A Photo-annealing Approach for Building Functional Polymer Layers on Paper**

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**Abstract:** A straightforward photo-annealing approach was developed for building functional polymer layers on paper. Conducting polyaniline with the ability for photothermal conversion can be readily annealed by near-infrared light. The annealed polymers become both insulating and hydrophobic. Selective photo-annealing produces a functional layer with patterned conductive arrays. This material exhibits real-time response to ammonium gas. Complete photo-annealing preserves the porous structure but changes the wettability of the polyaniline-nanofiber film.

Annealing treatments are commonly used to refine the nano- or micro-structures of polymeric materials by inducing changes in physical properties and phase separation. General annealing strategies, including thermal annealing and solvent annealing, are used to soften and reorganize polymer chains.[3] Regardless of scalability and simplicity, both methods are incapable of partial or selective annealing. The whole polymer film together with the supporting substrates has to be subjected to high temperatures or solvent vapors.[2] Inevitable destruction of the fragile substrates and poor control of the annealing area become important and pervasive problems. Photo-annealing by using intense light sources, for example, powerful lasers, can generate localized heat, thereby affording the convenience of melting polymers within a specific region.[3] However, the deep penetration of incident light can also cause thermal damage to the underlying substrate, thus limiting the use of photo- or thermo-labile supporting materials.

Rarely has attention been paid to achieving photo-annealing through the use of near-infrared (NIR) light with low irradiation doses. Mild NIR light can illuminate a desired position and causes little damage to supporting materials, however, the energy may be insufficient to soften the polymers. Dark materials with the ability to undergo photothermal conversion can satisfy this demand. Our previous work revealed that carbon nanotubes can tailor a rapid phase transition of individual polymer particles by NIR light.[4] Conducting polymers with deep color, in addition to distinct electrical performance, are able to absorb light with a wide range of wavelengths and generate heat without the aid of other agents.[5] Such photothermal conversions have been investigated as powerful tools for killing cancer cells in biological systems[6] or welding polymers in the dry state.[7]

A popular supporting material for preparing portable devices is cellulose paper owing to its high flexibility and low cost. Photo-annealing of conducting polymers paves the way to building functional layers on this fragile substrate. In this work, a rapid photo-annealing of polyaniline nanofibers on cellulose paper was remotely accomplished through the use of NIR light. Along with a change in their nanostructures, the conducting polymers undergo changes to their electrical performance and wettability. Besides its simplicity and generality, photo-annealing has two particular merits for modifying polyaniline on paper: 1) it affords great convenience for selective annealing to fabricate conducting arrays with desired pattern features, and 2) it is not damaging to the supporting materials if low-power light is used, thus leading to the formation of an asymmetric filter membrane.

A general route for building functional layers on cellulose paper is illustrated in Figure 1. A cellulose filter paper coated with a layer of polyaniline nanofibers (Figure 1b) was exposed to mild NIR light. The polyaniline nanofibers rapidly melted, concomitantly forming agglomerates within the exposed area. Such photo-annealed areas can be clearly distinguished from surroundings because of their altered color (Figure 1c). To prepare water-dispersible polyaniline nanofibers, a versatile interfacial polymerization was accomplished between a dichloromethane phase consisting of aniline and a water phase containing dissolved FeCl₃.[8] Polyaniline nanofibers were quickly formed at the interface owing to the oxidation of aniline by FeCl₃. As shown in Figure 2, this interfacial polymerization offers extraordinary control of the nanostructure of the polyaniline nanofibers. The nanofibers became thicker and branched upon increasing the oxidant concentration. Thinner nanofibers (Figure 2b) were hardly retained on the paper during a suction filtration process. However, the unique branched morphology (Figure 2h) acquired at high concentrations of FeCl₃ prevented the nanofibers from penetrating the paper, thus enabling optimal deposition of a polyaniline-nanofiber film onto paper. It should be noted that the use of saturated FeCl₃ also improved the polymerization capacity, thus leading to the generation of more nanofibers. As shown in Figure 2i, a standard batch of polymerization formulation, including

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aniline (1.0 \text{m}, 4 \text{mL}) and FeCl\textsubscript{3} (5.67 \text{m}, 4 \text{mL}), can ultimately produce 25 mg polyaniline nanofibers in 10 min. Photoirradiation under NIR light is able to actuate an electrical response in polyaniline nanofibers on the basis of the change in their conductivity. In order to validate this assertion, an electrical device was fabricated by bridging a paper chip deposited with a layer of polyaniline nanofibers (15 \text{\mu m} in thickness) with two gold electrodes (Figure S1 in the Supporting Information). This paper device outputs electrical signals on an electrochemical workstation with an applied direct voltage. To quantitatively view the photoresponse, the signal output was normalized by the absolute change of conductivity ($-\Delta G/G_0$) as in the following equation:

$$-\Delta G/G_0 \% = \left( \frac{I_0-I}{I_0} \right) \times 100\%$$

where $G_0$ and $I_0$ are the initial conductivity and current before the photoirradiation, and $I$ is the current after exposure to NIR light with a specific power density. To our surprise, the conductivity increased abruptly at the beginning of photoirradiation, whereas it dropped quickly with extension of the light irradiation (Figure 3a). The initial increase in conductivity is hypothesized to be due to the photo-effect of the NIR light (Figure S2). It is assumed that the excitons generated by light illumination dissociated into free electrons and holes, thus instantly improving the conductivity of polyaniline nanofibers.[9] This hypothesis is verified by a camera flashing with short exposure time. As shown in Figure 3b, a sharp increase in conductivity occurs at each exposure. With prolonged NIR irradiation, the thermo-effect becomes dominant. Photothermal conversion by polyaniline nanofibers generates a lot of heat, thereby significantly raising the local temperature within the conducting fibers. Rather than improving the conductivity as increased temperature usually does in semiconductors, the rising temperature caused by light irradiation enables the annealing of the proton-doped poly-
dramatic changes in the relative intensities of the peaks in the Fourier transformed infrared (FT-IR) spectrum revealed processes impair the conductivity of polyaniline. Analysis of crosslinking and chain oxidation may occur. Both of these processes impair the conductivity of polyaniline. A weak peak at 1758 cm⁻¹ suggests a partial oxidation of the polyaniline (see Figure S5). High local temperature may cause the loss of dopants from the polyaniline. The conductance is fully recovered if the paper device annealed by low intensity light is redoped by hydrochloric acid (Figure S4), thus indicating that dedoping also contributes to impairing the conductance. However, the conductance is only partially recovered by redoping if the paper device is annealed by high intensity light, as shown in Figure 3d. It can be concluded that dedoping causes a recoverable conductance decrease in the polyaniline while the occurrence of chemical reactions on strong light treatment results in permanent destruction of the conjugative structure.

The transition from a conductive to an insulating state affords great promise for constructing functional layers on paper with patterned conductance. Selective photo-annealing was achieved through the use of a striped mask on a paper substrate, as illustrated in Figure 4a. The exposed area becomes electrically insulated, while the covered area retains conductive performance. The paper chip has a low surface resistance of several KΩ in the longitudinal direction but the lateral resistance is infinite (Figure 4b). Owing to the sensitive of polyaniline to Lewis base, a thorough sensing assessment of the paper chips with conductive arrays was conducted by using ammonia. It has been widely accepted that ammonia can neutralize the doped protons of polyaniline, thereby leading to conversion of the conductive emeraldine salt to the insulating emeraldine base (Figure 4c). Sensing devices with control over array length and width were electrically bridged by two gold electrodes. As shown in Figure 4d, the conductivity change (\(\Delta G/G_0\)) grows to a plateau within few seconds when the device is placed in a thin ammonia atmosphere with a concentration of 50 ppm. Narrowing the array width can dramatically improve the sensitivity of detection. The conductivity change of a ×1200 μm array is five times larger than that of a ×4800 μm array. Furthermore, because the network of nanofibers provides a larger surface area, the polyaniline-nanofiber-based paper device is superior to a paper device with a polyaniline film produced through vapor polymerization and exhibits better performance in recognizing ammonium gas. The theoretical detection limit (DL) was estimated by analyzing a sensing curve at 50 ppm ammonia, with 100 consecutive points randomly selected to calculate the standard deviation (SD) of blank values and the average peak height (APH) according to the relationship DL = 3SD × 50/APH. A detection limit of 0.25 ppm was obtained from the calculation result. Excessive exposure did not cause the sensing chip to output stronger signals when the ammonia concentration was over 100 ppm (Figure 3c). However, this exposure limit is already three times higher than the point at which ammonia can be detected by the human nose.
In addition to the change in electrical performance, the surface wettability of polyaniline nanofibers can be changed by photo-annealing. As shown in Figure 5a, the film consisting of polyaniline nanofibers on filter paper was hydrophilic and water was quickly absorbed. However, the film became hydrophobic with a contact angle of 132° owing to the loss of dopants after an adequate photo-annealing (Figure 5b).

Interestingly, the water droplet gradually entered the hydrophobic film after standing on the surface for a few seconds (Video S1, S2). The contact angle of the region where water entered remained high, thus indicating that surface wettability was not influenced by water (Figure 5c). The rear layer of filter paper was found to be wetted by water droplets. Notably, one-way penetration is directed by the asymmetric structure with the combination of a hydrophobic film and a hydrophilic rear layer. Water injected onto the polyaniline surface passed through the structure as it was absorbed by the rear paper layer (Figure 5d). Turning the film over, water did not penetrate through the paper (Figure 5e). Mercury porosimetry revealed that the annealed polyaniline film retained porous features although the pore size distribution was shifted downwards (Figure S6). Water overcomes the porous barrier owing to powerful attraction by the backing paper. Through acting as a “water diode”, the asymmetric paper functions as a “water diode”, thus allowing water to pass only from the annealed layer towards the backing paper. This paper material is intriguing. In addition to facilitating oil/water separation, it could potentially extended to clinical applications, for example, vacuum assisted closure to treat wounds. Other light-absorbing materials, including some conventional polymers and supramolecular blends, will be considered for exploiting new functions through photo-annealing.

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