

### Nanotechnology



International Edition: DOI: 10.1002/anie.201907876 German Edition: DOI: 10.1002/ange.201907876

## Photothermal Welding, Melting, and Patterned Expansion of Nonwoven Mats of Polymer Nanofibers for Biomedical and Printing Applications

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Abstract: We report a simple method for the photothermal welding of nonwoven mats of electrospun nanofibers by introducing a near-infrared (NIR) dye such as indocyanine green. By leveraging the strong photothermal effect of the dye, the nanofibers can be readily welded at their cross points or even over-welded (i.e., melted and/or fused together) to transform the porous mat into a solid film upon exposure to a NIR laser. While welding at the cross points greatly improves the mechanical strength of a nonwoven mat of nanofibers, melting and fusion of the nanofibers can be employed to fabricate a novel class of photothermal papers for laser writing or printing without chemicals or toner particles. By using a photomask, we can integrate photothermal welding with the gas foaming technique to pattern and then expand nonwoven mats into 3D scaffolds with well-defined structures. This method can be applied to different combinations of polymers and dyes, if they can be co-dissolved in a suitable solvent for electrospinning.

Lectrospinning has been extensively explored to produce nanofibers for a variety of applications, including filtration, waste water treatment, catalysis, energy harvesting/conversion/storage, and medicine.<sup>[1-5]</sup> Typically, the electrospun nanofibers are collected as nonwoven mats in a layer-bylayer fashion, resulting in weak interaction between the nanofibers. Upon stretching, the mat will be easily deformed as a result of slipping between the nanofibers. An effective way for enhancing the mechanical strength of the mat is to weld the nanofibers at their cross points. Typical methods for welding the nanofibers involve thermal annealing,<sup>[6-8]</sup> chemical cross-linking,<sup>[9,10]</sup> and solvent or vapor treatment.<sup>[11-13]</sup> These methods have been applied to enhance the mechanical strength of nanofiber mats comprised of various polymers, including poly( $\varepsilon$ -caprolactone) (PCL), poly(lactic-*co*-glycolic acid), polyacrylonitrile, polysulfone, and a blend of poly(vinyl pyrrolidone) and In<sub>2</sub>O<sub>3</sub> precursor, by reinforcing inter-fiber connection.<sup>[6,11–13]</sup> In general, all these methods lack the feasibility and versatility for patterning (that is, welding the nanofibers in a spatially controlled manner) because all nanofibers in the mat will be welded, or, at least, affected. When treated with a solvent in the liquid or vapor format, the nanofibers may also suffer from dimensional shrinkage owing to the relaxation of polymer chains.<sup>[14]</sup>

Photothermal heating has been used to weld a variety of materials, such as polyaniline (PANi) fibrils,[15,16] a blend of PANi fibrils and carbon nanotubes,<sup>[17]</sup> and metal nanowires.<sup>[18,19]</sup> As a major advantage over the aforementioned methods, photothermal welding offers the ability to selectively weld the fibers in certain areas only through the use of a mask, enabling the formation of a well-defined pattern.<sup>[15,20]</sup> For instance, a grid pattern was easily created on a mat of PANi fibrils by placing a copper grid between the flash light and the mat.<sup>[15]</sup> Under flash irradiation, only those PANi fibrils in the regions not blocked by the grid were melted to form a dense film. Photothermal welding can also be achieved by doping the materials with plasmonic nanoparticles (e.g., Au or Ag nanostructures) or light-absorbing dyes. For instance, a layer of Ag nanoparticles was coated on a film made of poly(vinylidene fluoride) (PVDF).<sup>[20]</sup> Upon photothermal heating, the Ag nanoparticles would diffuse into the PVDF film to generate a composite, which could be further used for patterning and laser writing owing to the color change from reddish blue to yellow as a result of a blue shift for the localized surface plasmon resonance peak of the Ag nanoparticles. Photothermal welding has also been explored for biomedical applications, such as suture-free engraftment of a composite scaffold comprising of albumin fibers and Au nanorods<sup>[21]</sup> or laser-assisted vascular anastomosis by coating a scaffold with a light-absorbing mat of electrospun fibers made of a mixture of indocyanine green (ICG) and PCL.<sup>[22]</sup> Taken together, photothermal welding holds great promise for applications related to the fabrication of asymmetric mats, pattering, laser writing/printing, and biomedicine.

The previous methods for photothermal welding are typically limited to a specific type of material and/or a single application. Herein, we generalize the approach by doping the nanofibers with a light-absorbing dye to generate a nonwoven mat well-suited for photothermal welding. We also demonstrate the ability to control the extent of welding and the transparency of the resultant film, as well as the

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Supporting information and the ORCID identification number(s) for
the author(s) of this article can be found under: https://doi.org/10.1002/anie.201907876.

pattern of welding and expansion. We initially focused on PCL as a model polymer owing to its superior spinnability and biocompatibility.<sup>[23]</sup> We doped the nanofibers with a nearinfrared dye such as ICG by directly adding it into the solution for electrospinning. The chemical structure of ICG can be found in Figure S1, which has excitation and emission peaks at 780 and 800 nm, respectively. We chose ICG because of its low cost compared with plasmonic metals and its approval by the Food and Drug Administration (FDA) for clinical use.<sup>[24]</sup> Owing to the strong photothermal effect of ICG, the nanofibers in a nonwoven mat can be welded at their cross points upon irradiation with a near-infrared laser. In consequence, the mechanical strength of the nanofiber mat is significantly enhanced. It is worth noting that the nanofibers can also be over-welded (i.e., melted and/or fused together) to generate a dense, transparent film when the irradiance is high enough and/or the exposure time is sufficiently long. As such, we were able to fabricate a class of photothermal papers by covering a color plate with a thin mat of the ICG-doped nanofibers to realize direct laser writing by over-welding the nanofibers in selected regions. More significantly, by covering the mat with a photomask during laser exposure, we could spatially control the regions in which the nanofibers were welded or over-welded, offering flexibility and versatility for patterning the nanofiber mat. In this way, we generated a novel class of three-dimensional (3D) scaffolds by photothermally welding the nanofibers in a mat in a spatially defined pattern and then expanding the non-welded regions through gas foaming. This class of 3D scaffolds can be used to achieve full-thickness inward growth of cells into the expanded regions only while maintaining a freestanding structure with a spatially defined pattern.

We fabricated the ICG-doped PCL nanofibers by directly electrospinning PCL solutions containing ICG at concentrations of 1, 2, and 5%. Since the melting point of PCL is only 60°C, the nanofibers can be readily welded at their cross points and even over-welded upon irradiation with a diode laser for a sufficiently long period of time. The cross points between the nanofibers are expected to be welded at a faster rate relative to the regions away from the cross points. Since the light-absorbing dyes are homogeneously distributed in the nanofibers, the heat generated per unit area at the cross points is supposed to be higher than that at other regions. Additionally, the heat can diffuse along the nanofibers owing to their higher thermal conductivity relative to air. Altogether, the cross points between nanofibers are able to reach the melting point ahead of other regions. For example, by exposure to an 808-nm laser at irradiances of 0.2 and 0.4  $W \text{ cm}^{-2}$  for 2 s, the overall temperature of a mat of nanofibers electrospun from a solution containing 1% ICG only reached circa 36 and 40 °C, respectively, but welding already took place at the cross points between nanofibers while some regions of the mat even melted to prompt fusion, as shown by the scanning electron microscopy (SEM) images in Figure 1A,D. When the concentration of ICG was increased to 2%, the overall temperature of the nanofibers reached circa 42 and 46°C, respectively, upon laser irradiation under the same conditions, greatly increasing the extent of welding (Figure 1B,E). If the concentration of ICG was further increased to 5%, the



*Figure 1.* SEM images showing the morphology of ICG-doped PCL nanofibers electrospun from solutions containing ICG at concentrations of A,D) 1%, B,E) 2%, and C,F) 5% after exposure to an 808-nm diode laser at irradiances of 0.2 (A–C) and 0.4 W cm<sup>-2</sup> (D–F) for 2 s.

temperature of the nanofibers reached circa 48 and  $53^{\circ}$ C, respectively. In both cases, over-welding occurred across the irradiated area so that the nanofibers melted and fused together to generate a solid film (Figure 1 C,F).

We also stacked the nonwoven mats of ICG-doped PCL nanofibers into multi-layered films to determine the maximum thickness at which the films could still be welded upon laser irradiation. At an irradiance of 0.2 W cm<sup>-2</sup>, the maximum thicknesses for over-welding the nanofibers electrospun from solutions containing 1, 2, and 5% ICG were  $0.9 \pm 0.1$ ,  $1.9 \pm 0.2$ , and  $2.8 \pm 0.1$  mm, respectively (Figure S2). When the irradiance was increased to  $0.4 \text{ W cm}^{-2}$ , the maximum thicknesses were increased to  $2.7 \pm 0.3$ ,  $3.2 \pm 0.1$ , and  $3.6 \pm 0.4$  mm, respectively. Since the thickness of a directly collected nonwoven mat of electrospun nanofibers is typically within an upper limit of 0.5–1 mm,<sup>[25]</sup> the photothermal welding method should be well-suited for most of the applications involving nonwoven mats of electrospun nanofibers.

Since welding at the cross points could reduce the chance of slipping between the nanofibers when subjected to stretching, the welded mat showed a greater ultimate stress, elongation at break, and Young's modulus relative to the pristine sample. As such, photothermal welding can be used to increase the mechanical strength of a nonwoven mat of nanofibers. To this end, we compared the mechanical properties of ICG-doped PCL nanofibers electrospun from a solution containing 1% ICG, without and with welding at the cross points by exposure to the laser at an irradiance of  $0.2 \,\mathrm{W\,cm^{-2}}$  for 2 s. As shown in Figure S3, the ultimate stress, elongation at break, and Young's modulus were  $30.7 \pm$  $1.0 \text{ MPa}, 360.2 \pm 16.7 \%, 17.9 \pm 0.6 \text{ MPa}, \text{ respectively, for the}$ welded mats, which were all significantly higher than those of the pristine mats (17.3  $\pm$  1.0 MPa, 285.5  $\pm$  8.8 %, and 10.7  $\pm$ 0.5 MPa, respectively).

We further demonstrated that this photothermal welding method could be applied to enhance the mechanical properties of nanofibers made of other polymers, as long as ICG could be dissolved or dispersed in the polymer solutions prior

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to electrospinning. For example, we were able to weld and over-weld nanofibers made of PVDF, a piezoelectric polymer with a melting point as high as 170°C. Figure S4 shows SEM images of nonwoven mats of the ICG-doped PVDF nanofibers, electrospun from solutions containing ICG at concentrations of 1 and 5%, after laser irradiation at 2 W cm<sup>-2</sup> for 2, 5, and 10 s. By adjusting the irradiance of the laser, exposure time, and/or concentration of ICG, we achieved welding at the cross points only (Figure S4A) or generated a dense film through melting and fusion of the nanofibers (Figure S4F). We also tested the mechanical properties of the nonwoven mats of ICG-doped PVDF nanofibers electrospun from a solution containing 1% ICG, without and with welding at their cross points by exposure to the laser at  $2 \text{ W cm}^{-2}$  for 2 s. As expected, the mechanical properties of the welded mats were greatly improved in terms of ultimate stress (14.4  $\pm$ 0.8 MPa), elongation at break ( $309.8 \pm 16.6\%$ ), and Young's modulus ( $15.3 \pm 0.6$  MPa) relative to the values of the pristine mats  $(8.4 \pm 0.6 \text{ MPa}, 277.7 \pm 11.7 \%, \text{ and } 8.7 \pm 0.4 \text{ MPa},$ respectively), see Figure S5.

When over-welded, the nanofibers in a nonwoven mat are expected to melt and fuse together, creating a dense film while transforming the sample from a porous and opaque mat into a solid and transparent film. Such a change in optical transparency makes it feasible to exploit the mat for optically masked writing or printing. We demonstrated this concept using a nonwoven mat of the ICG-doped PCL nanofibers electrospun from a solution containing 1% ICG. Figure 2 shows infrared and SEM images of such a mat upon irradiation by the laser at  $0.4 \text{ W cm}^{-2}$ . With the increase of irradiation time from 1 to 3 and 5 s, the overall temperature of the mat increased from circa 34 to 50 and 57 °C, respectively (Figure 2A–C). As a result, the mat quickly lost the porous structure and evolved into a solid film (Figure 2D–F).

As shown in Figure 3A, the pristine mat was opaque, with essentially no transmittance for light in the visible region, owing to the scattering of light by the nanofibers.<sup>[26,27]</sup> When



**Figure 2.** A–C) Surface temperatures (measured using an infrared camera) and B–D) SEM images of the ICG-doped PCL nanofibers electrospun from a solution containing 1% ICG after exposure to the laser at an irradiance of 0.4 W cm<sup>-2</sup> for 1 s (A,D), 3 s (B,E), and 5 s (C,F). The region marked by a dashed circle indicates the location of the laser spot, which has a diameter of circa 1.5 cm.



**Figure 3.** A) UV/Vis transmittance spectra recorded from the mat of ICG-doped PCL nanofibers (electrospun from a solution containing 1 % ICG) before and after exposure to the laser at an irradiance of 0.4 Wcm<sup>-2</sup> for 5 s. Insets: SEM images of the corresponding nanofibers, scale bar = 1  $\mu$ m. B) Schematic of a photothermal paper fabricated by covering a yellow plate with a layer of the ICG-doped nanofibers. C) Direct writing on the photothermal paper using the laser at an irradiance of 0.4 Wcm<sup>-2</sup>. D) Another example of laser writing on a photothermal paper fabricated by covering a black plate with a layer of the ICG-doped nanofibers.

the mat was over-welded at  $0.4 \text{ W cm}^{-2}$  for 5 s, it became a solid and transparent film with a transmittance as high as 94% in the visible region. A previous study demonstrated that a nonwoven mat of nanofibers could be made highly transparent to visible light (90% transmittance) by filling the voids among the nanofibers with another polymer such as poly(dimethyl siloxane) that has a compatible refractive index.<sup>[28]</sup> Our demonstration suggests that the voids among the nanofibers could be permanently eliminated by overwelding the nanofibers through photothermal heating.

By coating a color plate with a layer of ICG-doped PCL nanofibers, we demonstrated a new class of photothermal

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papers for laser writing and printing (Figure 3B). The original coating showed a light green color because of the inclusion of ICG in the nanofibers, effectively blocking the color from the underlying plate. Upon writing with a laser, photothermal heating caused localized over-welding in the nanofiber coating. As a result, those regions irradiated by the laser became transparent to expose the color of the underneath plate. In this demonstration, we simply wrote "XIA LAB" on the photothermal paper using the diode laser at an irradiance of  $0.4 \,\mathrm{W\,cm^{-2}}$ . The color of the letters to be displayed is determined by the underlying color plate. When a yellow color plate was used as the background, the displayed letters showed a yellow-green color owing to the slight green color from the ICG dye (Figure 3C). When a stronger color such as black was used for the background, the letters only showed the color of the underlying plate (black in this case, Figure 3D).

Since the change in optical transparency of the mat solely resulted from the collapse of voids among the nanofibers during photothermal heating, there is no need to involve chemicals in order to create a letter or image, making the photothermal paper more eco-friendly and biocompatible relative to the traditional thermal papers based upon chemicals such as free bisphenol A and bisphenol S.<sup>[29,30]</sup> In principle, we can work with different types of polymers and photothermal dyes to generate the photothermal papers. To this end, we should be able to use an inexpensive polymer to reduce the material cost, a polymer with a high glass transition temperature to increase the stability of the written or printed letters in a hot environment, or a non-degradable polymer for long-term storage. Since the pores contained in the mat of nanofibers were circa  $5\,\mu m$  in diameter, much greater than the optical diffraction limit of the light used for exposure (around  $\lambda/2$  or 0.4 µm), the intrinsic spatial resolution of the writing/printing system should be mainly determined by the pore size. In practice, the spatial resolution is controlled by the spot size of the laser used to write the pattern or the size of opening on the photomask, which could be easily reduced down to 10 µm. This chemical- and tonerfree system holds great promise for applications related to laser writing/printing and high-definition display.

We could also pattern the nonwoven mat of nanofibers through the use of a photomask. When integrated with gas foaming, a technique capable of expanding a nanofiber mat,<sup>[31]</sup> we were able to further engineer the structure of a nanofiber-based scaffold. In one demonstration (Figure 4A-D), we masked four square regions in a mat of ICG-doped PCL nanofibers electrospun from a solution containing 1% ICG. We then over-welded the surrounding edges and the borders between the square regions by laser irradiation at  $0.4 \, \text{W} \, \text{cm}^{-2}$  for 3 s. Upon immersion in an aqueous NaBH<sub>4</sub> solution, the un-welded regions were expanded. As shown in Figure 4E-G, the over-welded region took a compact, single-layered structure while the expansion resulted in a porous and multi-layered structure along the vertical direction. According to the literature,  $H_2$ bubbles were generated in the solution owing to the decomposition of NaBH<sub>4</sub>.<sup>[32]</sup> The bubbles then escaped from the solution trapped in the matrix of the nanofibers, resulting in





Figure 4. A-D) Photographs showing the fabrication of a 3D scaffold through patterned welding and subsequent expansion. The welding was conducted by covering a mat of ICG-doped PCL nanofibers (electrospun from a solution containing 1% ICG) with four masks (A) and then exposing the remaining regions to the laser at 0.4 W cm<sup>-2</sup> for 3 s (B). C) Top-view and D) cross-sectional pictures showing the 3D scaffold after expansion in an aqueous NaBH₄ solution for 4 h. E) Optical micrograph and F,G) SEM images showing the cross section of the over-welded (F) and expanded (G) regions of the 3D scaffold shown in (D). Photographs showing H) the mat after welding at two opposite edges and I) the corresponding 3D scaffold after expansion. J) SEM image showing the cross section of the over-welded and expanded regions of the 3D scaffold shown in (I). K) Fluorescence micrograph showing the inward growth of NIH-3T3 fibroblasts into different regions of the 3D scaffold shown in (I) after culture for 3 days.

expansion. For the over-welded region, no expansion occurred because there was no void space to accommodate the NaBH<sub>4</sub> solution. In this way, we could vary the patterns and extent of welding, and thus tailor the geometric shapes of the resultant 3D scaffolds by controlling the width and height of the expanded regions.

This new class of scaffolds is expected to find use as 3D, in vitro models to investigate cell behaviors or cell infiltration and mass transport for the purpose of bulk tissue regeneration.<sup>[33]</sup> In a simple demonstration, we fabricated a 3D scaffold by over-welding the two opposite edges of a nanofiber



mat by laser irradiation at 0.4 Wcm<sup>-2</sup> for 3 s and then expanding the remaining region in the NaBH<sub>4</sub> solution (Figure 4H,I). The as-obtained 3D scaffold showed lateral dimensions of  $1 \text{ cm} \times 1 \text{ cm}$ , whereas the expanded region was about 3.5 mm in height. Figure 4J shows a cross-sectional SEM image of the over-welded and expanded regions. The multi-layered structure in the expanded region was completely different from the single-layered structure in the overwelded region. We also cut two samples from the interior of the expanded region and the over-welded region, respectively. As shown in the SEM images, the nanofibers inside the expanded region retained their morphology (Figure S6A), while the fibrous structure was essentially lost in the overwelded region (Figure S6B). When NIH-3T3 fibroblasts were cultured on such a 3D scaffold for 3 days, the fibroblasts were able to reach all the void space throughout the expanded region but only inhabit on the upper and lower surfaces of the over-welded region (Figure 4K). Although the bulk of the scaffold was filled with the infiltrated fibroblasts, it was able to retain its original structure after culturing under a dynamic condition. As shown in Figure S6C,D, the fibroblasts grew well on both expanded and over-welded regions. However, the fibroblasts tended to stretch and connect between each other with more and longer F-actin filaments on the sample cut from the interior of the expanded region relative to those grown on the over-welded region, as indicated by the white arrows in Figure S6. This difference can be attributed to the morphology for the underlying substrates. As reported in literature, fibroblasts, as well as other types of repairable cells such as Schwann cells, were supposed to spread on nanofibers, as indicated by their polar and elongated cytoskeleton, while they tended to cover a smaller area and take a more spherical morphology when cultured on a film made of the same material.<sup>[34,35]</sup> We also evaluated the stability of such a 3D scaffold. No obvious change was observed for both the structure and morphology of the scaffold even after immersion in phosphate-buffered saline and under shaking at 100 rpm for 10 days.

In summary, we have demonstrated a simple and versatile method for photothermal welding by doping polymer nanofibers with a light-absorbing dye. By adjusting the concentration of the dye, irradiance of the laser, and exposure time, we could control the extent of welding (i.e., welding at the cross points versus over-welding). The mechanical strength of such a mat was significantly improved by welding the nanofibers at their cross points. By depositing the dyedoped nanofibers on a color plate, we obtained a novel class of photothermal papers to realize laser writing/printing without any chemical species or toners. We could also spatially define the regions in which the nanofibers would be welded by covering the mat with a photomask during laser exposure. The masked regions were then expanded along the vertical direction by gas foaming, generating a novel class of 3D scaffolds with well-defined structures. Such a 3D scaffold allows us to control the spatial distribution of cells and maintain the original architecture of the scaffold when used under a dynamic culture condition. Altogether, this photothermal welding method holds promise for a variety of applications, including enhancement of the mechanical strength of nonwoven mats, patterning, photothermal writing/printing, and bulk tissue construction, among others.

#### Acknowledgements

This work was supported in part by a grant from the NIH (R01 EB020050) and startup funds from the Georgia Institute of Technology.

### Conflict of interest

The authors declare no conflict of interest.

**Keywords:** laser printing · nanofibers · patterning · photothermal effect · welding

How to cite: Angew. Chem. Int. Ed. 2019, 58, 16416–16421 Angew. Chem. 2019, 131, 16568–16573

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Manuscript received: June 24, 2019 Accepted manuscript online: August 2, 2019

Version of record online: September 20, 2019