Electronic Supplementary Material (ESI) for Chemical Communications.

A simple, scalable, eco-friendly and ultralow-temperature approach to forming Al2O3 water-repellent cotton coatings via UV photo-annealing.

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Supporting Information - Table of Contents

1. Experimental Details

1.1 General

The UV-absorbance of the aluminum precursors was measured using an Agilent Technologies Cary 60 UV-Vis photospectrometer measuring from 190 nm – 800 nm. Surface morphology images and composition were determined by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (SEM-EDS) using a ThermoFisher Helios Hydra Plasma FIB. To determine surface roughness of samples, atomic force microscopy (AFM) images were collected using a Bruker Dimension Icon atomic force microscope equipped with FastScan scanning 2 μm^2 areas of individual sample fibers. The wettability of the samples was determined by collecting images on a First Ten Angstroms FTA135 Contact Angle Analyzer. 10 µL of DI water was dropped onto the samples and images were collected on multiple spots of each sample. Images were processed using ImageJ contact angle plugin to determine water contact angle. Elemental composition of the prepared samples was investigated using X-ray photoelectron spectroscopy (XPS). Measurements were performed on a Thermo Scientific ESCALAB 250 spectrometer using a monochromated Al Kα X-ray source (150 W, 20 eV pass energy, 500 µm spot size). Peak fitting was done using ThermoScientific Avantage 4.75 software. A smart background subtraction was used for analysis and spectra were referenced to the C 1s hydrocarbon peak at 284.8 eV. Elemental ratios reported in this manuscript are the average of multiple spots measured across the same sample.

1.2 Preparation of f-Al_{13} and $Al(NO_3)_3 \bullet 9H_2O$ precursor solutions

The f-Al_{13} cluster $[Al_{13}(\mu\text{-}OH)_{24}(H_2O)_{24}](NO_3)_{15}$ was prepared using a previously published method.[1] In this simple precipitation method, $Al(NO_3)_3 \bullet 9H_2O$ (Acros Organics) and zinc metal powder (Sigma-Aldrich) were dissolved in nanopure water (ρ=18.2 MΩ cm) and filtered. The cluster then precipitated out of the filtrate solution as an amorphous white solid that was filtered, washed with isopropyl alcohol, and collected.

1.3 Preparation of UV-annealed textile coatings

A 10 mM precursor solution of the f-Al_{13} cluster was made in an acetone/water mixture (5:1 ratio by volume) and filtered through a 0.45 micron filter. For comparative studies, analogous $Al(NO_3)_3 \bullet 9H_2O$ solutions were prepared containing the equivalent aluminum concentration (130 mM). The precursor solutions were then drop casted or spray casted onto 2 x 2 cm square pieces of native cotton fabric using a Master G233 Pro Set airbrush with N_2 flow.

Once samples were coated with precursor solution, they were photo-annealed using a Novascan PSD Pro Series digital UV ozone system equipped with a mercury grid lamp emitting at 253.7 nm (90%) and 184.9 nm (10%). Samples were placed in the UV chamber, purged under N_2 atmosphere for 10 minutes and then subjected to 2 hours of UV treatment at ambient temperature. Radiant heat from the lamp increased the temperature to 30 °C. Samples that were thermally annealed were placed on a hot plate and heated at 120 °C for 1 hour. The

prepared samples are labeled based on the precursor used and the relative post treatment. For instance, a native cotton sample treated with the f-Al_{13} cluster precursor solution and post annealed using UV light and thermal will be labeled as "Al_{13}-UV/Thermal".

It is important to note that the coatings were annealed with a lower powered mercury lamp (7–8 mW cm^{-2}). It is likely this process can be significantly optimized through the use of a high-powered lamp that generates more ambient heat. Therefore, when considering the potential for scaling up this process, the use of external thermal energy may not be necessary as a high-powered lamp would alleviate the need for extra heating.

2. Characterization Data

2.1 UV-Vis Absorbance

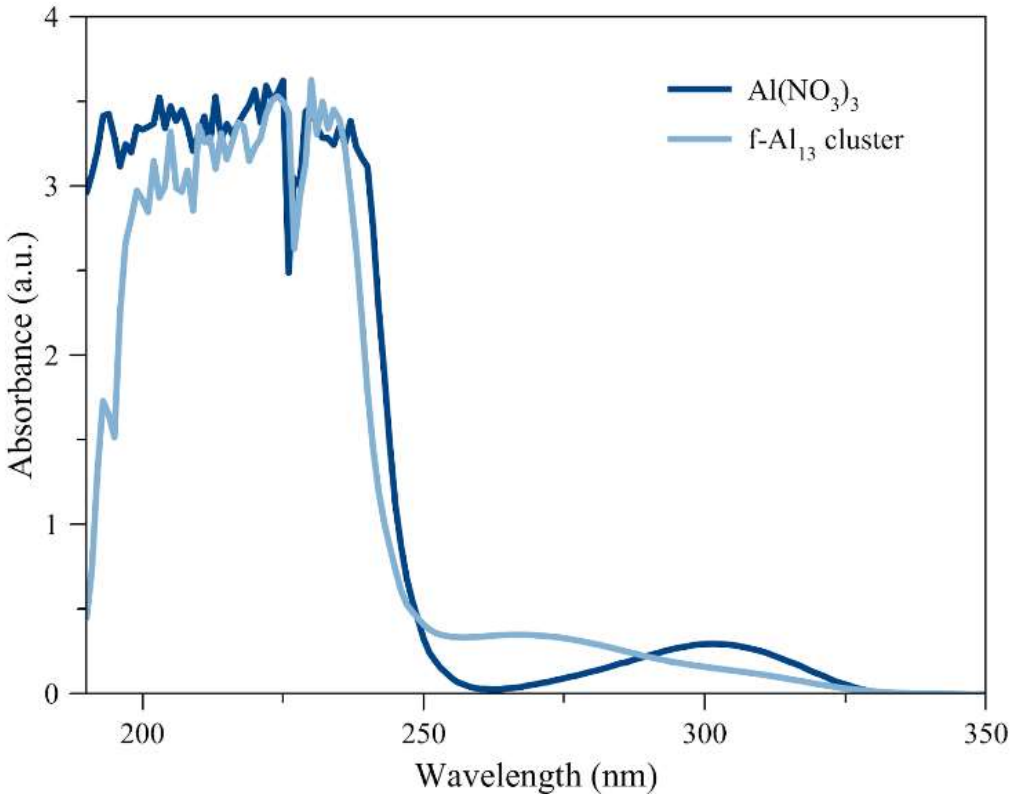

Figure S1 UV absorbance spectra of $Al(NO_3)_3 \bullet 9H_2O$ and f-Al_{13} cluster in nanopure H_2O.

2.2 Water Contact Angles

Table S1 Water contact angle measurements of native and Al_2O_3 coated cotton.

Sample	WCA (°)
Native Cotton	**< 10**
Al_{13} – UV	**122.3**
$Al(NO_3)_3$ – UV	**118.1**
Al_{13} – UV/Thermal	**140.2**
$Al(NO_3)_3$ – UV/Thermal	**127.2**

2.3 SEM Imaging

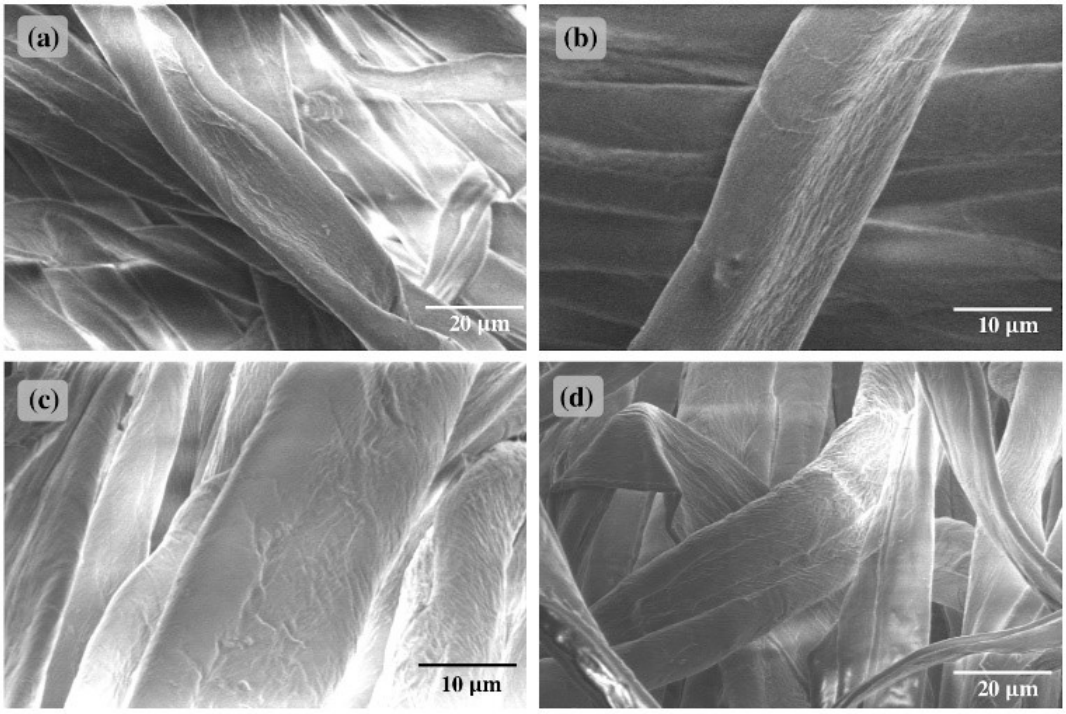

Figure S2 (a) SEM images of native cotton, and (b) Al_{13}-UV, (c) $Al(NO_3)_3$-UV , and (d) Al_{13}-UV/thermal.

Figure S2a shows an SEM image of the native cotton and the inherent striations of the cellulose fibers can be discerned. In Figure S2b, the fiber is coated with Al_2O_3 from the f-Al_{13} cluster solution and the striations can still be discerned, indicating a relatively thin and uniform Al_2O_3 coating on the individual fibers. However, the fibers coated from the $Al(NO_3)_3$ precursor

solution in Figure S2c appear significantly rougher, which is likely due the increased number of nitrate counterions that have to burn off which leads to a rougher coating with more morphological defects.

2.4 Atomic Force Microscopy

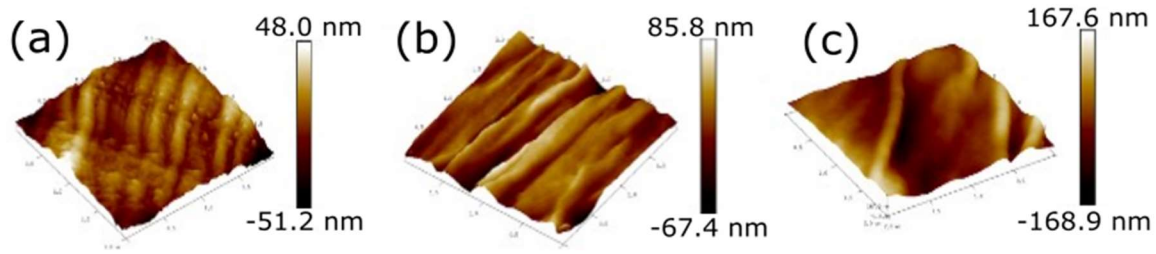

Figure S3 (a) 2 μm^2 AFM scans of native cotton, (b) Al_{13}-UV and (c) $Al(NO_3)_3$ – UV.

[1] W. Wang, K. M. Wentz, S. E. Hayes, D. W. Johnson, D. A. Keszler, *Inorg. Chem.* 2011, 50 (11), 4683–4685.