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Solvent-Free Reactive Vapor Deposition for Functional Fabrics: Separating Oil–Water Mixtures with Fabrics

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Abstract: A facile, solvent-minimized approach to functionalize commercial raw fabrics is described. Reactive vapor deposition of conjugated polymers followed by post-deposition functionalization transforms common, off-the-shelf textiles into distinctly hydrophobic or superhydrophilic materials. The fabric coatings created by reactive vapor deposition are especially resistant to mechanical and solvent washing, as compared to coatings applied by conventional, solution-phase silane chemistries. Janus fabrics with dissimilar wettability on each face are also easily created using a simple, three-step vapor coating process, which cannot be replicated using conventional solution phase functionalization strategies. Hydrophobic fabrics created using reactive vapor deposition and post-deposition functionalization are effective, reusable, large-volume oil–water separators, either under gravity filtration or as immersible absorbants.

Keywords: reactive vapor deposition; hydrophobic; Janus material; absorbant; separation

1. Introduction

Industrial water contamination is a pernicious worldwide problem that wreaks tremendous, long-lasting environmental damage and particularly cripples developing economies. Numerous research efforts are dedicated to developing materials for cleaning up oil-contaminated water [1]. Conventional separation materials such as dispersants, solidifiers, and booms and skimmers suffer from high manufacturing costs, secondary pollution, frequent fouling and low separation efficiency [2,3]. Due to these limitations, membranes with special wettability (superhydrophobicity and oleophilicity) have received intense recent attention. Nanostructured hydrophobic materials, such as polymer membranes and metal meshes, have been reported for oil–water separation, but complex and non-scalable fabrication process are typically encountered, in addition to the frequent need for high-cost, fine chemicals during synthesis [4–8].

In theory, natural fabrics such as cotton and wool are excellent candidates for contaminant absorbing/filtering materials because of their naturally-occurring microscale roughness and inherent porosity. Natural fabrics are also outstanding decontaminants because of their low cost and reusability [9]. Methods of functionalizing commonly-available fabrics for water decontamination include surface modification with inorganic nanoparticles [10–12], silane treatment [13], graft polymerization [14,15] and polymer lamination [16].

However, paradoxically, the industrial processes used to manufacture textiles are, themselves, major contributors to global water pollution [17]. Conventional textile and garment production is water-intensive, consuming approximately 700 gallons of fresh water to produce a T-shirt and 1800 gallons of fresh water to produce a pair of jeans. In 2015, the World Bank estimated that 20% of

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global water pollution was caused by textile processing [17]. Treating such large volumes of waste water is time and energy-intensive, and expensive. Moreover, the inorganic nanoparticles that are widely used to modify the surface of textiles are known to cause unique environmental damage and human health issues upon inevitable leaching into water sources [18,19]. Therefore, alternative, less solvent-intensive approaches to process and dye textiles are sorely needed.

Here, we report a facile, solvent-minimized approach to functionalize commercial raw fabrics. Reactive vapor deposition of conjugated polymers [20–23] followed by post-deposition functionalization transforms common, off-the-shelf textiles into distinctly hydrophobic or superhydrophilic materials that are effective filters and/or absorbants to remove oil-based contaminants from fresh water, even in the presence of surfactants. The vapor coating method reported herein has the potential to significantly curtail the solvent use associated with mainstream textile manufacturing processes while also creating functional fabrics that can decontaminate polluted water.

2. Materials and Methods

All chemicals were purchased from Millipore Sigma and used without further purification. Fabrics were purchased from fabric stores and used without cleaning.

The reactive vapor deposition of the monomer 3,4-(hydroxymethyl)ethylenedioxy-thiophene (HMEDOT) to create poly(3,4-(hydroxymethyl)ethylenedioxy-thiophene) (PHMEDOT) films on various substrates was carried out in a custom-built, tubular vacuum chamber (Figure 1) whose design and operating principles were previously described [20]. The process pressure was maintained close to 150 mTorr during deposition. The crucible containing the oxidant, $FeCl_3$, was placed 5 inches from the monomer vapor inlet. The substrates, glass slides and fabrics, were placed between the monomer and oxidant vapor source in the tube with only one side exposed to the vapor. First, with the monomer valve closed, the oxidant $FeCl_3$, the substrates, and the monomer HMEDOT, were heated at 170 °C, 95 °C, and 120 °C, respectively, for 8 min. Second, the monomer valve was opened, and the polymer films started to form in the middle of the two vapor sources. The polymerization was halted by closing the valve after 20 min. Third, the polymer films were cooled to room temperature and rinsed with solutions in the following sequence: methanol (20 min), 1 M HCl solution (15 min), and methanol (20 min). The samples were dried in air. Chemical characterization of PHMEDOT films is previously reported [22].

PHMEDOT-coated fabrics, glass slides or pristine fabrics were placed in a sealed glass container together with a few small droplets (approximately 0.1–0.5 mL) of neat trichloro-(1H,1H,2H,2H-perfluorooctyl)-silane and the container was placed in an oven held at 60 °C overnight. Then, the samples were rinsed with ethanol for 20 min (2×) and dried in a vacuum oven at 50 °C for 2 h.

Commercial, untreated fabrics were immersed in a 1 wt.% solution of trichloro(1H,1H,2H,2H-perfluorooctyl)silane in Tetrahydrofuran (THF) and the solution was maintained at 50 °C overnight. Then, the samples were extracted from the solution, rinsed with fresh THF for 20 min (2×) and dried in a vacuum oven at 50 °C for 2 h.

3. Results and Discussion

Fabrics were investigated as potential filters/absorbants for three reasons. First, fabrics are already manufactured in a high volume and can be recycled. This is important for cleaning high-volume pollution events, as a large quantity of contaminant absorbing/separating materials are needed. Second, fabrics have highly-textured surfaces with a large surface area, which should afford unmatched contaminant separation from dilute media [24]. Third, fabrics are naturally porous materials with nanoscale and microscale pores that can be tuned by judiciously choosing the constituent fiber (cotton, silk, wool) and weave or knit pattern, affording numerous experimental handles with which to systematically study and control contaminant transport, sequestering and/or capture.

However, commonly-available, untreated fabrics indiscriminately absorb any liquid to which they are exposed and are, therefore, not capable of selectively removing contaminants from aqueous mixtures. For example, when an oil/water bilayer is gravity-filtered through a commercially-available raw cotton fabric, the fabric absorbs a portion of both the oil and water, and minimal overall separation is effected (see video in Supplementary Materials). Here, reactive vapor deposition [20–23] was investigated as a solvent-minimized method to functionalize the surface of untreated textiles and create fabric filters and/or absorbants for water decontamination.

Figure 1 illustrates the stepwise process used to functionalize commercial, raw fabrics. First, off-the-shelf textiles were coated with PHMEDOT in a custom-built reactor that allows rough and/or fragile substrates to be nondestructively coated with a variety of conjugated polymer films [20]. The PHMEDOT coating changed the color of the starting fabric into a dark blue and created a superhydrophilic surface. For all the fabrics reported in this work, the PHMEDOT coating thickness was 300 nm (as measured on a flat silicon test silicon coupon that was coated concomitantly with the fabrics [20–22]). As previously reported, the PHMEDOT coating on all investigated fabrics, irrespective of weave density, was conformal and the intrinsic porosity and hand-feel of the starting fabrics was maintained [21,22]. Next, the fabrics were exposed to vapors of trichloro(1H,1H,2H,2H-perfluorooctyl)silane [25] to make a hydrophobic surface labelled F-PHMEDOT. No color change was observed after this post-deposition functionalization. The total weight of all investigated fabrics increased by less than 0.1% relative to the pristine samples after the two-step coating process.

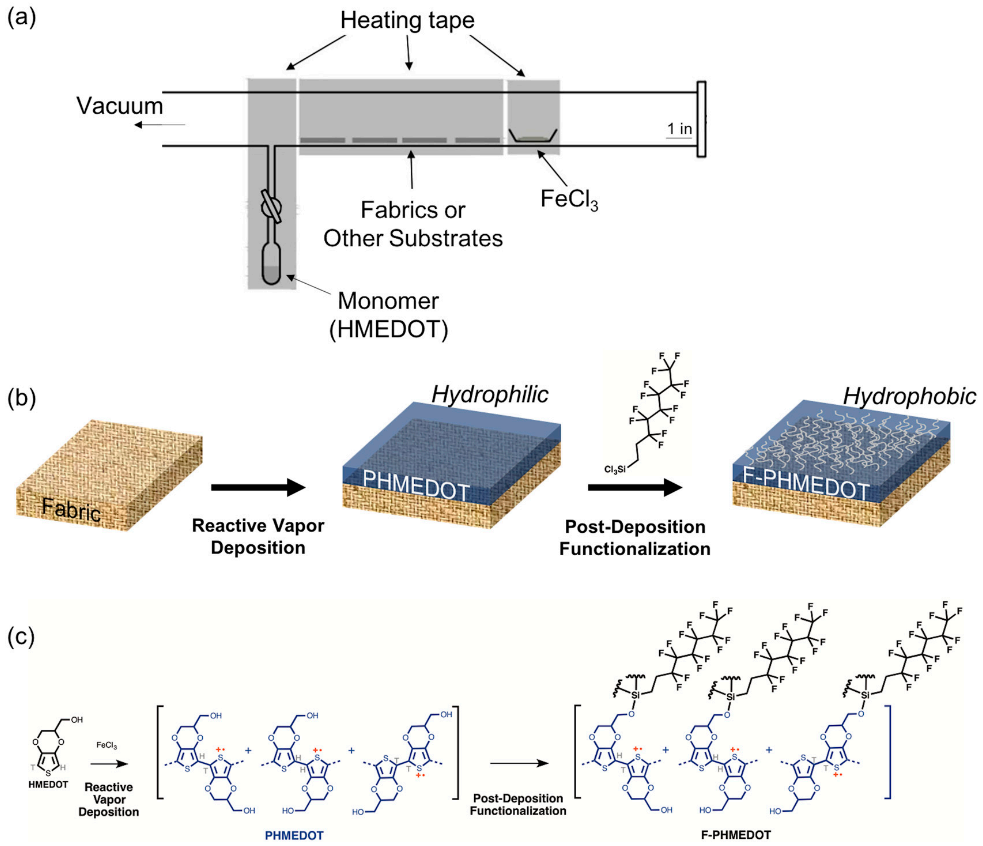

Figure 1. (**a**) Schematic of custom-built reactor used to coat untreated fabrics via reactive vapor deposition. (**b**) Illustration of the process to tune the wettability of off-the-shelf fabrics using reactive vapor deposition and post deposition functionalization. (**c**) Chemical structures of poly(3,4-(hydroxymethyl)ethylenedioxy-thiophene) (PHMEDOT) and F-PHMEDOT polymer coatings on fabrics.

As the example of an untreated cotton fabric, the pristine, as-purchased sample was naturally hydrophilic, with an apparent contact angle of 62.8° (Figure 2a), but this pristine fabric sample slowly absorbed the water droplet over approximately 10 min. After coating with PHMEDOT, the fabric surface became superhydrophilic. An apparent water contact angle was unmeasureable for PHMEDOT-coated fabrics because the water droplet was immediately absorbed by the fabric upon contact (Figure 2b). After post-deposition functionalization to transform PHMEDOT into F-PHMEDOT, the surface of this same fabric became hydrophobic, with an apparent water contact angle of 140.7° (Figure 2c). Therefore, reactive vapor deposition can be used in combination with post-deposition functionalization to create either hydrophilic or hydrophobic fabrics.

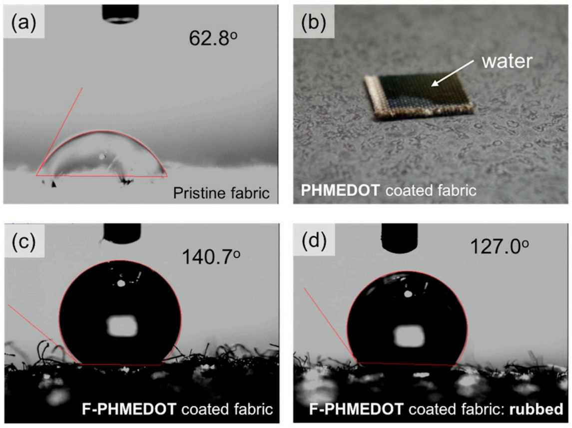

Figure 2. (**a**) Apparent water contact angle of a pristine, tight-woven, raw cotton fabric. (**b**) Photograph of a tight-woven, raw cotton fabric after vapor coating with PHEMDOT, showing the extreme hydrophilicity of the fabric surface. A water droplet placed on this coated fabric surface is immediately absorbed into the fabric. (**c**,**d**) Apparent water contact angles of (**c**) a tight-woven cotton fabric after vapor coating with F-PHMEDOT, and (**d**) the same vapor-coated fabric after mechanical rubbing.

The hydrophobic surface of the F-PHMEDOT-coated fabric is mechanically and chemically stable (Figure 2d, Figure 3). In our previous report, we proved that vapor-deposited conjugated polymer films on fabrics were remarkably stable to bending/folding, rubbing, dry ironing and cold laundering [21]. Here, we tested the stability of the post-deposition functionalized F-PHMEDOT coating by comparing the apparent water contact angle of F-PHMEDOT-coated fabrics before and after 500 times of mechanical rubbing and solvent (dichloromethane) washing (Figure 3). Further, the ruggedness of our vapor-deposited F-PHMEDOT coating on fabrics was compared to that of a hydrophobic coating created using conventional, solution-phase methods. The control sample was made by soaking the pristine fabric in 1 wt.% solution of trichloro(1H,1H,2H,2H-perfluorooctyl)silane in THF overnight. The F-PHMEDOT coated fabrics displayed apparent contact angle changes of less than 10% after mechanical rubbing and solvent washing. While the apparent water contact angle of the control sample remained unchanged after solvent washing, the apparent contact angle decreased by more than 30% after mechanical rubbing and the water droplet was fully absorbed by the fabric after 30 s. Therefore, the vapor-deposited coatings described herein possess superior ruggedness compared to fabric coatings created by conventional solution-processing.

An unmatched feature of reactive vapor deposition is that it can be spatially controlled to allow the selective coating of one face of a prewoven fabric. Mass transport of the reactive radical species created during reactive vapor deposition can be predictably controlled by the chamber pressure, substrate stage temperature, intrinsic adhesive properties of the reactants, and substrate roughness/porosity [21,22,26,27]. For the reactor and deposition conditions used in this report, the weave density and porosity of the substrate textile was found to be the primary variable controlling the area of surface coating. As seen in Figure 4, use of a prewoven fabric with a loose weave pattern (high porosity) created a uniform PHMEDOT coating across all exposed surfaces of the fabric and no uncoated surfaces were noted. In contrast, when a fabric with a tight weave density (low porosity) was subjected to reactive vapor coating in our chamber, two distinct sides of the fabric were observed, one coated (blue) and one uncoated.

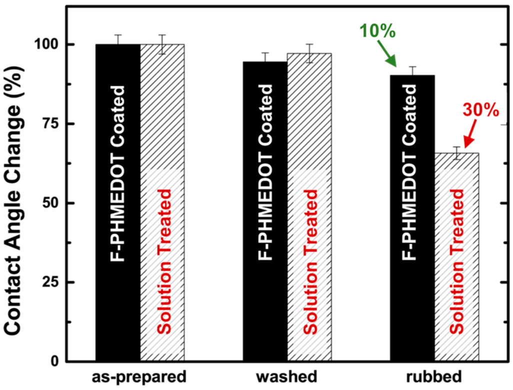

Figure 3. Change in apparent water contact angles of a vapor-coated (F-PHMEDOT) and solution-coated cotton fabric before and after solvent washing and mechanical rubbing.

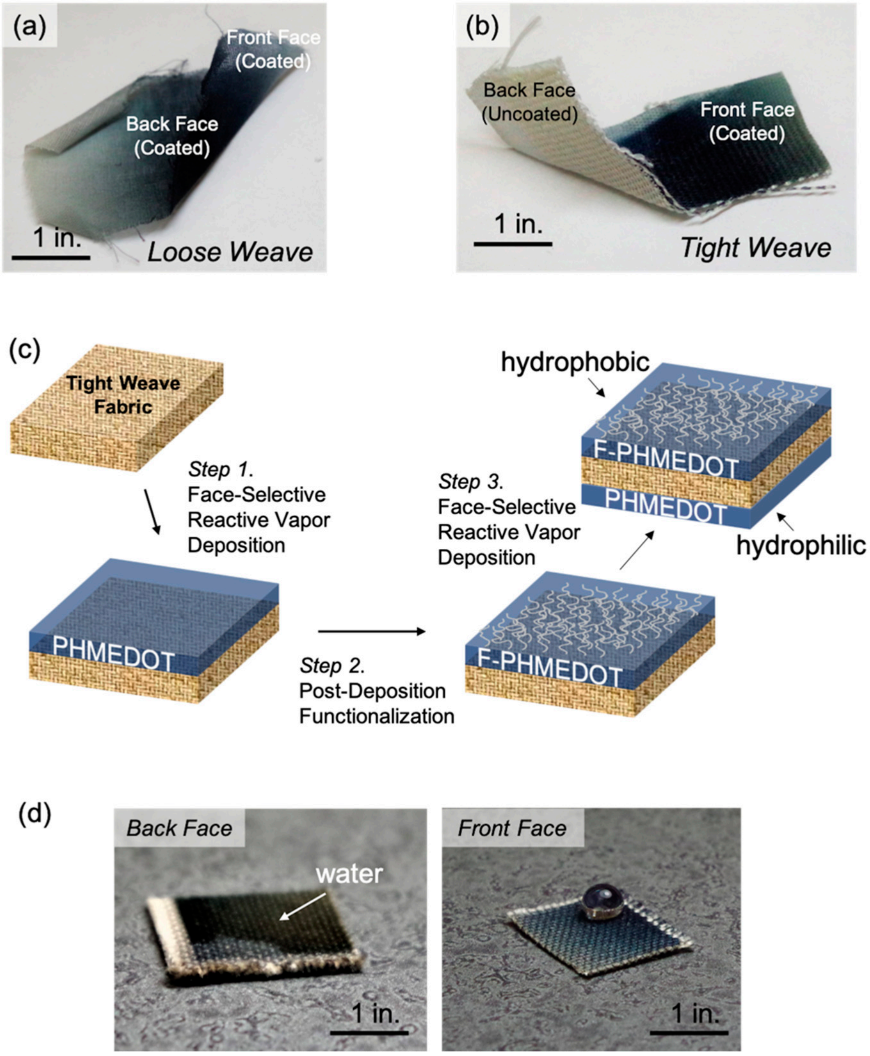

Figure 4. (**a**) Optical image of a loose weave, untreated cotton fabric vapor coated with PHMEDOT. (**b**) Optical image of a tight weave, untreated cotton fabric vapor coated with PHMEDOT. (**c**) Stepwise process for creating Janus fabrics with dissimilar wettability on each face. (**d**) Optical images of a water droplet on the front and back sides of the Janus fabric.

Taking advantage of this selective coatability feature, tight-woven textiles were transformed into Janus fabrics that displayed two distinct wettabilities on each face/side. By depositing PHMEDOT on the clean, uncoated side of an F-PHMEDOT coated fabric, Janus fabrics with one hydrophilic face and one hydrophobic face were created (Figure 4). Figure 4d shows the distinctive wettability of each face of the Janus fabric. A video demonstrating the dissimilar hydrophilic and hydrophobic properties of each face of the fabric is provided in the Supplementary Materials. Janus fabrics will be useful for separating both oil-in-water emulsions and water-in-oil emulsions [28,29].

Next, the ability of the F-PHMEDOT-coated fabrics to separate oil/water mixtures was evaluated in two ways. The oil phase used here was hexanes-dyed with Oil Red O. In the first method, a two-phase oil/water bilayer was poured into a funnel containing an F-PHMEDOT-coated tight woven cotton fabric as the filter (Figure 5a–c). The two-phase oil water mixture was separated into two distinct components by gravity, without extra applied pressure. The gravity-driven separation process was very fast (2 s) and occurred concomitantly with liquid flow through the fabric filter. A video demonstrating oil/water separation in real time is provided in the Supplementary Materials. The fabric filter remained unfouled even after large volumes of oil/water mixtures (two litres total) were continuously filtered through, indicating that large volume of oil-contaminated water can be purified using this fabric filter.

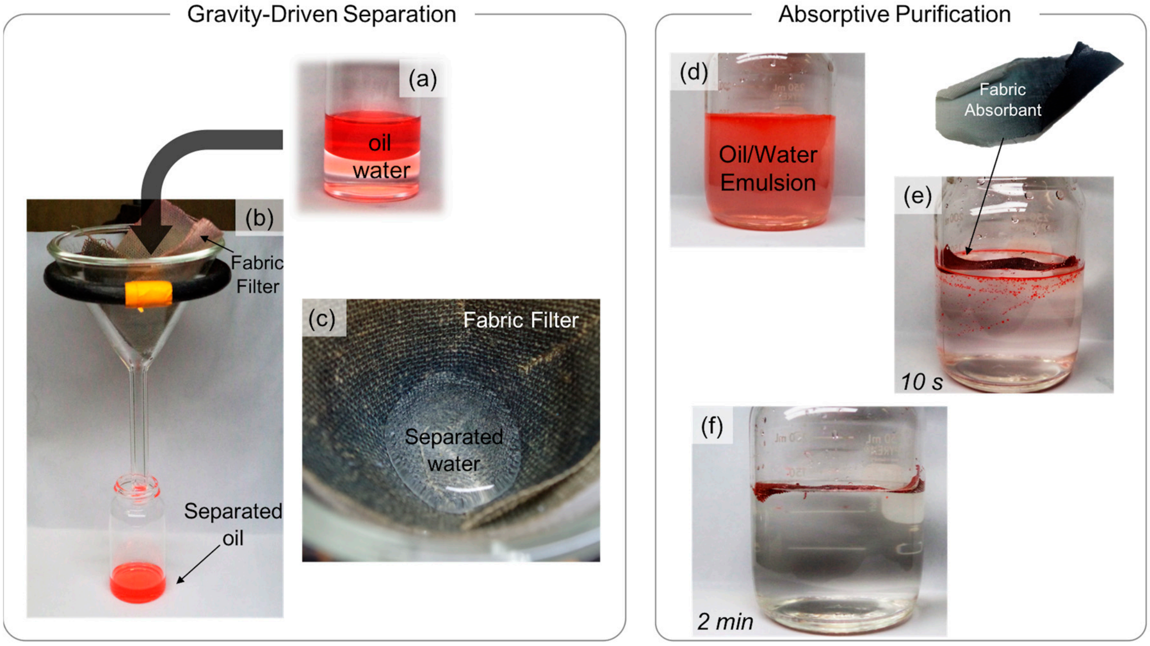

Figure 5. Gravity-driven separation of a two-phase oil/water mixture (**a**) using an F-PHMEDOT coated tight woven cotton fabric as a pass-through filter (**b**). The water phase remains in the fabric filter (**c**) while the oil phase is filtered through and collected (**b**). Removal of oil from a surfactant-stabilized oil/water emulsion (**d**) by immersing an F-PHMEDOT coated loose woven cotton fabric into the emulsion. The fabric absorbant selectively soaks up the oil particles after a short time (**e**) and oil is completely sequestered in the fabric after 2 min (**f**).

In the second method, a surfactant-stabilized oil/water emulsion was clarified (Figure 5d–f). The surfactant-stabilized mixture had an oil to water ratio of 1:100 by volume and was stabilized with commercial hand-washing soap. A 1 inch × 2 inch piece of an F-HMEDOT-coated loose woven cotton fabric was fully immersed in the mixture. Within 10 s, the red-colored oil was absorbed by the fabric and the mixture became clear after 2 min (Figure 5f). The fabric absorbant depicted in Figure 5f could be further re-used to purify another oil/water emulsion after simply wringing it out and air drying;

this process was repeated five times without any noticeable failure in the oil-absorbing capacity of the 1 inch × 2 inch piece of fabric.

4. Conclusions

A combination of reactive vapor deposition and post-deposition functionalization affords fabrics with distinctive hydrophobic or superhydrophilic surfaces. The surface coatings created by reactive vapor deposition are especially resistant to mechanical washing, as compared to surface coatings applied by conventional, solution-phase silane chemistries. Janus fabrics with dissimilar wettability on each face can also be created using a simple, three-step vapor coating process, which cannot be replicated by solution-phase methods. The hydrophobic fabric reported herein acts as an effective, reusable, high-volume oil-water separation material, either under gravity filtration (for phase-separated mixtures) or as an immersible absorbant (for surfactant-stabilized oil/water emulsions).

Conventional textile and garment production is water-intensive, consuming approximately 700 gallons of fresh water to produce a T-shirt and 1800 gallons of fresh water to produce a pair of jeans. In 2015, the World Bank estimated that 20% of global water pollution was caused by textile processing [17]. Treating such large volumes of waste water is time and energy-intensive, and expensive. Therefore, alternative, less solvent-intensive approaches to process and dye textiles are needed.

Reactive vapor deposition allows for the solvent-free functionalization of raw, off-the-shelf fabrics and has the potential to significantly curtail the solvent use associated with mainstream textile manufacturing processes [30]. Currently, however, vapor coating methods are not broadly adopted by textile scientists and manufacturers because of the perceived difficulty and high cost of scaling up vapor coating chambers to satisfy the high volume demand of the textile industry. Burgeoning reactor designs for stain-guarding carpets [31] prove that vapor coating methods are indeed conducive to large-scale, high-throughput manufacturability. Nevertheless, further research in the academic sector is needed to optimize reactor designs and coating stages to continuously process and coat large spools of thread. Innovations in vapor phase polymerization chemistries are also required to decrease the duration of each coating cycle (currently 20 min) and eliminate the use of heavy metal oxidants during the coating process.

Supplementary Materials: Videos of oil-water separation in real time. The following are available online at http://www.mdpi.com/2079-6439/7/1/2/s1, Janus Fabric (.mp4), Functionalized Fabric Gravity Filter (.mp4), Ineffective Raw Fabric Filter (.mp4).

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