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COMMUNICATION

Paper miniaturization via periodate oxidation of cellulose

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Abstract Cellulose-based paper is a versatile material with a diverse array of applications. While paper is not commonly thought of as a material that shrinks, here we present a method for miniaturizing paper via periodate oxidation. Chromatography paper was exposed to varying concentrations of periodate (0.1–0.5 M) over a 96-h period. Following optimization of miniaturization parameters, fourteen different types of paper were miniaturized and reductions in surface area ranging from 60 to 80% were observed. All cellulose paper types, but not cellulose-derivatives, displayed successful miniaturization. Results were highly tunable dependent upon periodate concentration and reaction time. Potential applications of the technique are discussed, including its use as a microfabrication method.

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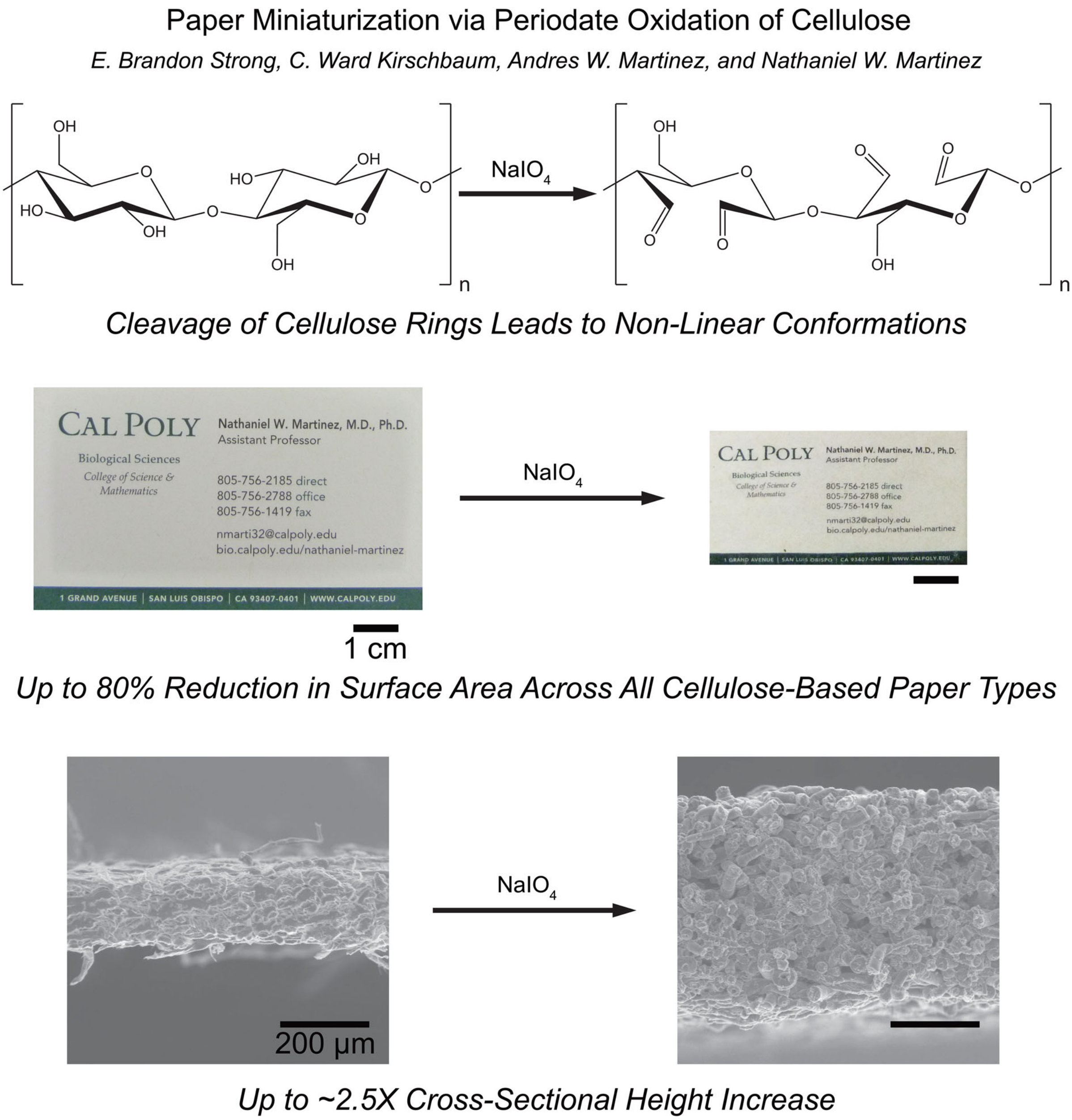
Graphical Abstract



Keywords Malaprade reaction · Shrinking paper · Sodium metaperiodate · Shrinkage of paper · Filter paper · Chromatography paper · Printer paper · Periodic acid · $NaIO_4$ · HIO_4

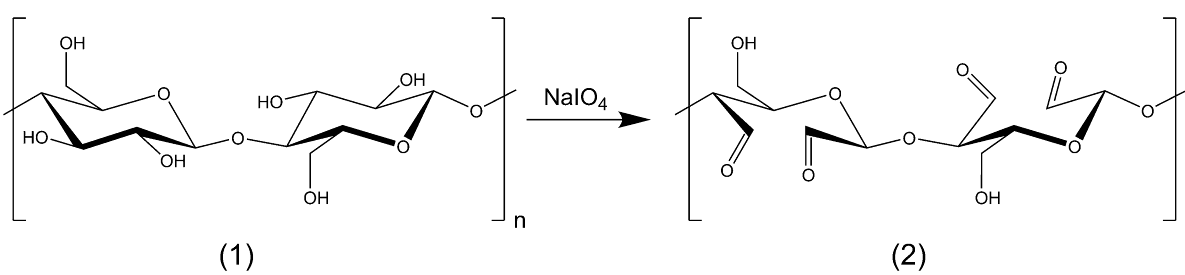
Introduction

Originally discovered in 1838 by Anselme Payen, cellulose $(C_6H_{10}O_5)_n$ is the most abundant organic polymer on Earth (Klemm et al. 2005). Today, cellulose is utilized in a diverse array of applications, including the production of fibers (e.g., cotton, rayon, cellophane, etc.), consumables (e.g., powdered cellulose as an inactive drug filler or food additive), biofuels (e.g., converted to butanol), and as a tool for laboratory techniques (e.g., chromatography and filtration). However, by far the most common application of cellulose is in paper products (e.g., currency, books, cardboard, tissues) (Klemm et al. 2005). Paper, traditionally defined as a thin sheet of pressed cellulose fibers, is generally produced via the following process: raw material (e.g., wood) preparation, pulp manufacturing, pulp washing/screening, chemical finishing (dependent on purpose), and finally, pressing/drying. This fabrication process can be used to produce paper types varying in thickness, density, pore size, and finish.

While cotton (another cellulose-based material) is known to shrink slightly when laundered (Fletcher and Roberts 1953; Juciene et al. 2006), paper is not typically thought of as a material that shrinks. To our knowledge, only two methods for miniaturizing cellulose-based paper have been reported: (1) multiple cycles of exposure to liquid ammonia followed by drying (Hermann 1997), and (2) saturation in aqueous solutions of periodate (Jackson and Hudson 1937; Davidson 1941). The method involving liquid ammonia was used previously to produce miniaturized paper currency (~ 55% reduction in surface area) (Hermann 1997). Alternatively, periodate oxidation of cellulose via the Malaprade reaction (Scheme 1) (Malaprade 1928, 1934) has been investigated extensively for the production of cellulose derivatives (Guthrie 1962; Potthast et al. 2007), as well as for making covalent modifications to the surface of paper (Su et al. 2007; Wang et al. 2012). Two studies from the first half of the twentieth century briefly mentioned the shrinkage of filter paper via periodate oxidation. Jackson and Hudson (1937) first made note of this phenomenon upon saturating paper in 0.271-M periodic acid (HIO_4) over a 37-day period, resulting in a 75% reduction in surface area. Davidson (1941) achieved a 72% reduction in the surface area of paper following saturation in 0.094-M periodic acid; the time required was not specified. We recently rediscovered the use of periodate for miniaturizing paper, and investigated its effect on multiple paper types. We did not examine the use of liquid ammonia due to the associated risks, more complex procedure, and reduced miniaturization effects as compared to periodate oxidation.

Experimental

Solutions of sodium metaperiodate ($NaIO_4$) with concentrations of 0.1, 0.2, 0.3, 0.4, and 0.5-M were prepared in deionized water. The maximum solubility of $NaIO_4$ in water at room temperature (~ 25 °C) was found to be ~ 0.5-M. Whatman No. 1 chromatography paper (4.5 × 4.5 cm) was saturated in 25 mL of each $NaIO_4$ solution in a covered glass dish at room temperature and in the dark (to minimize light sensitivity). The paper was removed at varied intervals ranging from 3 to 96 h. After removal, the paper was placed in a deionized water bath on a rocker for 15 min to remove any excess periodate. Without washing, the paper may turn a light-yellow color upon desiccation. Following washing, the paper was dried for 1 h in a slab gel dryer (Bio-Rad Model 443) at 60 °C and 300 Torr. Paper can also be dried between blotting paper at room temperature over a 24-h period (no gel dryer necessary). To minimize paper distortion during the miniaturization process, the paper can be sandwiched between two panes of glass. Following optimization of miniaturization conditions, an array of paper types was miniaturized in 0.5-M $NaIO_4$ for 48 h (n = 3 per paper type). Paper surface area measurements were performed with a ruler, and cross-sectional



Scheme 1 Oxidation of cellulose (1) with sodium periodate to generate 2,3-dialdehyde cellulose (2)

width was measured with a scanning electron microscope (FEI Quanta 200). The presence of aldehydes (Scheme 1) was confirmed via Raman spectroscopy (Figure S1).

Results and discussion

Slight miniaturization was observed in as little as 3 h; however, the optimal concentration and incubation period was determined to be 0.5-M $NaIO_4$ (max solubility of $NaIO_4$ in water at room temperature) and 48 h (Fig. 1). Most of the observed miniaturization effects occurred while in solution, but some additional shrinkage was observed following desiccation. While extended incubation periods did lead to slightly greater reductions in surface area, there was only a 1% difference in surface area between paper incubated for 48 and 96 h. In addition to an 80% reduction in surface area (Table 1), Whatman No. 1 CHR paper displayed a 166% increase in cross-sectional width (Fig. 2b). Surface area reduction, paired with cross-sectional width increase, is a trend that is also observed when miniaturizing thermoplastic shrink films (Grimes et al. 2008). While not examined in this study, the rate of cellulose oxidation by periodate has also previously been shown to be affected by temperature, electrolyte concentration, and pH (Nevell 1957).

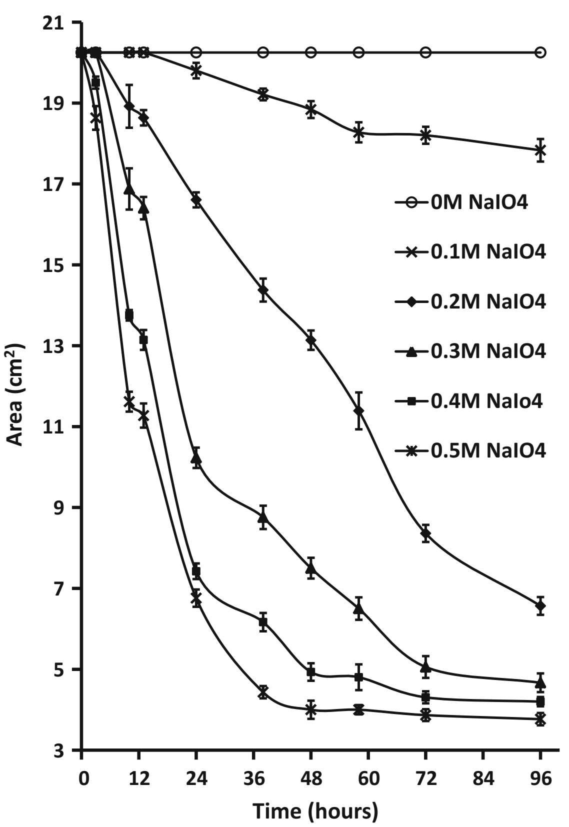


Fig. 1 Miniaturization of Whatman No. 1 Chromatography paper over time in increasing concentrations of aqueous sodium periodate ($NaIO_4$). The optimal concentration and incubation period for the miniaturization of paper was determined to be 0.5-M $NaIO_4$ and 48 h

Following optimization of the miniaturization method using chromatography paper as a model, the method was tested on other paper types with the optimized conditions of 0.5-M $NaIO_4$ and 48-h incubation. All types of cellulose paper shrank anisotropically, with an average area reduction of 72% (Table 1, Fig. 2a). It is hypothesized that this shrinkage can be attributed to the formation of intramolecular hemiacetals between aldehyde groups and the primary alcohol in 2,3-dialdehyde cellulose (oxidized form of cellulose, Scheme 1) (Guthrie 1962). This intramolecular reaction cannot occur in a chair conformation, and would therefore lead to non-linear conformations and buckling, ultimately resulting in miniaturization (Guthrie 1962). Non-uniform linear shrinking can likely be attributed to the anisotropic nature of paper fibers, and was similarly observed in the shrinking of paper with liquid ammonia (Hermann 1997). Both mixed ester and nitrocellulose paper displayed no size reduction upon exposure to periodate (Table 1). Put together, these findings indicate successful miniaturization of all types of cellulose paper, but not cellulose derivatives, which would be expected based on the mechanism of the Malaprade reaction (Scheme 1).

Additional observations on miniaturized paper included slightly increased hydrophobicity, less distortion of thicker paper, high fidelity of the miniaturization process (Fig. 2a), and slightly reduced levels of miniaturization for 'hardened' filter paper (− 63% change, Table 1). Increased hydrophobicity may be attributed to reduced pore volume upon miniaturization (Fig. 2b), or the reduced number of hydroxyl groups in the oxidized form of cellulose (Scheme 1). As a side note, hydrophobic cellulose has been previously shown to increase in thickness upon desiccation (Chen et al. 2015), and may be a contributing factor to this observed phenomenon in miniaturized paper (Fig. 2b). Overall, our optimized

Table 1 Miniaturization of different paper types (n = 3)

Brand	Type	Chemistry	Dimension 1 % change[a]	Dimension 2 % change	Area % change
Whatman No. 1	Chromatography	Cellulose	− 57.0	− 54.1	− 80.2
Whatman No. 3	Chromatography (3 mm)	Cellulose	− 50.7	− 44.8	− 72.8
Hammermill	Printer (75 g/m^2)	Cellulose	− 47.4	− 40.7	− 68.8
Fisherbrand	Weighing (low nitrogen)	Cellulose	− 58.1	− 48.5	− 78.4
Whatman No. 1	Filter (standard, 11 μm)	Cellulose	− 46.3	− 41.5	− 68.6
Whatman No. 3	Filter (standard, 8 μm)	Cellulose	− 48.3	− 43.3	− 70.7
Whatman No. 4	Filter (standard, 20–25 μm)	Cellulose	− 44.4	− 43.0	− 68.3
Whatman No. 5	Filter (standard, 2.5 μm)	Cellulose	− 50.0	− 47.2	− 73.6
Whatman No. 31	Filter (low ash)	Cellulose	− 52.2	− 45.0	− 73.7
Whatman No. 40	Filter (ashless, 8 μm)	Cellulose	− 58.1	− 48.5	− 78.4
Whatman No. 42	Filter (ashless, 2.5 μm)	Cellulose	− 47.0	− 45.6	− 71.1
Whatman No. 52	Filter (hardened low ash, 7 μm)	Cellulose	− 43.3	− 36.3	− 63.9
Whatman No. 541	Filter (hardened ashless, 20–25 μm)	Cellulose	− 41.5	− 34.8	− 61.9
Micro filtration systems No. 2	Filter (standard, 90 g/m^2)	Cellulose	− 48.1	− 44.8	− 71.4
		Average	− 49.5	− 44.2	− 71.6
Fisherbrand	Filter (0.45 μm)	Nitrocellulose	0.0	0.0	0.0
Millipore sigma	Filter (0.45 μm)	Mixed cellulose esters	0.0	0.0	0.0
		Average	0.0	0.0	0.0

All paper saturated in 0.5-M $NaIO_4$ for 48 h. Only cellulose paper displayed miniaturization. Initial dimensions: 4.5 × 4.5 cm

[a]Dimension 1 was arbitrarily determined to be the side with greater percent change

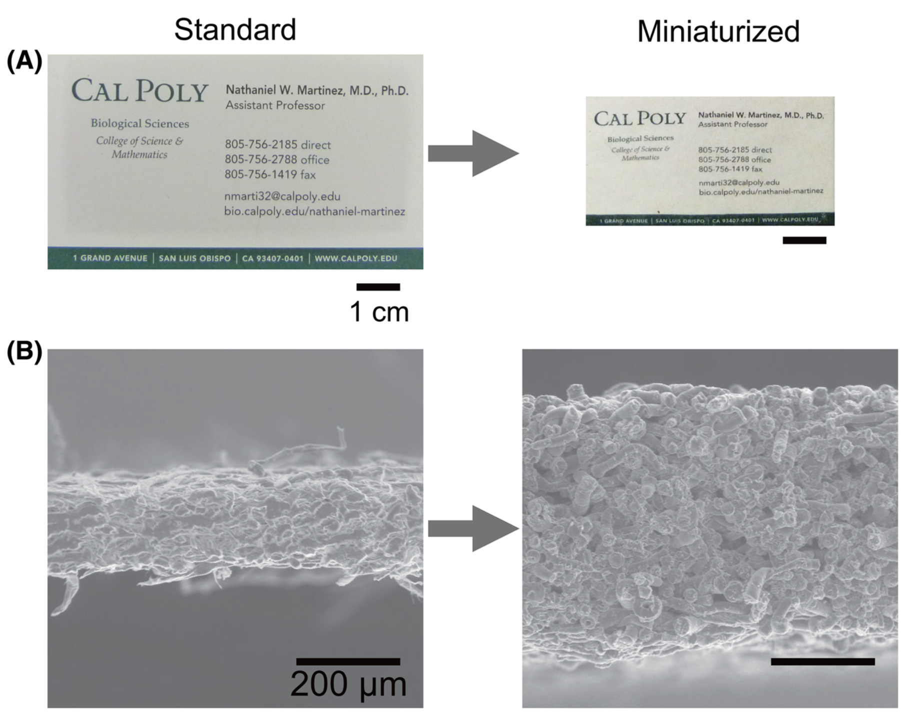


Fig. 2 Miniaturization of paper via periodate oxidation of cellulose. **a** Photograph of standard business card (8.9 × 5.1 cm, 3.5 × 2 in.) pre- and post-miniaturization (60% reduction in surface area). Photographs display high fidelity of the miniaturization process. **b** Scanning electron microscope cross-sectional images (166% width increase)

method of miniaturizing paper has significant advantages over those published previously by Davidson (1941) and Jackson and Hudson (1937). We observed complete miniaturization of cellulose filter paper after only 48 h and without having to replace the periodate solution (Table 1), as compared to the previously reported incubation period of 37 days combined with multiple periodate solution cycles (Jackson and Hudson 1937). Additionally, we tested this method on an array of cellulose paper types to demonstrate that it is effective for miniaturizing cellulose-based membranes but not membranes made from cellulose-derivatives (Table 1). Finally, our results indicate that this method of paper miniaturization is highly tunable, dependent upon periodate concentration and reaction time (Fig. 1).

Paper miniaturization via periodate oxidation of cellulose can be utilized in a wide array of applications, including as a novel microfabrication technique. The concept of shrinking materials has long been used as a method of microfabrication due to the ease with which larger, lower-resolution structures can be converted into smaller, higher-resolution structures without the need for sophisticated equipment. This has been previously demonstrated using thermoplastic shrink films (Grimes et al. 2008), as well as hydrogels, which can shrink upon desiccation or in response to environmental changes (e.g., pH or temperature) (Aldalali et al. 2014). More specifically, our lab is currently investigating the possibility of creating higher-resolution wax-patterned features in paper-based microfluidic devices via this process. Beyond microfabrication, our lab is also investigating paper miniaturization as a method of inserting wrinkles into monolayer graphene sheets (Deng et al. 2016), and as a demonstration of paper chemistry suited for use in both high school and university-level classes. It is our hope that this brief report will provide researchers with a novel tool for working with cellulose-based membranes, and thus find innovative ways to incorporate this technology.

Conclusions

We recently rediscovered a method of miniaturizing cellulose paper via saturation in an aqueous periodate solution, and subsequently optimized this method. Optimal miniaturization conditions were determined to be 0.5-M periodate and a 48-h incubation period. Under these parameters, fourteen cellulose-based paper types displayed between 60 and 80% reduction in surface area, while cellulose-derivatives displayed no such miniaturization effects. Results were highly tunable dependent upon periodate concentration and reaction time. Potential applications of this technology are discussed.

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Authors' Contributions EBS: study design, data collection, data analysis, manuscript drafting and revision, final approval of the version to be published, accountability for all aspects of the work; CWK: data collection, data analysis, final approval of the version to be published, accountability for all aspects of the work; AWM: study design, data collection, data analysis, manuscript drafting and revision, final approval of the version to be published, accountability for all aspects of the work; NWM: study design, data collection, data analysis, manuscript drafting and revision, final approval of the version to be published, accountability for all aspects of the work.

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