

A4 Paper Chemistry: Synthesis of a Versatile and Chemically Modifiable Cellulose Membrane

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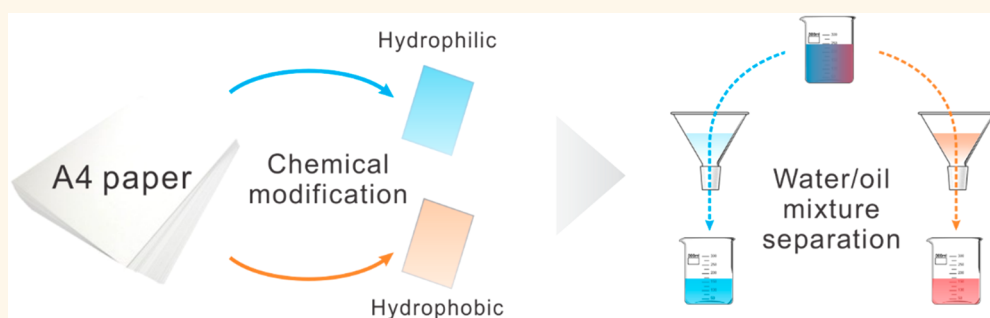
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ABSTRACT: Multifunctional cellulose membranes were developed from A4-sized printing paper via chemical modification. A4 paper is a widely used and easily accessible product with high cellulose content. Inspired by cellulose chemistry, we report a simple modification of the A4 paper, converting it from a common office supply to a user-modifiable functionalized cellulose membrane for practical applications. The hydroxyl groups of cellulose enable a facile tuning of its internal structure and polarity via chemical modification. In addition, the functionalized cellulose membrane has more stable mechanical strength compared to commercial cellulose-based filtration membranes. As a proof-of-concept, we demonstrate the separation of a water/oil mixture using the functionalized A4 membrane; we have extended this idea to origami-assisted membrane applications. Finally, this versatile A4 paper chemistry may offer a promising strategy for the development of functional membranes.

KEYWORDS: cellulose chemistry, A4 printing paper, chemical grafting, water/oil separation, origami membrane

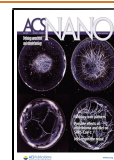
Cellulose-based membranes are widely used in separation chemistry applications, including gravimetric filtration, energy storage systems, and medical science, owing to their versatile properties.^{1–4} Cellulose-based membranes are ecofriendly, economical, recyclable, biocompatible, and flexible.^{5,6} Cellulose-based membranes also possess mechanical stability owing to the highly networked intra- and intermolecular hydrogen bonding of hydroxyl groups based on repeating glucose units. While the homogeneous process is widely employed in the industrial sector to produce cellulose acetate-based membranes,⁷ the heterogeneous process is currently attracting more attention owing to its high potential for chemical modifications to the functional moiety in cellulose nanofibers, including acid hydrolysis,⁸ esterification or etherification reactions,⁹ and polymer grafting.¹⁰ These functionalization processes have facilitated and popularized the use of cellulose-based materials by enhancing their dispersity and compatibility with other solvents and nanomaterials.^{11–13}

Chemically modified cellulose functional membranes have been investigated from the viewpoint of their applications in energy storage devices and biomedical devices owing to their physicochemical properties. Despite significant merits, the fabrication of cellulose membranes from bulk wood requires intensive processing, including chemical and physical treatments, as well as reassembly techniques, after the dispersion of cellulose fibers in solvents.^{14,15} As cellulose exists in the form of complex lignocellulose composites which are mainly composed of lignin and hemicelluloses, its selective extraction from biomass and use requires considerable effort and

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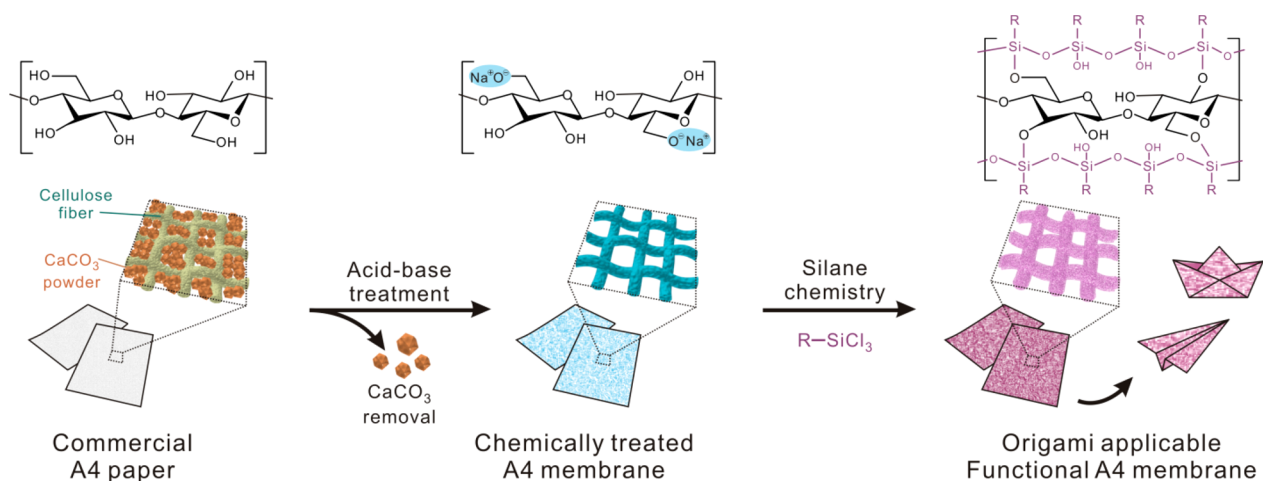


Figure 1. Schematic illustration of chemical treatment processing in A4 paper chemistry.

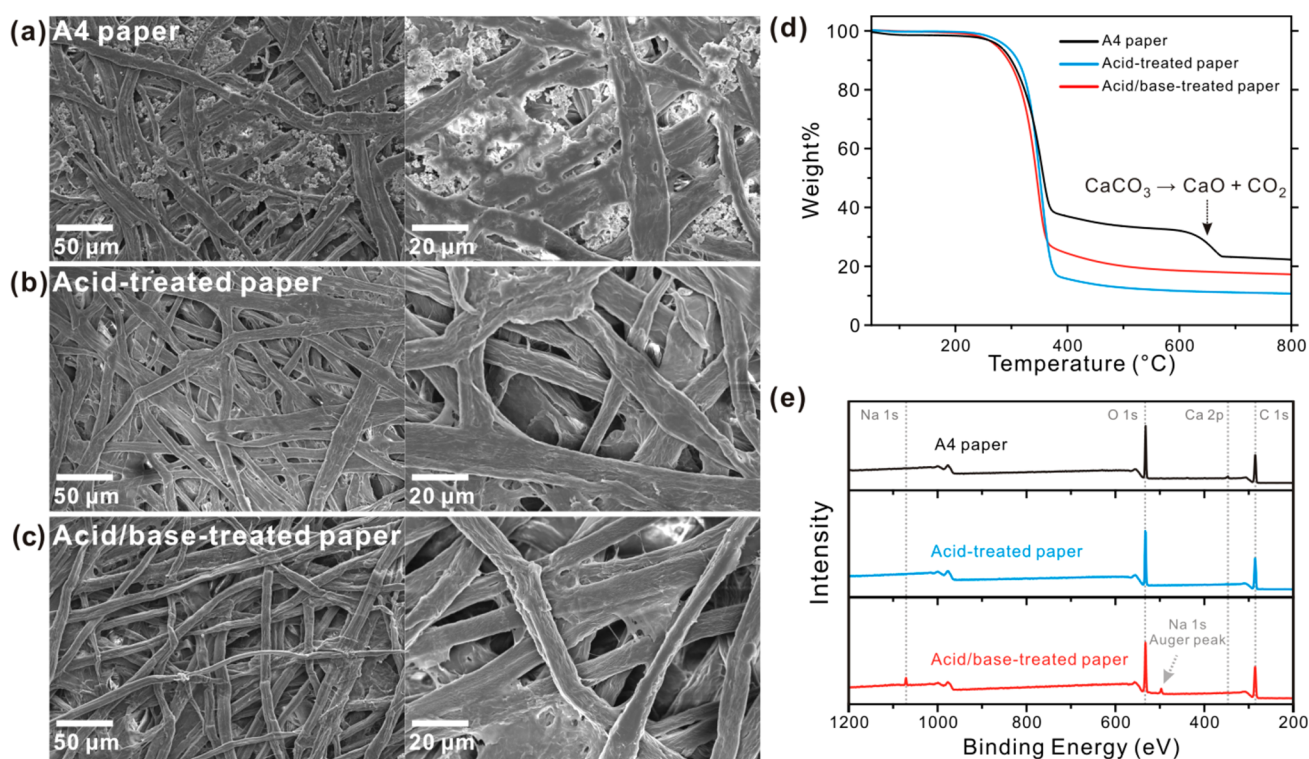


Figure 2. Morphology and characterization of samples derived from A4 paper. (a–c) SEM morphologies of (a) A4 paper, (b) acid-treated A4 paper, and (c) acid/base-treated A4 paper showing microporous cellulose structures. (d) TGA and (e) XPS spectra of paper samples before and after chemical treatments. Note that the white powder observed in the raw A4 paper is calcium carbonate.

processing.^{16,17} In a series of exemplary reports, Hu and co-workers have studied the selective extraction of cellulose from lignocellulose complexes and its modifications into diverse structures such as flexible membranes,¹⁸ buoyant aerogels,¹⁹ and physically strengthened wood blocks.²⁰ These applications are highly practical as macroscopic cellulose chemistry has limitless and sustainable possibilities.

In the macroscopic vision of cellulose chemistry, we observed that commercially available A4-sized printing paper (abbreviated as “A4 paper”) is one of the many cellulose abundant products which is easily accessible and can be processed to obtain a material with standardized size, shape, and composition. Paper production technologies have been steadily improved since 1965, thereby decreasing the cost of

production and energy consumption by more than half, while the total production of printing papers has increased more than 4-fold over the same period. On the basis of these efforts, the paper industry produces around 97 million tons of printing papers per year worldwide which provides us with a cost-effective and limitless handy source of cellulose composites (Figure S1). The industrial production of A4 paper involves multiple treatment steps including the removal of the lignocellulose complex (*i.e.*, “pulping”), by the addition of reinforcing agents (*e.g.*, starch and calcium carbonate) to enhance the physical properties (*e.g.*, printability and mechanical strength) and chemical properties (*e.g.*, water-resistance and brightness).^{14,15}

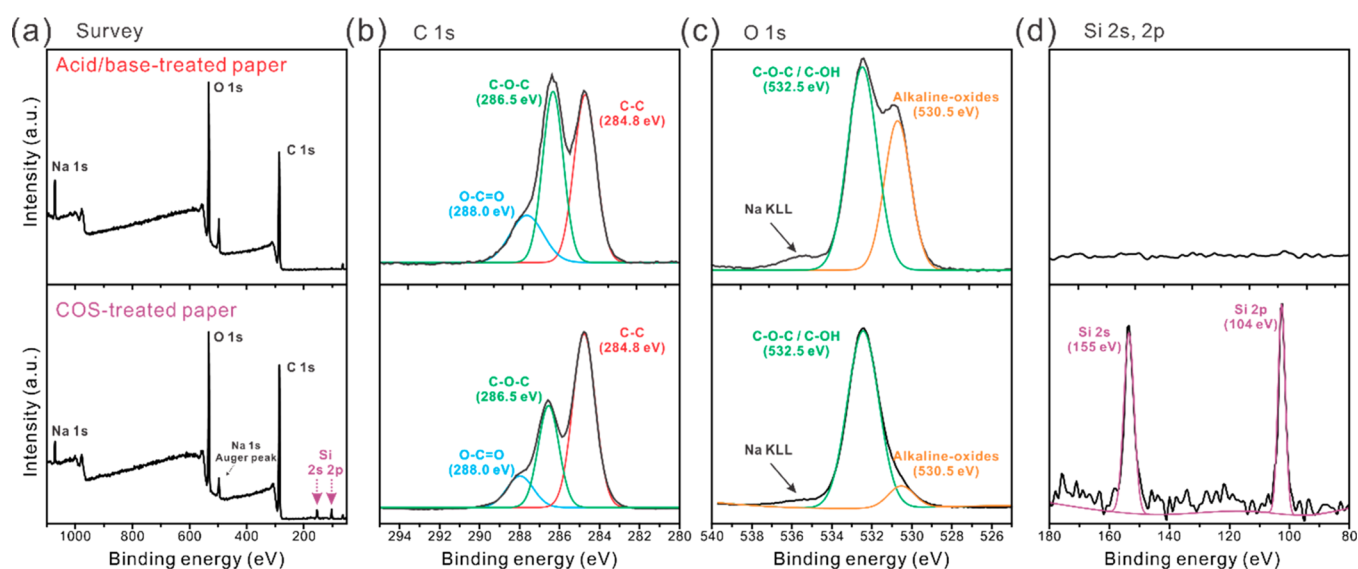


Figure 3. XPS characterization of (top panels) acid/base-treated and (bottom panels) COS-treated A4 papers including (a) survey spectrum with elemental deconvolution, (b) C 1s, (c) O 1s, and (d) Si 2s, 2p.

Herein, we demonstrate a method for developing highly efficient and tunable cellulose-based membranes, starting with commercially available A4 paper, followed by facile chemical modifications. Therefore, a few purification and functionalization steps could transform the A4 paper into user-modifiable and multifunctional cellulose membranes.

RESULTS AND DISCUSSION

As described in Figure 1, A4 paper was purified and chemically modified via a solution-processable two-step acid and base treatment to remove calcium carbonate and add alkoxide functional groups. In the following step, we introduced a hydrophobic silane on the cellulose surface, thereby switching the membrane affinity from hydrophilic to hydrophobic. The A4 paper modified cellulose membrane maintained high porosity with controllable pore diameters during processing. The chemical treatment steps on the A4 paper were monitored using elemental, morphological, and mechanical analyses, and the final product exhibited comparable membrane performance to those of commercial cellulose membranes.

The functionalized A4 paper based membrane exhibited a 3D porous structure along with chemically modifiable characteristics. Furthermore, the functionalized A4 membrane demonstrated significant separation behavior in water/oil mixture filtration and origami-assisted oil absorbency in the proof-of-concept process.^{21–23} We envision that our approach “A4 paper chemistry” will broaden the boundaries of cellulose chemistry and membrane technology.

The A4 paper chemistry is composed of two experimental parts: (1) pretreatment followed by (2) chemical modification. In Figure 2, we demonstrate how the pretreatment step influences the A4 paper membranes, preparing them for the subsequent chemical functionalization process. The pretreatment steps are composed of two sequential acid and base treatments by a simple dipping process. First, the calcium carbonate fillers in the A4 paper were removed by using 200 mM HCl solution, following the decomposition reaction under acidic condition: $\text{CaCO}_3(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + \text{CaCl}_2(\text{aq})$. The appearance of CO_2 bubbles from the paper was rapid and ceased within 1 min (Figure S2). After dipping

in HCl solution for 5 min, no peaks corresponding to calcium carbonate were observed in X-ray diffraction (XRD) and thermogravimetric analysis (TGA), suggesting the complete removal of the calcium carbonate filler in the A4 paper (Figure S2).^{24–27}

Subsequent base treatment with NaOH introduced a surface functional moiety on the cellulose fibers. The average diameter of the initial cellulose fibers was measured to be $12.98 \pm 2.12 \mu\text{m}$. However, it decreased to 11.64 ± 2.23 and $7.86 \pm 1.49 \mu\text{m}$ after the acid and acid/base treatment steps, respectively (Figure 2a–c). In accordance with this observation, the shrinkage of the cellulose-based frames after NaOH treatment is attributed to the selective degradation of lignin and hemicellulose compounds.¹⁸

Furthermore, the TGA result of the raw A4 paper indicated the thermal decomposition of calcium carbonate into calcium oxide and carbon dioxide at approximately 640–670 °C (Figure 2d).^{28–30} After the acid treatment, the weight percent of the final residue decreased from 21.6 to 10.7 wt % owing to the removal of calcium carbonate. Although the exact composition of A4 paper is classified industrial information, the approximate composition of cellulose/starch/calcium carbonate was ca. 80/5/15 in the A4 paper used in this study. In concert with this compositional ratio, TGA analysis indicated ca. 14–21% of calcium carbonate contained in the A4 papers. The removal of calcium carbonate after acid treatment is confirmed by the X-ray photoelectron spectroscopy (XPS) spectra, which indicate the absence of calcium ions (Figure 2e). Interestingly, the residual weight percent of the acid-treated paper increased from 10.7 to 17.3 wt % after the base treatment. This mass increase is mainly attributable to the introduction of sodium ions in the hydroxyl groups of cellulose, converting them to corresponding sodium alkoxide salts (see Figure 3 and following discussion). Although the pK_a value of the hydroxyl moieties in cellulose is estimated to be 12.0–12.5, the strong alkaline condition ($\text{pH} > 13$) from the base treatment facilitates ionization of the corresponding cellulose with an effective charge of -1.0 to -1.5 , as reported in previous literature.³¹ This functional moiety is critical for

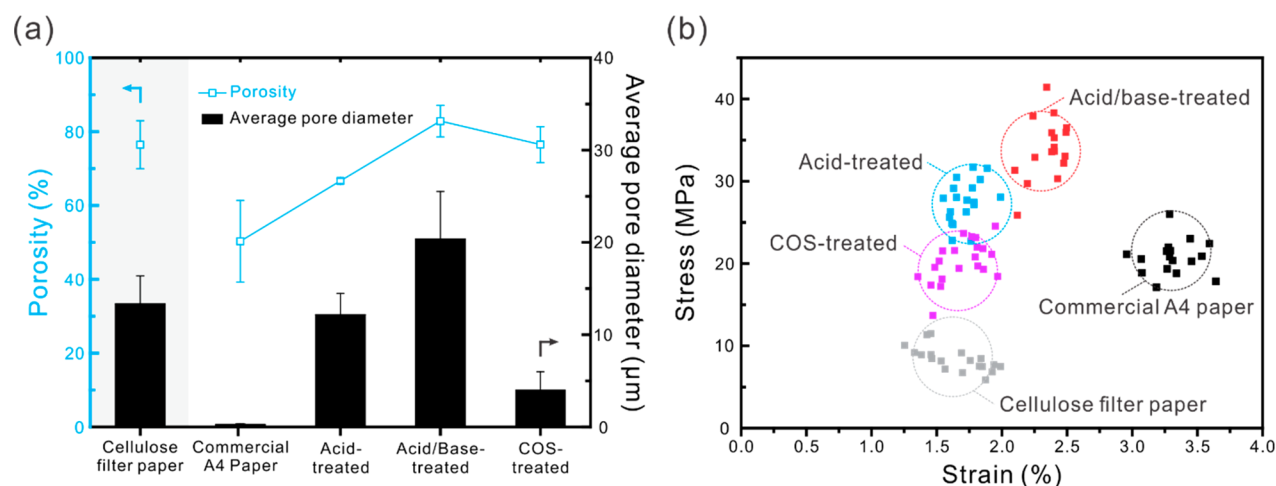


Figure 4. (a) Average pore diameters and porosities measured by mercury intrusion porosimetry and (b) mechanical properties of a commercial cellulose membrane and the functionalized A4-paper membranes prepared in the study. The mechanical property was collected for more than 30 samples for each membrane set.

introducing further chemical modifications to the acid/base-treated A4 paper membrane.

Following the pretreatment steps, further chemical functionalization involving silylating chemistry was performed on the acid/base-treated A4 paper. As a representative example, we chose trichlorooctylsilane (COS) for the modification of the hydroxyl groups on the surface of cellulose. The silylation reaction was controlled in a COS solution in hexane in an ambient environment.

The functionalization of COS molecules on the surface of the acid/base-treated membrane was carefully characterized using XPS, energy dispersive X-ray spectroscopy (EDS), and Fourier transform infrared (FT-IR) spectroscopy. XPS analysis indicated three important changes after COS functionalization: the increase of C–C bonding from 45.1% to 57.0% owing to the long aliphatic chains of the COS molecule in the C 1s peak, the appearance of the silicon peak to 3.3%, and the decrease of alkoxide portion in the O 1s peak.^{32–34} The FT-IR spectrum suggests that the cellulose structures remain intact during the acid and base treatment steps. Moreover, C–H stretching at ca. 2857–2927 cm^{-1} was observed after COS treatment step (Figure S3).³⁵

It is also important to note that the base-treatment step and the resulting alkoxide groups were necessary prior to the COS-treatment step. As confirmed by EDS analysis, the water-rinsing step after acid/base treatment removes the alkoxide groups, which diminishes the reactivity toward the COS molecule and inhibits the effective functionalization of the membranes (Figure S4). Meanwhile, the hexane-rinsing step maintained the alkoxide group for an effective functionalization with COS. To trace small quantities of the elements, we used inductively coupled plasma mass spectrometry (ICP-MS) to confirm the changes during chemical treatments. Sodium ions were partially removed (ca. 11%) after the COS treatment owing to the substitution with silane; however, complete removal was difficult as the initially hydrophilic cellulose membrane became hydrophobic. Calcium ions were initially abundant in the A4 paper, but they were mostly removed after the acid treatment step from 24 100 to 749 ppm. After the base treatment step, plenty of sodium ions were introduced from 65.5 to 31 500 ppm. Most importantly, the silylation of COS

chemicals increased silicon content from 593 to 3480 ppm (Figure S5 and Table S1).

The changes in the internal structure after the chemical modifications were observed by using mercury intrusion porosimetry (MIP). The internal structure of the prepared A4 paper-based membrane can be elucidated by measuring the porosity after each chemical treatment (Figure 4a). The initial average pore diameter and porosity of the commercial A4 paper were 0.31 μm and 50.3%, respectively, owing to the densely compressed cellulose fibers with calcium carbonate fillers from the manufacturing process. After the acid/base-treatment step, the overall average pore diameter and porosity increased to 12.2 μm and 82.9%, respectively, because of the removal of calcium carbonate and the partial decomposition of the cellulose fibers in acidic and alkaline conditions. The average diameter and porosity of the COS-treated membrane decreased to 4.01 μm and 76.5%, respectively. The properties of the prepared membrane are comparable to those of commercially available cellulose filter papers, having a similar porosity but the former having a smaller pore diameter. The decrease of the average pore diameter in the COS-treated membrane is due to newly generated microscale pores from the cross-linking of silane which was confirmed by the incremental mercury intrusion vs pore diameter curves (Figure S6). We also compared the permeability of each membrane using the Gurley test (Figure S7). The air permeation time was shortened by half (from 32 to 16 s) after the removal of the calcium carbonate fillers, implying the generation of macro-scale pores. The result of capillary flow porosimetry (CFP) revealed a similar average pore size, which was increased after the acid treatment step due to the removal of calcium carbonate fillers (Table S2). In this study, the pore size and distribution of membranes were evaluated with both MIP and CFP to understand their micro- and macroscale structural changes of cellulose fibers during chemical modification steps. While MIP measures the pore size of both through pores and blind pores at the nano- and microscale, CFP determines only the size of through macropores in solution. Thus, a relatively small variation of pore diameters in CFP analysis compared to MIP implies that macropores for fluid pathways were not affected during chemical modification steps.

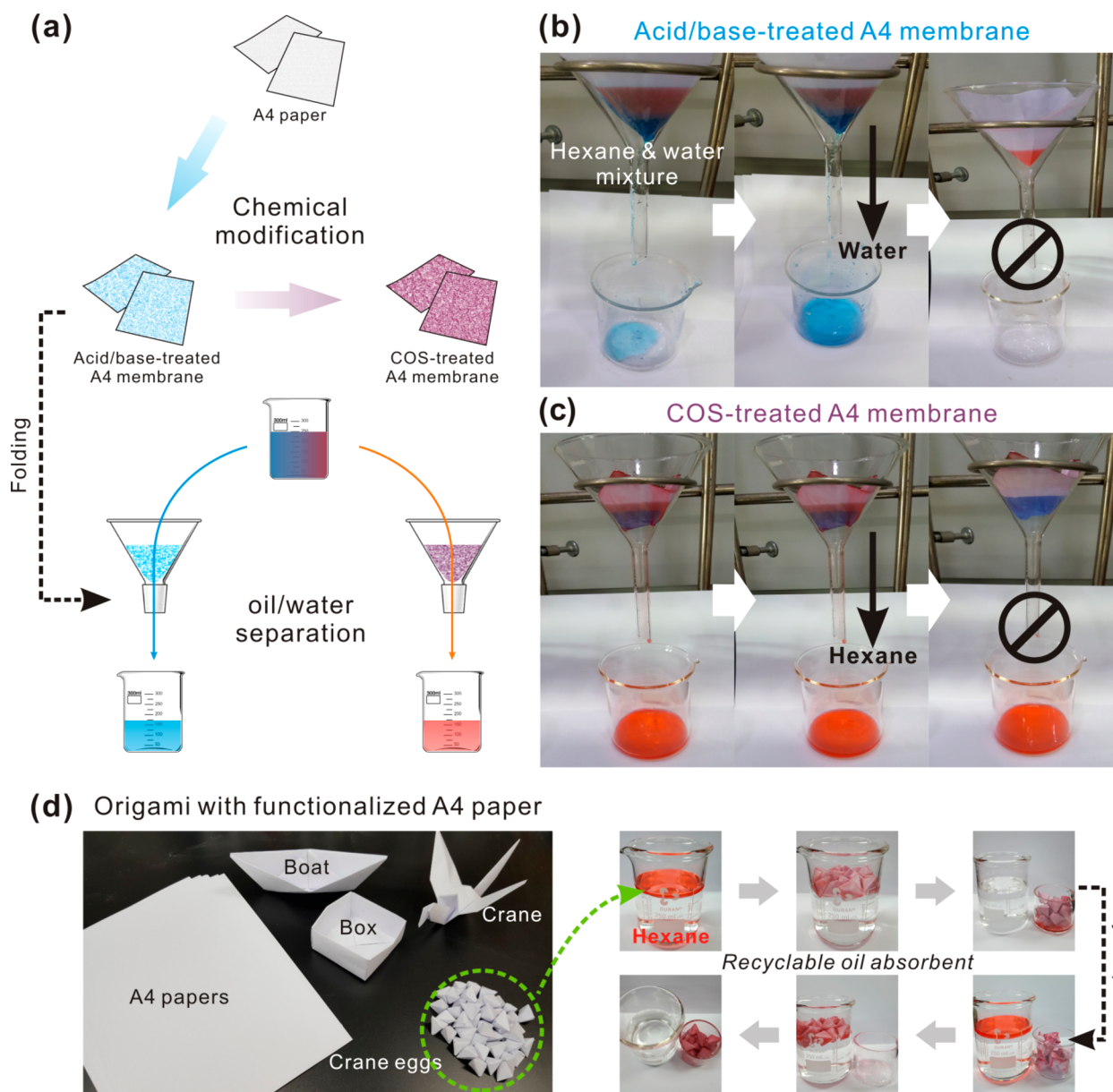


Figure 5. (a) Schematic illustration of chemically modified filtration membrane from A4 paper. Filtration tests with (b) acid/base-treated A4 paper membrane and (c) COS-treated A4 paper membrane. Water and hexane were colored with methylene blue (blue) and Sudan IV (red), respectively, to visualize the colorless solvents. (d) Origami-assisted application of a crane-egg-shaped COS-functionalized A4 paper membrane for oil absorbency.

The mechanical strength of the prepared membrane is essential for the modification of the A4 paper. The mechanical strength of the prepared A4 paper membranes was measured with a universal testing machine (UTM) (Figure 4b). All chemically modified A4 membranes displayed a similar or significantly higher ultimate strength and toughness than the ultimate tensile strength of the commercially available cellulose filter paper (6.10 MPa), indicating the applicability of the prepared membranes (Figure S8 and Table S3). The A4 papers exhibited an ultimate strength of approximately 20.7 MPa with a highest toughness of 50.1 MJ m^{-3} . The acid treatment step significantly reduced the toughness to 31.3 MJ m^{-3} , owing to the decomposition of the internal hydrogen bonds; nevertheless, base treatment was shown to improve the mechanical strength greater than that of other chemically modified A4 paper membranes.^{36,37} This phenomenon could be attributed

to the embedded sodium ions, as the subsequent COS treatment step dramatically decreased the mechanical strength owing to the elimination of the sodium ions by silane cross-linking, as observed by XPS. Understanding the mechanical properties of these prepared membranes in the presence of external ionic species will be the subject of our ongoing effort.

Encouraged by the successful functionalization of the A4 paper membrane, we further investigated its performance as an oil/water separation membrane. As a proof-of-concept, the performance of an acid/base-treated membrane and a COS-treated A4 paper membrane in water/oil filtration was tested, specifically in separating colored hexane and water via gravimetric filtration (Figure 5a). The acid/base-treated A4 membrane only allowed water to pass through while retaining the hexane (Figure 5b). In contrast, the COS-treated A4 membrane showed a selective permeability to hexane but

inhibited the permeation of water (Figure 5c). The control membranes, both commercial A4 paper and cellulose filter paper, could not separate the water/hexane mixture, which again highlights the role of proper surface chemistry for membrane utilization (Figure S9). It is important to note that the average pore diameter of the cellulose membrane is much larger (i.e., by the order of a few micrometers) than that of water and hexane molecules. The filtration test result implies that functional moieties on the surface are more important than the membrane pore sizes for selectivity.

Furthermore, the origami concept was adopted with A4 paper chemistry to expand the utility of the functionalized A4 membranes (Figure 5d). COS-functionalized A4 paper was transformed into crane eggs for oil absorbency, and these were reusable after the drying step. The quantitative analysis of pigment absorption in the UV-vis spectrum showed that approximately 0.2 mg of Sudan IV was absorbed in a single crane egg, which corresponds to 6.4 mg (128 ppm) of adsorbed pigments per single A4 paper (Figure S10). The modified A4 membranes were stable for over 10 min after filtration, with residual solvent on the membrane, demonstrating their mechanical stability for practical use. Another simple oil/water separation device of a lidless star-shaped boat was designed using an A4 paper based membrane coupled with origami (Figure S11). The COS-treated star-shaped boat can freely float on water when placed on a hexane/water mixture. Owing to the hydrophobicity of the COS-treated miniboat, water was repelled, while hexane was spontaneously collected inside the boat. After hexane was removed from the mixture using the boat, only clean water remained in the container with nearly 98% separation efficiency.

CONCLUSION

In summary, we developed a cellulose membrane capable of separating water and oil using commercial A4 paper via simple chemical treatment and modification. The calcium carbonate fillers present in the A4 paper were easily removed by acid treatment, and the subsequent alkaline treatment introduced alkoxide functional groups on the cellulose, thus providing additional sites for chemical reactions. Elemental analysis by XPS confirmed the removal of fillers from the A4 paper and the presence of chlorosilane-based chemicals after the modification steps. The porous structure of the A4 membrane changed as the microporous structure of the newly added silane compound expanded, which occurred during the modification steps. The functionalized A4 paper membrane demonstrated successful water/oil separation and was further applied to origami-assisted oil absorbency. This study provides possibilities for the future use of commercially available A4 papers as user-modifiable versatile cellulose-based membranes.

METHODS

Materials and Chemicals. Commercial A4 paper (Miilk, 75 g m⁻²) was manufactured by Hankuk Paper Mfg. Co., Ltd. Cellulose filter paper (Whatman Qualitative Filter Paper: grade 1) used for the control group experiments was purchased from GE Healthcare. All chemicals were of analytical grade and used as received without further purification. The reagents, including HCl, NaOH, and hexane, were purchased from Samchun Chemical, and deionized water (DI water, Milli-Q system) was used to process the A4 paper. Trichlorooctylsilane (COS), methylene blue, and Sudan IV were purchased from Sigma-Aldrich.

Chemical Treatments of A4 Paper and Filtration Tests. *Acid-Treated Paper.* Commercial A4 paper was prepared at the desired size

and shape and then dipped into 200 mM HCl solution for 5 min. The paper was then rinsed with DI water for 1 min to remove residual acid.

Acid/Base-Treated Paper. Acid-treated paper samples were dipped into 200 mM NaOH solution for 5 min. After the treatment, the paper was dried in vacuum oven at 40 °C for overnight to remove the residual moisture. It should be noted that the rinsing step with DI water was omitted for the following COS functionalization.

COS-Treated Paper. Fully dried acid/base-treated samples were first dipped into hexane for 1 min and then dipped into 300 mM trichlorooctylsilane (COS) in hexane solution for 5 min. Finally, the paper was rinsed with hexane for 1 min to remove residual chemicals. During the treatment, the container was enclosed to ensure a moisture-free environment.

Water/Hexane Filtration. Chemically treated papers were gently folded into a cone-shape and placed on a glass funnel. A mixture of colored water/hexane solution was poured slowly on the membrane. Colored solutions were poured periodically on the filtration paper. Water and hexane were colored with methylene blue (blue) and Sudan IV (red), respectively, to visualize the colorless solvents.

Origami-Assisted Separation Applications. For the absorbency test, the A4 paper was first folded into the crane egg shape before following the same process as above. The crane eggs were placed in a perforated plastic box to be fully immersed in the reaction and rinsing solutions, as they naturally float on the solution for either water or hexane. COS-treated crane eggs were dipped into the colored hexane and water mixture for 1 min and moved to a vacuum oven at 40 °C to dry for 30 min to remove absorbed hexane, and the same cycle was repeated. Similar to the crane eggs, a star-shaped miniboat was subjected to the same procedures and placed over a colored water/hexane mixture. After enough hexane was collected in the miniboat, a pipet pump was utilized to remove the hexane. The separation efficiency was calculated based on the following equation, $\eta = \frac{m_1}{m_0} \times 100\%$, in which η is the separation efficiency and m_0 and m_1 are the mass of hexane before and after the separation process, respectively.

Measurements and Characterizations. Scanning electron microscopy (SEM) measurements were recorded on S-4800 (Hitachi) and Nova NanoSEM (FEI) instruments at an accelerating voltage of 10 kV. Energy dispersive X-ray spectroscopy (EDS) coupled with SEM was employed at an accelerating voltage of 15 kV. TGA was carried out on a Q50 system (TA Instruments) at a scan rate of 10 °C min⁻¹. X-ray diffraction (XRD; SmartLab, Rigaku), X-ray photoelectron spectroscopy (XPS; K-alpha, Thermo Fisher), inductively coupled plasma-mass spectroscopy (ICP-MS; NexION300, Perkin-Elmer), and Fourier transform infrared (FT-IR) analysis (670-IR, Varian) were used for elemental and qualitative analysis of the membranes. UV-vis spectroscopy (Cary 5000, Varian) was used to quantify the concentration of dye in hexane solution.

Porosity and Average Pore Size Distribution. Porosity/pore size analysis was performed using mercury intrusion porosimetry (PM33GT, Quantachrome) and capillary flow porosimetry (1100-A CFP, Porous Media Inc.). Here, two independent instruments were used for the cross-validation of the data. Mercury intrusion porosimetry (MIP) was used to determine the pore volumes and pore size distributions of the membranes using pressure ranges from 0.2 to 33 000 psi. Capillary flow porosimetry (CFP) was used to determine the pore size and its distribution. To fully wet the membranes prior to CFP analysis, they were incubated with the wetting liquid (surface tension = 15.4 dyn/cm) for 1 day. A Gurley permeability tester (4340 Automatic Densometer, Gurley Precision Instruments) was utilized to confirm the relative air permeability of the membranes.

Mechanical Properties. Stress-strain curves were determined using an Instron (Instron 5943, UK) universal testing machine (UTM) loaded with a 1 kN load cell at a constant speed of 1 mm min⁻¹ at 25 °C. The test specimens had a dog-bone shape, with a length, width, and thickness of 25.5, 3.11, and 3.1 mm, respectively. All test samples were performed according to ASTM D638-03.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsnano.0c02211>.

Characterization data of XRD, TGA, FT-IR, SEM-EDAX, ICP-MS, mercury intrusion porosimetry, capillary flow porosimetry, Gurley test, UTM, UV-vis, and water/hexane separation experiment (PDF)

Video clip of the water/hexane separation process (MP4)

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Author Contributions

The manuscript was written with the contributions of all authors. All authors have approved the final version of the manuscript. E.A. and B.-S.K. contributed to the overall idea development and experimental design. E.A. performed the membrane preparation and characterizations. T.K. contributed the elemental characterizations. Y.J. contributed the morphological characterization with SEM.

Notes

The authors declare no competing financial interest.

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