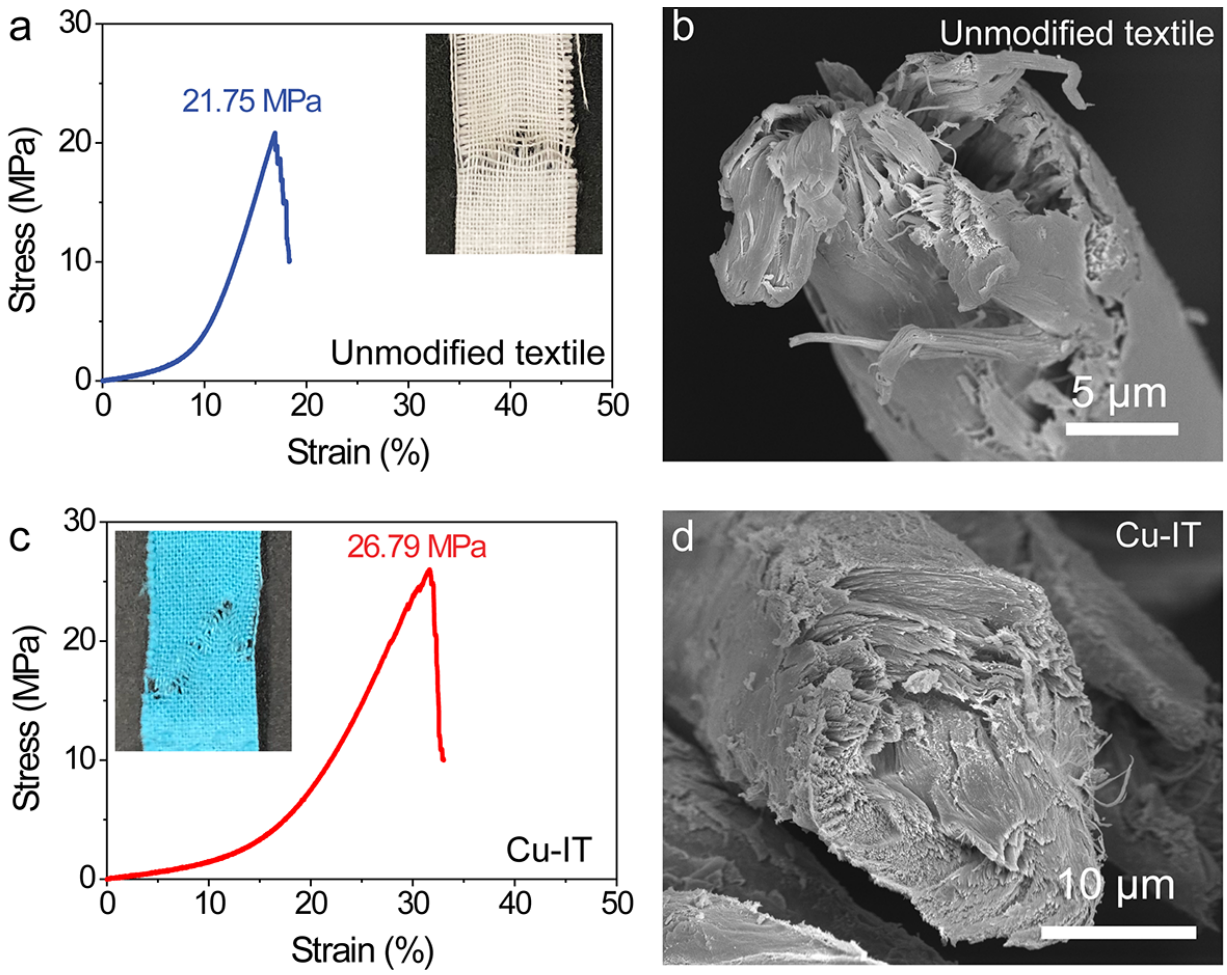
Supplementary Fig. 18: Abrasion resistance testing results of the Cu-IT and unmodified textile. **(a)** Photographs of the samples before and after abrasion. **(b)** SEM micrographs of the Cu-IT and unmodified textile after abrasion. **(c)** The TGA curves of the Cu-IT sample before and after abrasion.

After the abrasion tests, no apparent damage was observed in the Cu-IT (Supplementary Fig. 18a). In contrast, some parts were worn and broken in the unmodified textile. SEM images of the unmodified textile and Cu-IT after abrasion (Supplementary Fig. 18b) show that increasing deflection of the fibers occurred in the unmodified textile during the continuous rubbing process

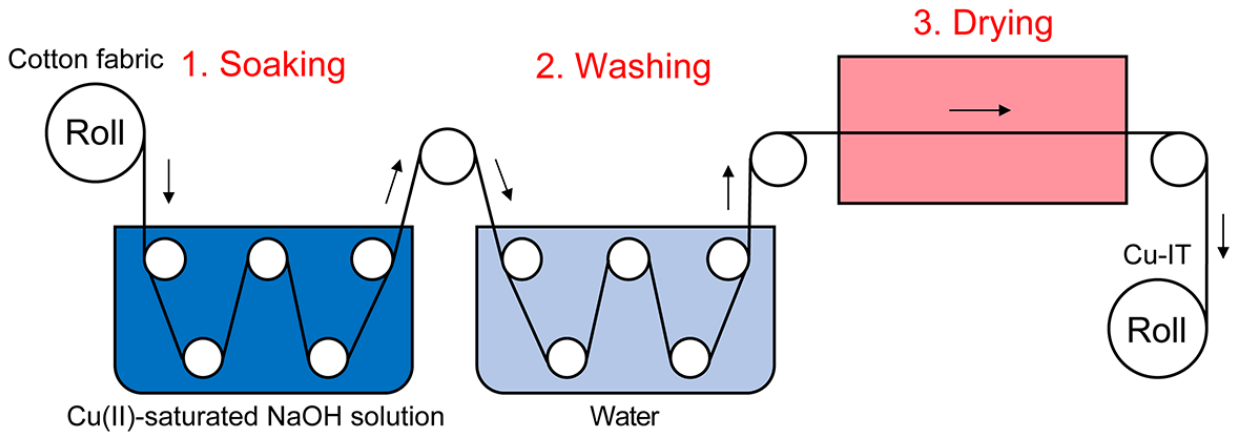
and finally led to a rupture of the fibers, while no rupture occurred in the Cu-IT sample. These results confirmed the enhanced abrasion resistance of Cu-IT. Furthermore, we performed TGA measurements on the Cu-IT samples before and after abrasion (Supplementary Fig. 18c). The TGA curves overlapped, indicative of the even distribution of Cu ions throughout the fibers in the Cu-IT, even after abrasion.



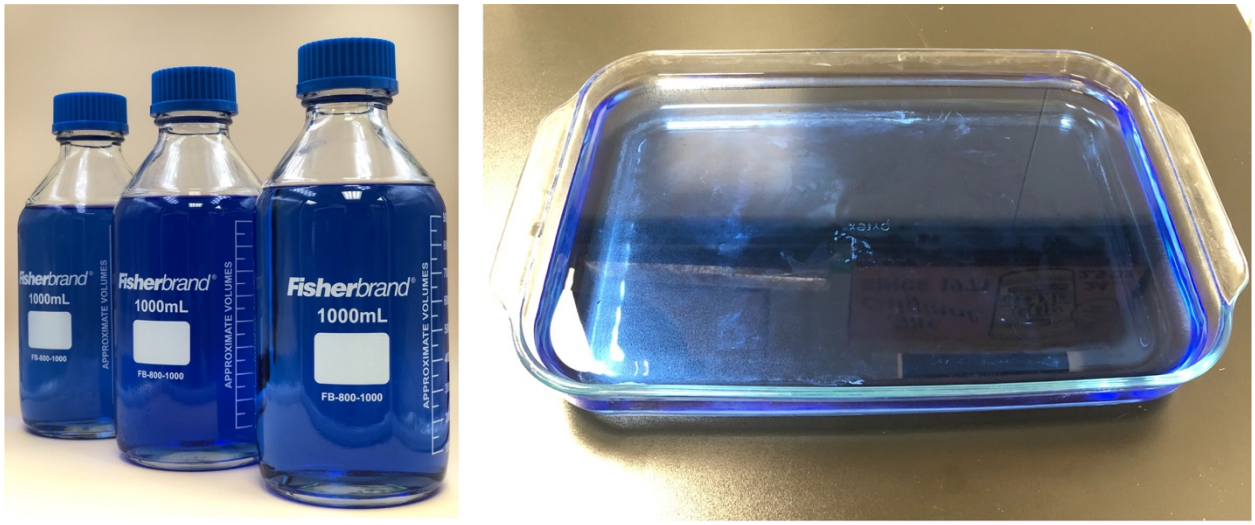
Supplementary Fig. 19: (a) Tensile stress-strain curves of the unmodified textile after being soaked in 10% NaOH solution for three days, followed by a wash to remove NaOH (Cotton-NaOH). The inset shows a photograph of the sample after the tensile tests. **(b)** SEM micrograph of the corresponding fracture surface. The textile treated in NaOH solution shows a strength of 20.35 MPa, lower than that of the unmodified cotton textile (21.75 MPa), which is attributed to the depolymerization of cellulose polymer under alkaline conditions.[13,14] The fracture surface of the Cotton-NaOH sample is loose, showing characteristics of a typical fibrillar fracture.[15,16]



Supplementary Fig. 20: Tensile stress–strain curves (left) and SEM micrographs (right) of the fracture surfaces of the **(a, b)** unmodified textile and **(c, d)** Cu-IT, respectively. The fracture area of the Cu-IT is compact, differing from that of the unmodified textile that shows a loose morphology.



Supplementary Fig. 21: Continuous roll-to-roll manufacturing schematic of Cu-IT. The process involves simple soaking of the cotton fabric in the Cu(II)-saturated NaOH solution, followed by washing and drying. The compatibility of Cu-IT with roll-to-roll manufacturing suggests its potential for large-scale production.



Supplementary Fig. 22: Cu(II)-saturated NaOH solution (at a NaOH concentration of 10 wt%). As an example, 3 L of Cu(II)-saturated NaOH solution can be prepared within 1 day. The process is easy to scale up and NaOH can be recycled from the waste solution (Fig. 5a).

Supplementary Table:

Supplementary Table 1: Cu (II) acetate standard fitting parameters**.**

Scattering Path	S_o^2	CN (+/- 10%)	R (Å) (+/- 0.02 Å)	σ^2	E_0 shift (eV)
Cu-O	0.77	4.2	1.93	0.005	-0.4

Supplementary Table 2: Structural parameters of the Cu-IT samples obtained by fitting the EXAFS data.

Samples	CN (+/- 10%)	R (Å) (+/- 0.02 Å)	σ^2	E_0 shift (eV)
Original Cu-IT	4.0	1.93	0.005	-0.5
After washing	4.0	1.93	0.005	-0.5
After sweat treatment	4.0	1.93	0.005	-0.5

The quantitative EXAFS fitting results are given above in Supplementary Tables 1-2. The Cu (II) acetate standard has 4 Cu-O coordination at a bond distance of 1.93 Å. The Cu textile samples were fit using a scattering path generated based on the Cu (II) acetate standard. Using this method, all of the Cu textile samples have the same quantitative local coordination: a Cu-O coordination number of 4 at a bond distance of 1.93 Å.

σ^2, known as the Debye-Waller factor, is a parameter of structural disorder in the EXAFS equation. The Cu (II) acetate has a σ^2 value of 0.005, which is the same for all the Cu-IT samples. This value is characteristic of light atom scattering paths, such as Cu-O coordination. The amplitude reduction factor, denoted as S_0^2, is an adjustment made to account for the fact that the initial state and the final state of the X-ray absorbing are not the same, and the value is determined from the Cu (II) acetate reference compound.

Supplementary Table 3: Inhibitory effect of Cu-IT on IAV evaluated using a focus assay: infectivity of low (3×10^4 PFU mL^{-1}) and high (3×10^6 PFU mL^{-1}) concentration IAV after incubation with original and washed Cu-IT.

IAV FFU/mL	No textile (virus only)	Original Cu-IT	Washed Cu-IT
High concentration IAV	2.1×10^6	0	0
Low concentration IAV	2.0×10^4	0	0

Supplementary Reference:

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