ZnO Microstructures as Flame-Retardant Coatings on Cotton Fabrics

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Supporting Information

ABSTRACT: In this study, we report a unique strategy that utilizes ZnO and ZnS microparticles and rods as fire-retardant materials when coated onto cotton fabrics. ZnO and ZnO/ZnS microparticles or rods were grown or adsorbed to the surface of cotton fibers. Properties such as heat release rate, total smoke release, and mass loss rate of the materials were tested using a cone calorimeter. ZnO and ZnO/ZnS rods were able to reduce the heat release rate and total smoke release from 118 kW/m² and 18.3 m²/m² to about 70.0 kW/m² and 6.00 m²/m², respectively. The maximum average rate of heat emission and fire growth rate index, which is used to evaluate the fire spread rate, the size of the fire, and the propensity of fire development, were improved with these coatings and indicate that there are potential applications of these materials as fire retardants.

INTRODUCTION

Cotton fabrics have played an important role in the manufacturing of clothing and furniture in the military and civilian sectors because of their desirable properties such as biodegradability, water absorbency, breathability, and the vast availability of raw materials for large-scale production.1,2 Cotton fabrics, however, can be easily ignited and pose a high risk for fires because cellulose fibers have a low limiting oxygen index, a low onset ignition temperature (360−425 °C), and provide a rich source of hydrocarbon fuels during combustion, which makes these materials highly flammable.3−5 According to recent statistics, fires cause approximately 1.3 million accidents annually, which result in more than 3000 deaths, 15,000 injuries, and an estimated $11.6 billion in direct property losses.8 Home fires, where the main fire hazard is the combustion of textiles, are responsible for 80% of civilian fire deaths.9

The most widely used flame-retardant strategy for cotton fabrics consists of weaving or coating the cellulose fibers with a flame-retardant polymer or compound to form a composite material.8,10−16 Cotton fabrics can be directly coated with halogenated, nitrogen-containing or phosphorus-containing additives to improve their fire-resistant properties, but many of these compounds are limited in use because of their demonstrated toxicity. Halogenated flame retardants react with oxygen or hydroxyl radicals in the gas phase to effectively interrupt combustion.6 However, toxic species released from the combustion of halogenated flame retardants are hazardous to human health and to the environment.17−20 Because of these concerns, the use of halogenated flame-retardant materials has been rigorously restricted.21−23 In addition to the gas-phase flame-retardant mechanism, nitrogen- and phosphorus-containing compounds also exhibit flame-retardant action in the condensed phase, which is attributed to the formation of a ceramic-like char during thermal degradation, which provides a layer of insulation to the underlying polymer.24 Char-forming compounds such as ammonium polyphosphate, tetrakis(4-hydroxyethyl) phosphonium chloride, sodium hypophosphite (SHP), and spirocyclic pentaerythritol diphosphoryl chloride have been widely used as effective and durable flame-retardant coatings for cotton fabrics.25,26 Nevertheless, studies suggest that phosphorus-containing compounds produce large amounts of smoke, may be toxic, potential mutagens, or pose unwanted risks to human health and the environment.27−30 New flame-retardant strategies are based on incorporating insulating inorganic materials into cotton fabrics, a strategy that mimics the formation of a char layer of nitrogen- and phosphorous-containing compounds. Silicate nanoclays and

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ZnO nanoparticles have been introduced into phosphorus-based polymeric flame retardants using the sol–gel method, dual-cure processes, and layer-by-layer assembly. Lam and co-workers combined N-methylol dimethylphosphono propionamide with nano- and microscale ZnO particles and showed that ZnO can act as a cocatalyst to promote the formation of a char layer to enhance the flame-retardant action of cotton fabrics. Sharaf’s group also observed improved flame retardancy when they combined nano-ZnO with polycarboxylic acids and SHP with cotton fabrics.

On the basis of these promising reports and the work previously performed by our co-workers, we investigated the combustion properties of cotton treated with spherical and rod-shaped particles of ZnO and ZnS as potential fire retardants using cone calorimetry. To the best of our knowledge, no studies have investigated the flame-retardant properties of these ZnO-based coatings on cotton surfaces alone without the aid of other, usually harmful, flame-retardant additives. The designed Zn-based microparticle coatings were expected to act as a protective layer of insulation and as a smoke suppressant because zinc salts have been shown to reduce the production of smoke during burning. ZnO and ZnO/ZnS rods were grown on cotton fabrics using a hydrothermal method previously published by our group. In this paper, we show that even loosely adsorbed spherical microparticles of ZnO and ZnS can reduce the heat release rate (HRR) when coated on cotton fabrics independent of an organic flame retardant. We also show that the uniform protective coating of ZnO and ZnO/ZnS rods on the cotton surface results in a lower peak HRR (PkHRR), a lower fire growth rate (FIGRA) index, a lower maximum average rate of heat emission (MARHE), and a lower specific extinction area (SEA) compared to cotton alone.

## RESULTS AND DISCUSSION

### Characterization of Cotton Samples

ZnO and/or ZnS particles were coated onto cotton surfaces by physisorption. ZnO and ZnO/ZnS rods were grown on the cotton fibers through a seed-mediated two-step hydrothermal process, as described in the Procedures section. Commercially available ZnO and ZnO + ZnS microparticles were physisorbed onto a cotton surface by dip-coating in a suspension of ZnO (~10 μm) and ZnS microparticles (~10 μm) sequentially. Figure 1a,b shows the SEM images of the ZnO and ZnO + ZnS spherical microparticles adsorbed to the cotton surface. Poor adhesion between the cotton surface and the microparticles resulted in the clustering of ZnO and ZnS particles, as can be seen from the elemental maps of Zn and S (Figure 1c,d). Figure 2a–d shows the representative SEM images of cotton fibers coated with ZnO and ZnO/ZnS core/shell rods generated by a 24 h reaction, which were fabricated using a hydrothermal process previously reported by Athishda et al. (see the Procedures section). ZnO rods were produced with an average length of 1300 ± 285 nm and a width of 137 ± 39 nm (Figure 2a,c). A slight reduction in the average sizes of the ZnO/ZnS core/shell rods occurred during the sulfidation process (l = 1207 ± 323 nm, w = 234 ± 42 nm) (Figure 2a,c). Figure 2e shows that single crystals of ZnO coated the entire cellulose fiber. The average thickness of the polycrystalline ZnS shell was 42.4 ± 7.5 nm, as measured from TEM images (Figure 2f).

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![Figure 1. SEM images of cotton coated by (a) ZnO microparticles and (b) ZnO + ZnS microparticles. Elemental maps of (c) zinc and (d) sulfur show the uneven distribution of ZnO and ZnS microparticles adsorbed to the cotton surface.](image-url)

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images of cotton fibers coated with ZnO short rods ($l = 201.1 \pm 35.33$ nm, $w = 210.1 \pm 14.6$ nm) generated by a 5 h hydrothermal reaction. Short ZnO rods grew evenly on the fiber surface and formed a thin uniform layer.

**Cone Calorimetry.** The percent mass loading, $A$, of the coatings was calculated according to the following formula:

$$A = \frac{W_f - W_0}{W_0} \times 100\%$$

where $W_f$ is the weight of samples after treatment with particles and $W_0$ is the weight of the scoured cotton. Table 1 shows the percent mass loading of the seven sets of cotton samples analyzed. ZnO/ZnS core/shell rods had a higher mass loading percentage (85–92%) because they were chemically attached to the cotton fiber (Figures 1 and 2), unlike ZnO and ZnS microparticles. Prior studies have shown that ZnO rod coatings on cotton fabrics withstand laundering conditions. None of the coatings qualitatively changed the flexibility of cotton fabric.

The results of the combustion are presented in Table 2 from triplicate experiments. The data show similar trends. The various zinc coatings did not significantly or systematically improve the TTI of the cotton fabrics. However, the THR was reduced by all of the coatings except for coatings bearing ZnO + ZnS microparticles. ZnO short rod coatings had a slight improvement in the THR compared with ZnO microparticles at a similar mass loading. Cotton samples coated with ZnO and ZnO/ZnS rods released the least total amount of heat during combustion when compared to untreated cotton and cotton samples treated with microparticle coatings (Table 2). ZnO/ZnS core/shell rod coatings were more efficient at reducing the THR compared to ZnO rods. This is likely due to the endothermic decomposition of the ZnS shell on the ZnO surface. A similar trend was observed for the EHC data (Table 2). All coatings reduced the EHC, but the effect was more pronounced for ZnO, ZnO/ZnS rod, and ZnO short rod coatings. Figure 4 shows the HRR of Zn coatings compared to untreated cotton. After ignition, the HRR of untreated cotton increased rapidly in the first 60 s and, subsequently, PkHRR occurred at 60 s. The PkHRR was reduced by all of the coatings, and importantly, the time to reach the PkHRR increased (Figure 4). The HRR curves of ZnO seed, ZnO short rod, ZnO microparticle, and ZnO + ZnS microparticle cotton samples had similar features, but the peaks were shifted by 65–75 s compared to the untreated cotton. Cotton samples coated with microparticles and ZnO seeds reduced the PkHRR by about 20–24% at a mass loading of 1.6%, and ZnO short rods reduced the PkHRR by 33% at a mass loading of 13.70%. The HRR of ZnO and ZnO/ZnS rod-coated cotton samples increased dramatically within the first 25 s, just like the untreated cotton, but a slowdown was evident in the following 80 s, which indicates that the flame-retardant mechanism of the rod coatings was initiated at 25 s. ZnO and ZnO/ZnS core/shell rod coatings were more effective at retarding burning because the PkHRR was delayed (95–110 s) and reduced by 50%. This is mainly due to the uniform coverage of the ZnO and ZnO/ZnS rods on the fiber surface, which provides a protective layer during combustion. The lower thermal

**Table 1. Mass Loading of Particles on Cotton Samples**

<table>
<thead>
<tr>
<th>sample</th>
<th>wt %</th>
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<tr>
<td>scoured cotton</td>
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<tr>
<td>ZnO microparticles</td>
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<td>ZnO + ZnS microparticles</td>
<td>21.01</td>
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<tr>
<td>ZnO seeds</td>
<td>1.60</td>
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<tr>
<td>ZnO short rods (5 h)</td>
<td>13.70</td>
</tr>
<tr>
<td>ZnO rods (24 h)</td>
<td>85.24</td>
</tr>
<tr>
<td>ZnO/ZnS rods</td>
<td>92.55</td>
</tr>
</tbody>
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Figure 2. Electron microscopy images of ZnO and ZnO/ZnS rods grown on natural cotton. SEM images of (a) ZnO and (b) ZnO/ZnS rods on individual cellulose fibers. High-magnification SEM images showing the hexagonal habit of the (c) ZnO rods and the rough texture of the polycrystalline (d) ZnS shell generated on the surface of the ZnO rod after sulfdation. Representative TEM images of (e) ZnO and (f) ZnO/ZnS core/shell rods detached from the cotton surface.

Figure 3. Electron microscopy images showing (a) ZnO short rods on a natural cotton fiber and (b) the hexagonal morphology of the short rods at high magnification.
conductivity of the rod layer retards burning by slowing down heat transfer and spreading and reduces the thermal pyrolysis rate of cotton.46–48 These data suggest that more time would be available to escape, providing a better chance of survival.

CO₂ production rate curves from calorimetry experiments are represented in Figure S1. Cotton samples with coatings had a lower average CO₂ yield and longer burning time. Figure S1 reveals that the fire-retardant mechanism occurs in the condensed phase.49 This indicates that the combustion was retarded by coatings as a result of the protective layer of the crystals on the surface of the fibers. Specific extinction area (SEA) and CO and CO₂ yield are also shown in Tables 2 and S2. SEA is a smoke measurement that represents the instantaneous amount of smoke released and the effective optical obscuring area generated per unit mass loss of specimen.50 Untreated cotton produced an optical obscuring area of 14.66 m² per 1 kg mass loss during burning (Table S2). Zn coatings reduced the SEA, which means that the coatings could improve visibility to allow individuals to escape in case of a real fire. This is consistent with the work by others showing that Zn salts can act as smoke suppressants and reduce the SEA as well.50 Compared to microparticle and seed coatings, rod coatings reduce the SEA more effectively. This trend correlates well with the THR and EHC data, which also result from the protective insulation layer on the fiber surface that reduces the rate and intensity of combustion. ZnO microparticles, ZnO seeds, and ZnO long and short rod coatings reduced the CO yield, which results from slower and more complete combustion of the fabric. ZnO + ZnS microparticle- and ZnO/ZnS rod-coated cotton samples release more CO than untreated cotton. This is because sulfur radicals produced from ZnS radicals to generate SO₂, which affects the combustion reactions in the flame zone and leads to incomplete combustion (less CO₂ production).51–53 (The TSR data are shown in Figure S1 and Table S2.) The mean MLR (MeanMLR) of the untreated cotton samples during combustion was 8.54 g/s. This value was reduced by all of the coatings, with ZnO and ZnO/ZnS rod coatings having the highest reduction in MeanMLR of approximately 32%. This result is consistent with ZnO and ZnO/ZnS rods forming a protective barrier to prevent burning and/or reduce the intensity of combustion compared to loosely adsorbed microparticles and small ZnO seed crystals.

The FIGRA index and MARHE are the two accepted evaluation parameters of the ratio of a material to fire. The FIGRA index is used to evaluate the fire spread rate and the size of the fire and calculated as the ratio of PkHRR to time to PkHRR. MARHE is used to evaluate the propensity of fire development and calculated as a ratio of the accumulative heat emission to time. From the samples tested, coatings with ZnO/ZnS core/shell and ZnO long rods exhibited a similar FIGRA index and MARHE compared to ZnO long rod coatings and show a slight improvement compared to ZnO short rod coatings (Table 2). At high temperatures, it has been reported that ZnS decomposes endothermically to release sulfur radicals, which react with oxygen to generate the nonflammable gas sulfur dioxide, which further retards combustion.20,52,54 The nanolayer of ZnS on the core/shell rods is likely not thick enough to show a significant improvement in the FIGRA and MARHE values compared to long rods of ZnO.

Images of the cotton samples taken after the combustion tests are shown in Figure 5. After burning, the untreated cotton sheets were completely turned to ash, as shown in Figure 5a. Cotton samples coated with ZnO microparticles, ZnO + ZnS microparticles, and ZnO seeds leave a white and/or light yellow solid residue, which adheres to the aluminum holder (Figure 5a–d). The aluminum sample holders were burned through because of the high intensity of heat loading from combustion. ZnO short rod-, ZnO long rod-, and ZnO/ZnS rod-coated cotton samples maintain the original shape of the cotton fabric, and as a result, the aluminum holders survive intact after combustion (Figure 5e–g). SEM images of ZnO and ZnO/ZnS rod-coated cotton samples were taken after cone calorimetry experiments and are shown in Figure 6. ZnO and ZnO/ZnS rod coatings preserved the woven structure of the cotton fabric, as seen in Figure 6a–c. Individual cotton fibers were completely consumed, but a hollow shell of ZnO rods remained in place.
Short ZnO rods exhibited a hollow shell structure after combustion, analogous to the longer ZnO rods, but the walls were much thinner, and the shell is effectively more porous because of lower mass loading (Figure 6f). High-magnification SEM images of ZnO rods that form the protective layer around the cotton fibers are shown in Figure 6gh. No damage or sintering of neighboring rods was observed after combustion. Decomposition of the ZnS shell on the ZnO/ZnS core/shell rods leaves behind ZnO rods with textured surfaces, as shown in Figure 6h. Figure 6i shows a high-magnification SEM image of ZnO short rods after burning. ZnO coatings were thermally stable and maintained their size and shape at high temperatures regardless of size. Energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) experiments confirm that the ZnS shell is no longer present on the surface of ZnO/ZnS core/shell rods after combustion (Figures S2 and S3). SEM data together with the cone calorimetry experiments suggest that the flame-retardant mechanism is the formation of a protective layer of ZnO rods that acts as a barrier to limit radiative heat and flames from penetrating the cotton surface. ZnO materials also exhibit size-dependent thermal conductivity, that is, reduced thermal conductivity with decreasing particle size.47,48 This may be one reason why even ZnO seeds show good fire-retardant properties, and it also presents an opportunity to further tune or exploit this property to produce fire-retardant products and textiles.

**Vertical Flame Tests.** Flame tests were carried out in the vertical orientation, and the data are shown in Table 3. None of the samples exhibited self-extinguishing properties. ZnO microparticle, ZnO + ZnS microparticle, ZnO seed, and ZnO short rod coatings became flaky and brittle and detached from the frame, leaving behind no residue (Figure S4). Light flakiness was observed for ZnO and ZnO/ZnS rod coatings. Residues were observed for cotton coatings of ZnO long rods and ZnO/ZnS core/shell rods, and the residues maintained the
original shape of the fabric after the vertical flame tests. This data are consistent with the results obtained from the cone calorimeter (Figure 5). The after-flame time was reduced for ZnO short and long rod coatings only, and the after-glow time was reduced the most by ZnO long rods and ZnO/ZnS core/shell rods compared to the control. These data suggest that even at high mass loadings, these coatings do not exhibit self-extinguishing behavior. Although the ZnO coatings reduce the HRR of cotton fabrics, ideally, the coatings must be coupled with a chemical flame retardant to exhibit self-extinguishing properties.

**Thermal Stability.** Thermal decomposition was studied by TGA and differential thermal analysis (DTA) performed in air and nitrogen (Figure 7). The TGA curves collected in air (Figure 7a) show that the onset temperature of degradation of untreated cotton was around 340 °C and peak decomposition rate occurred at 350 °C (Figure 7b), as previously reported.55,59,60 The onset temperature of degradation for untreated cotton was found to be higher in nitrogen (Figure 7c) at around 350 °C. The peak decomposition rate occurred at 360 °C (Figure 7d), which is due to the slower pyrolysis of cellulose under an inert atmosphere.57,58 Compared to untreated cotton, the onset temperature and peak decomposition rate were not significantly changed by ZnO micro-particle coatings in air and nitrogen, which indicates that the coating did not improve the thermal stability of cotton. The curve of ZnO + ZnS microparticle coatings shows a decomposition onset temperature of 290 °C and a steeper percentage weight loss from 290 to 340 °C, which is due to the catalytic effect of sulfur on the decomposition of cellulose, which causes mass loss at a lower temperature compared to untreated cotton.55,59,60 This is a result of direct contact of ZnS particles with the cotton surface. ZnO seed-coated cotton samples show a trend similar to that of untreated cotton below 350 °C in both air and nitrogen. A significant weight loss event was observed in TG experiments of ZnO seed-coated cotton performed in air at 370 °C (Figure 7a) and at 475 °C in DTA curves (Figure 7b). This is attributed to the collapse of the thin protective layers of ZnO seeds on the fiber surface and further oxidation and decomposition of the char residue of the cotton, which is missing in tests performed under nitrogen (Figure 7c,d).61 A similar onset temperature of degradation was observed for coatings consisting of long and short ZnO rods under both air and nitrogen, suggesting that these coatings also did not improve the thermal stability of cotton samples. The onset temperature of mass loss is lowered by ZnO/ZnS rod coatings, which is likely from the endothermic decomposition of the ZnS shell.62,63 The leftover residue for all coated samples is ZnO (which does not decompose) and an oxidized char of cotton (0.54 mass %).43,64,65 The TGA data are consistent with the TTI data and show good correlation with the residue mass results from the calorimetry experiments.

**CONCLUSIONS**

We show that ZnO materials, in general, are effective at reducing the PkHRR even when unassisted by an organic fire retardant. ZnO particles chemically grown on cotton formed a uniform protective coating on the cotton surface, resulting in lower PkHRR, lower FIGRA, and lower MARHE compared to cotton. However, the lack of self-extinguishing properties suggests that coupling ZnO materials with other chemical/molecular flame-retardant materials could improve flame retardancy. The functional properties of ZnO, such as low thermal conductivity, high mechanical strength,67 UV absorption,68 favorable whiteness index,69 and biocompatibility,70 coupled with the combustion behavior indicate that these materials have a promising future as eventual fire-retardant coatings on cotton fabrics.

**MATERIALS**

Sodium hydroxide (ACS reagent, ≥97.0%, pellets), Triton X-100 (BioXtra), zinc acetate dihydrate (ACS reagent, ≥98%), triethylamine (≥99%), zinc nitrate hexahydrate (≥99.0%, crystallized), hexamethylenetetramine (ACS reagent, ≥99.0%), zinc oxide (ACS reagent, ≥99.0%, powder), and zinc sulfide (10 μm, 99.99%, powder) were purchased from Sigma-Aldrich (St. Louis, MO). Citric acid (ACS reagent, ≥99.0%, crystal) was purchased from Spectrum Chemical Mfg. Corp. (New Brunswick, NJ). Sodium sulfide (nonahydrate, ≥99.0%) was purchased from Fisher Science Education (Nazarath, PA). Isopropyl alcohol (ACS reagent, ≥99%) and ethyl alcohol 200 proof (absolute, anhydrous, and ACS/USP grade) were purchased from Pharmco-AAPER (Shelbyville, KY). Bleached, desired cotton fabric (400) was purchased from TestFabrics (West Pittston, PA). Polytetrafluoroethylene...
(PTFE) sheets (1/8" thick, 6" × 6"), nylon 6/6 black wing nuts, and nylon off-white with shoulder screws (0.75" length) were purchased from McMaster-Carr (Douglasville, GA). Square PTFE frames were machined using an Epilog Mini 24 laser cutting system (40 W) at the Oklahoma State University Visual Resource Center, with a thickness of 1/8", outer dimensions of 6" × 6", and inner dimensions of 4" × 4" (empty space).

**Procedures.** *Pretreatment of Cotton Fabric.* The cotton scouring solution was prepared by dissolving 2.50 g of NaOH, 0.75 g of Triton X-100, and 0.38 g of citric acid in 250 mL of high purity Nanopure water (18 Ω/cm). Five cotton swatches (7" × 7") were placed in a 500 mL round-bottom flask containing 250 mL of the scouring solution. The mixture was stirred at 100 °C for 1 h. The scoured swatches were removed from the solution, rinsed thoroughly with high purity water (18 Ω/cm), and dried under ambient conditions.

**Synthesis of ZnO Rods on Cotton Fabric.** ZnO rods were grown on the cotton surface using a previously published protocol by Athauda et al. A 50 mM solution of ZnO seeds was grown on the cotton surface using a previously published protocol by Athauda et al. A 50 mM solution of ZnO seeds was made by dissolving 12.61 g of ZnO in 900 mL of deionized water while stirring overnight at 60 °C. A 200 mM Na2S solution was made by dissolving 43.23 g of Na2S in 900 mL of deionized water while stirring overnight at 60 °C. A 100 mM growth solution was made by dissolving 2.75 g of Zn(CH3COO)2·2H2O in 250.0 mL of isopropanol. The resulting solution was stirred vigorously (300 rpm) at 85 °C for 20 min. Then, 1.745 mL of triethylamine was added dropwise to the solution and stirred at 85 °C for an additional 15 min. This seed solution was allowed to cool to room temperature. Pretreated cotton swatches were submerged in the seed solution for 15 min and dried in a furnace (Binder) at 120 °C for 1 h.

A 100 mM growth solution was made by dissolving 12.61 g of hexamethylenetetramine in 900 mL of high purity water (18 Ω/cm). Then, 26.77 g of Zn(NO3)2·6H2O was added, and the resulting solution was stirred for 24 h at room temperature. The ZnO growth solution was filtered (Whatman, 150 mm) prior to use. Cotton treated with the ZnO seed solution was mounted onto a Teflon frame, submerged in 2.7 L of growth solution in a 4 L glass tank, and kept in a furnace at 95 °C for 5 and 24 h to generate cotton coated with ZnO short rods (13% mass loading) and long rods (85% mass loading). The cotton was then rinsed with deionized water and dried under ambient conditions.

**Preparation of the ZnO/ZnS Rod-Coated Cotton Samples.** A 200 mM Na2S solution was made by dissolving 43.23 g of Na2S in 900 mL of deionized water while stirring overnight at room temperature. Precipitates were removed using filter paper (Whatman, 150 mm). The Na2S solution (2700 mL) was added into a 4000 mL glass jar. The cotton swatches functionalized with ZnO rods with 85% mass loading were mounted in a PTFE frame and submerged in the filter-aided Na2S solution at 60 °C for 4 h. The cotton was then rinsed with deionized water and dried in air.

**Preparation of the ZnO and ZnO/ZnS Microparticle-Coated Cotton Samples.** Suspensions of commercially available ZnO (24.41 g/L) and ZnS (19.49 g/L) microparticles were prepared in ethyl alcohol and stirred at room temperature overnight. The cleaned cotton swatches were soaked in a dispersion of colloids while stirring for 1 h followed by drying in an oven at 120 °C for 1 h. For samples containing ZnO + ZnS microparticles, cotton swatches were first soaked in the suspension of ZnO and, subsequently, in a suspension of ZnS.


