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# Combined Nanocellulose/Nanosilica Approach for Multiscale Consolidation of Painting Canvases

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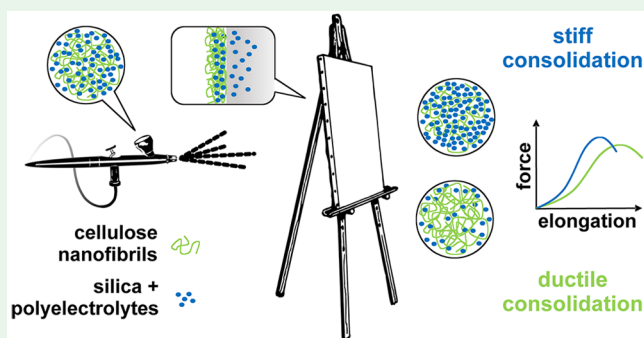
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## S Supporting Information

**ABSTRACT:** The restoration of painting canvases is a complex problem that, because of the hierarchical nature of the canvas, requires intervention at several length scales. We propose an approach combining polyelectrolyte-treated silica nanoparticles (SNP) and cellulose nanofibrils (CNF) for canvas consolidation. The formulations, applied on model-degraded canvases, gave a total weight increase of <5 wt %. Scanning electron microscopy and micro-X-ray fluorescence measurements were used for determining the component distribution across the canvas depth, while tensile testing demonstrated the mechanical efficiency of the consolidation. CNF formed a film at the canvas surface that increased the ductility. SNP penetrated deeper and reinforced at the fiber scale, yielding higher stiffness. The two effects could be balanced by varying the SNP/CNF ratio to reach a suitable reinforcement. This approach offers an alternative to the conventional treatments based on, e.g., relining with a new canvas or application of synthetic film-forming compounds.

**KEYWORDS:** conservation, restoration, canvas, cellulose nanofibrils, silica nanoparticles



From a structural point of view, canvas is one of the most important components of easel paintings, with its main function being to provide support to the paint layers. Canvases are generally woven from natural cellulose-based fibers and therefore are prone to aging.<sup>1</sup> Besides inducing color changes, aging results in deterioration of the mechanical properties and in extreme cases in a loss of integrity of the canvas. This weakening generates stress on the paint layer, potentially leading to irreversible damage. The two main processes by which canvas degrades are of environmental origin: (i) stress changes as a result of temperature and humidity variations<sup>2</sup> and (ii) chemical degradation of cellulosic chains due to oxidation and acid-catalyzed hydrolysis.<sup>3</sup>

The problem of canvas consolidation has traditionally been tackled by the application of an adhesive layer (e.g., rabbit glue, lacquer), which can be followed by lining, i.e., attachment, of a new canvas onto the back side of the painting.<sup>4,5</sup> Owing to the hygroscopic character of cellulose-based canvas, the use of water-based adhesives is often problematic because it causes variations of the canvas dimensions. Generally speaking, the treatments are invasive and provide only a partial solution to the problem because the canvas is only treated on the outermost surface.<sup>6</sup> Furthermore, they are not reversible. Part of the problem is derived from the structure of the canvas, which is complex due to the hierarchical assembly of cellulose fibers. The fibers are interlocked into yarns, and the yarns are

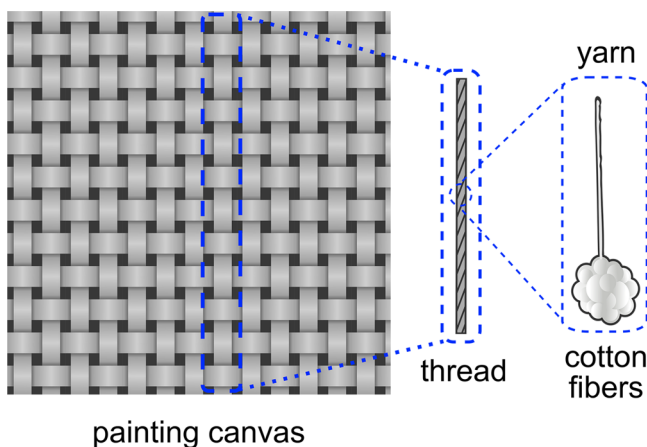
twisted into threads to be woven into textile (see Figure 1). Therefore, the consolidation can only be truly efficient if it operates at all of the different length scales.

The growing trend of minimal intervention and reversibility of the applied treatment promotes the use of nanomaterials in art restoration.<sup>7</sup> Nanomaterials can be very efficient even at low concentration, and because of their small size, they penetrate well into the material to be treated. The utilization of nanomaterials has been growing in many areas of conservation, e.g., cleaning,<sup>8</sup> deacidification,<sup>9</sup> and consolidation.<sup>10,11</sup> Furthermore, as a result of the toxicity of some of the widely used synthetic adhesives, e.g., Beva 371, and despite the water sensitivity of canvas, the trend goes toward waterborne treatments.<sup>5,12</sup> One of those is nanocellulose, which has recently been demonstrated as a natural consolidant for painting canvases.<sup>13</sup> Owing to a very large aspect ratio (i.e., the thickness is in the nanoscale, while the length is generally in the microscale), the application of nanocellulose gave a continuous film on the canvas surface without much penetration. It may therefore be beneficial to introduce an

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**Figure 1.** Schematic illustration of the complex structure of a painting canvas.

additional component that penetrates further into the material to provide consolidation at a different length scale.

We present here a combined approach based on (i) polyelectrolyte-treated silica nanoparticles (SNP) and (ii) cellulose nanofibrils (CNF) in a one-pot formulation that provides the potential for such multiscale reinforcement. While SNP provide consolidation at the single fiber level, CNF act on the canvas surface. To the best of our knowledge, this is the first time that this synergistic approach has been explored.

For consolidation purposes, colloidal silica is a strong candidate. Besides being abundant, nontoxic, and inexpensive,<sup>14,15</sup> it has proven to be a good reinforcing agent for other fibrous materials such as paper<sup>16,17</sup> and textile.<sup>18</sup> It is alkaline in nature and may provide deacidification, an issue that is practically important but remains beyond the scope of this paper. The second component of the formulations, CNF, belongs to the recently developed group of cellulose-based materials called nanocellulose.<sup>19</sup> Both components have previously been shown to provide good reinforcement on paper<sup>20,21</sup> and on cotton canvas when used individually.<sup>13,22</sup>

CNF have the same chemical nature as the canvas and may therefore be expected to interact well with the fiber surface. In order to enhance the interaction of SNP with cellulose, we coated SNP with polyelectrolyte multilayers (PEMs), which consisted of the cationic polymer poly(ethylenimine) (PEI) and the anionic polymer (carboxymethyl)cellulose (CMC), using a procedure that allowed the formation of multilayers without almost any aggregation and that ended with a layer of cellulosic nature. A detailed description of the preparation of SNP (referred to here as CMC@SNP) can be found elsewhere and in the [Supporting Information](#).<sup>23</sup> The outermost CMC layer rendered the SNP negatively charged, thus preventing flocculation with the likewise negatively charged CNF. The two polyelectrolytes have previously been used in different applications related to art restoration and have proven to be stable under normal conditions.<sup>12,24</sup> Because PEI tends to turn yellow at temperatures above 100 °C or when exposed to UV radiation,<sup>25</sup> its concentration in the preparation of CMC@SNP was reduced to a minimum (see the [Supporting Information](#)). Under the normal conditions of aging, no color change could be noticed.

Aqueous formulations with different CMC@SNP:CNF mass ratios were applied by spraying onto the model surfaces of degraded cotton canvases and evaluated using scanning

electron microscopy (SEM), X-ray fluorescence (XRF), and tensile testing. Pure dispersions of silica/CMC complexes and of CNF were used as reference formulations. The model surface of the degraded cotton canvas was obtained by accelerated aging in H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub>.<sup>26</sup> The mass gains of the treated canvases are listed in [Table 1](#).

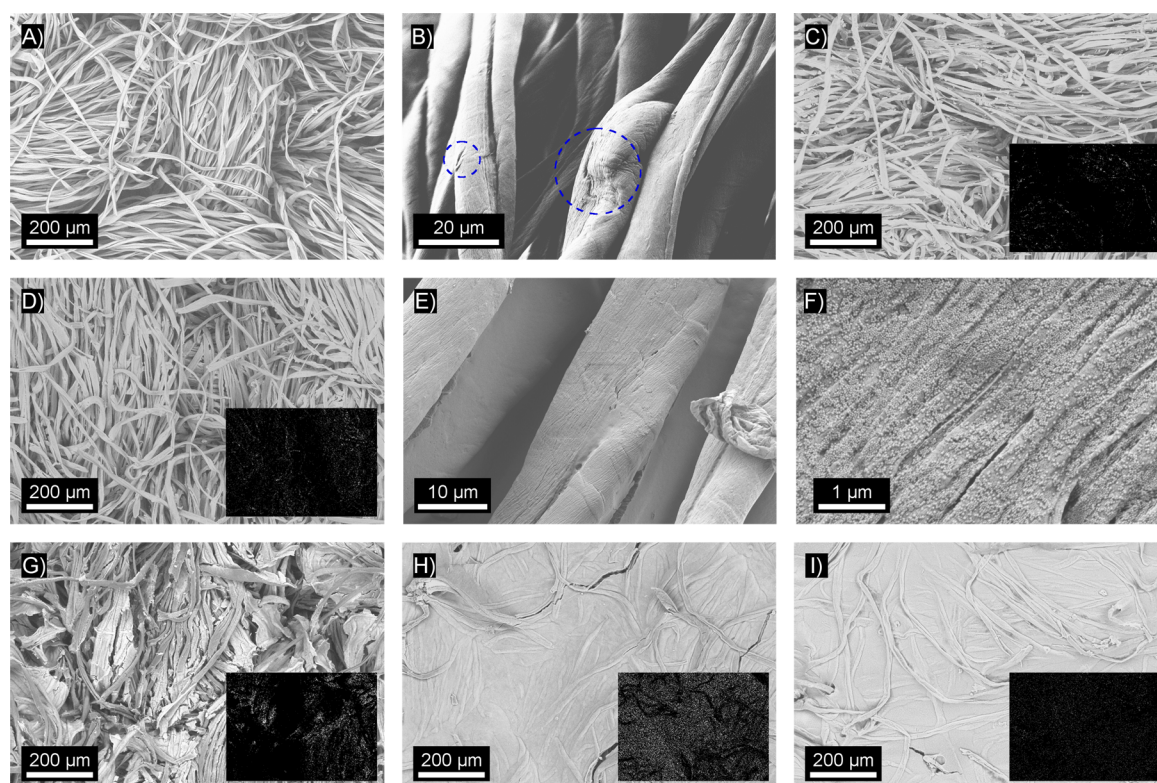
**Table 1. Mechanical Properties of Degraded Canvas before and after Application of Formulations<sup>a</sup>**

CMC@ SNP:CNF (w/ w)	no. of coatings	breaking force (kN/m)	elongation at break (%)	mass uptake (wt %)
no treatment		4.24 ± 0.38	35.4 ± 1.0	
0:1	1	4.46 ± 0.20	36.8 ± 1.0	1.2
	2	5.04 ± 0.42	41.0 ± 2.4	2.5
	3	4.74 ± 0.32	40.3 ± 3.4	3.2
1:9	1	4.79 ± 0.30	37.8 ± 1.0	1.3
	2	4.75 ± 0.40	39.5 ± 1.8	2.5
	3	4.87 ± 0.29	39.5 ± 1.3	3.3
1:1	1	4.77 ± 0.28	36.7 ± 1.2	1.1
	2	5.10 ± 0.25	37.6 ± 1.1	2.2
	3	5.05 ± 0.55	39.3 ± 3.3	3.4
9:1	1	5.46 ± 0.41	33.1 ± 2.4	3.7
	2	5.80 ± 0.59	34.0 ± 2.1	7.2
	3	5.89 ± 0.39	34.2 ± 1.9	9.4
1:0	1	5.02 ± 0.22	28.6 ± 1.6	5.3
	2	5.30 ± 0.26	27.9 ± 0.7	8.6

<sup>a</sup>The extreme right column presents mass uptake of the samples due to the treatment.

SEM images of the canvas surfaces before and after treatment are shown in [Figure 2](#). The nontreated canvas surface is shown in [Figure 2A](#), while [Figure 2B](#) shows a closeup of the cracks formed during degradation (see the dashed circles). Parts C and D of [Figure 2](#) display the canvas surface after application of SNP and CMC@SNP dispersions, respectively. As can be seen from the magnified fibers in [Figure 2E,F](#), the deposited CMC@SNP tends to form homogeneous monolayers. This is the result of the presence of PEMs, which prevented uncontrolled SNP gelling during drying. The results from formulations having CMC@SNP:CNF ratios of 9:1, 1:1, and 1:9 are demonstrated in parts G–I of [Figure 2](#), respectively. The insets show silica abundance on the surface of the treated samples (indicated by white color) obtained by energy-dispersive X-ray (EDX) analysis. With the application of formulations solely based on SNP, the silica signal on the surface was relatively low, which indicates that the nanoparticles penetrate into the canvas, probably promoted by the capillary action of the fibrous network. The presence of CNF significantly increased the silica signal intensity on the surface of the samples. It is, however, difficult to draw conclusions regarding the effect of the entangled network formed by CNF on the penetration because EDX is surface-sensitive and has a very limited depth of penetration. Previous results for CNF-treated painting canvases<sup>13</sup> and cotton fabrics<sup>27</sup> have demonstrated the film-forming properties of CNF and the tendency to accumulate at the surface of the fabric. Evidently, the introduction of SNP did not change this behavior. The SEM pictures also indicate that increasing the CNF content led to films with higher flexibility. The film shown in [Figure 2I](#) had very few cracks compared to the specimen with the lowest CNF content displayed in [Figure 2G](#).





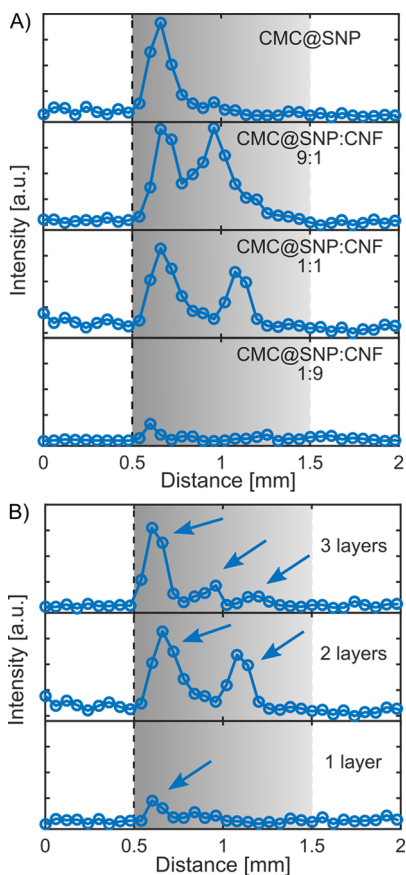
**Figure 2.** SEM pictures of degraded cotton canvas (A and B) before and after treatment with (C) silica, (D–F) CMC@SNP, and different CMC@SNP:CNF mixtures with mass ratios of (G) 9:1, (H) 1:1, and (I) 1:9 after application of two layers of each formulation. The insets show the results of EDX analysis of silica abundance on the surface of the investigated samples. The dashed circles indicate cracks on the surface of the fibers.

To further analyze the penetration of silica particles into the canvas, micro-XRF measurements were performed on cross sections (Figure 3). Being chemically identical, it was not possible to distinguish the canvas from CNF and we only tracked the silica signal. Figure 3A shows the effect of the mass ratio CMC@SNP:CNF on the penetration of the SNP through the canvas, and Figure 3B presents the influence of the number of applications of the formulations. Surprisingly, the colloidal silica treated with polyelectrolytes did not diffuse deep into the canvas. This is probably because the suspension used has a high concentration, 4.5 wt %, which gives a high viscosity counteracting the penetration. When CNF are added, the silica concentration is decreased. CNF remain at the canvas surface, while silica penetrates the canvas. With the silica content being lower, the viscosity decreases, allowing deeper transport.

The samples treated with the formulations containing CNF also exhibited unexpected results, with more than one maximum for the silica abundance signal. The only exception was the sample 1:9 CMC@SNP:CNF, which can be explained by the low silica content. The number of maxima corresponds to the number of passes of application of the formulation on the canvas surface (see Figure 3B). During each pass of application, performed by spraying, the samples are wet again, allowing further penetration to occur because of capillary transport. This observation is in agreement with the scenario described above. Furthermore, the CMC@SNP mixed with CNF penetrated deeper into the canvas than the reference formulation based on CMC@SNP only, and the diffusion was not affected by the increasing content of CNF. This clearly indicates that the CNF film did not hinder deep penetration of the silica particles through the canvas, proving the possibility of treating the sample, in a one-pot operation, at multiple scales.

The mechanical properties of the treated canvases were evaluated by mechanically stressing the treated samples to the breaking point, which is, in fact, well beyond the stress imposed on a painting. This procedure allowed benchmarking of the overall performance of the treatments. Representative tensile curves are shown in Figure 4, and the mechanical properties are listed in Table 1, in the form of the breaking force (expressed as a force per perimeter of canvas) and elongation at break. The insets in Figure 4 show the elongation regimes at which painting canvases are usually exposed when mounted on a stretcher (0–300 N/m and 0–3% elongation).<sup>28,29</sup> These values correspond to the limit after which the canvas starts to be torn.<sup>30</sup> In terms of consolidation of the painting canvas, which undergoes dimensional changes due to different environmental impacts, the applied reinforcement needs to be stiff to provide mechanical integrity to the paint layer, while it also needs to exhibit a certain ductility. Tensile measurements suggest that CNF and CMC@SNP strengthen the degraded canvas in different ways. CNF (Figure 4A) increased the breaking force value and elongation at break, while the stiffness of the sample was not affected much (inset in Figure 4A). CMC@SNP increased the breaking force and decreased the extension at break (Figure 4E), and the stiffness (inset in Figure 4E) was increased compared to that of CNF, as indicated by the increase of the slope of the curve.

By the combination of both components into one formulation, it is possible to synergistically improve the stiffness compared to the treatments with the individual components and to tailor the reinforcing behavior by changing the component ratio. The formulation with the highest CNF content (Figure 4B) improved the breaking force, as well as the extension at break. With increasing silica content, the treated



**Figure 3.** Results of micro-XRF measurements showing silica abundance over the cross section of (A) samples treated with formulations of CMC@SNP and different CMC@SNP:CNF ratios (two layers) and (B) samples treated with 1:1 CMC@SNP:CNF with varying amounts of application layers. The gray area denotes the canvas thickness; the dashed line shows the side of the samples from which the treatment was applied.

canvases had higher breaking force and became less ductile (Figure 4C,D); however, the elongation at break for CNF-containing samples was always higher than that for pure CMC@SNP. Interestingly, even a small addition of CMC@SNP to CNF resulted in a significant increase of the stiffness. This is in agreement with the general knowledge that silica-based materials tend to be brittle.<sup>31</sup> Overall, the best mechanical performance was obtained, with the formulations having a CMC@SNP:CNF mass ratio of 9:1 (Table 1). With three layers of this formulation, the breaking force was increased by 38.9% (from 4.24 to 5.89 kN/m), while the elongation at break was only marginally decreased (from 35.4 to 34.2%).

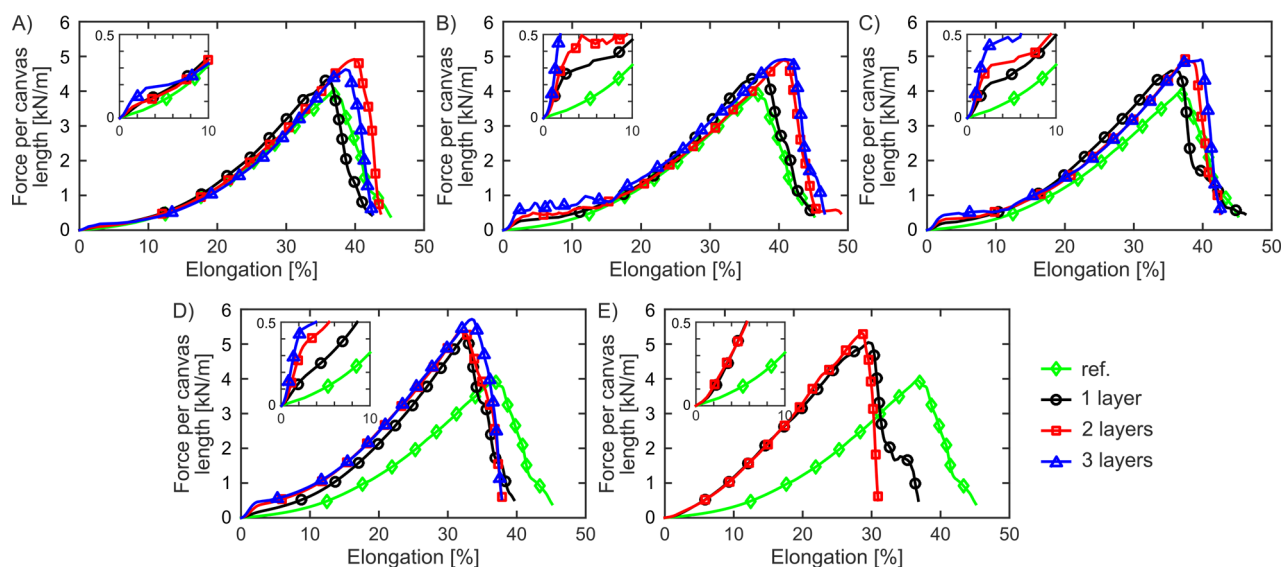
In summary, we show that a strategy based on formulations combining CMC-treated SNP and CNF is suitable for effectively addressing the loss of mechanical integrity of the degraded painting canvas. Because of the size difference between the components, they provide consolidation at different length scales, which is crucial for the macroscopic behavior. The CNF formed a film on the surface of the canvas, while the silica particles penetrated into the inner part of the canvas. The reinforcing properties of the formulations could be tuned by changing the ratio between the silica particles and CNF. A high content of CNF in the formulation resulted in a ductile behavior, whereas a high silica content yielded a stiffer canvas. In comparison with the classical treatments, which only coarsely address the problem, we show that a multiscale approach offers the possibility of reinforcing the degraded canvas toward the original behavior.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsanm.8b00262.

Description of materials and methods, preparation of polyelectrolyte-treated silica nanoparticles (CMC@SNP), preparation of strengthening formulations, AFM



**Figure 4.** Tensile test curves of degraded cotton canvas treated with (A) CNF, (E) CMC@SNP, and different CMC@SNP:CNF mixtures with mass ratios of (B) 1:9, (C) 1:1, and (D) 9:1. The treatments were applied with up to three repetitions (layers). The insets present the curves in the low-elongation region.



image of nanocellulose, and size distribution of CMC@SNP (PDF)

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### Notes

The authors declare no competing financial interest.

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