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## Smart polydiacetylene nanowire paper with tunable colorimetric response†

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**We report the synthesis of mesostructured conjugated nanowires and fabrication of their freestanding papers. The nanowires are formed through non-covalent self-assembly of conjugated diacetylene precursor 5,7-octadecadiynoic acid via hydrogen bonding and  $\pi$ - $\pi$  stacking in a simple sol-gel process. Resultant nanowires exhibit lamellar mesostructure and can be dispersed uniformly in aqueous solutions. The nanowire papers are fabricated through filtration of nanowire solutions. The papers exhibit mechanical robustness allowing them to be freely folded and cut like regular printer papers, and show rapid sensitivity to different ions, solvents, and UV irradiation, as well as reversible blue  $\leftrightarrow$  red chromatic switching induced by UV irradiation and solvatochromic transition.**

One-dimensional (1D) nanowires have been widely fabricated into macroscopic devices to realize properties resulting from their unique features such as 1D external morphology and increased surface area in comparison with bulk materials.<sup>1,2</sup> To date, microfabrication through combining conventional patterning, etching, and cleaning processes has very often been used to fabricate nanowire devices.<sup>1,2</sup> Such a method requires the nanowires to survive cycles of aggressive chemical and physical processes such as etching, cleaning, heating, *etc.* therefore, it is not ideal for integration of organic nanowires that are soft and delicate. In this work, we use an infiltration method to fabricate semiconducting organic nanowires into freestanding nanowire papers that offer smart multifunctions and mechanical robustness for integration of macroscopic sensing membranes. Polydiacetylenes (PDAs) with conjugated backbone alkane chains exhibit strong colorimetric responses (blue  $\rightarrow$  red) due to external stimuli, including changes of temperature, pH, ions, solvent, stress, or receptor-ligand interactions.<sup>3,4</sup> Such visual color changes of PDAs make them smart materials for sensing applications. The color changes have been demonstrated directly related to molecular

ordering of PDA. Through design of head group interactions, reversible switch blue  $\leftrightarrow$  red has been demonstrated, which is essential for development of sensing devices. In addition to molecular ordering, it has been recently shown that nanostructured PDA composites show enhanced color responses. Through formation of a mesoporous network, Lu *et al.* demonstrated that nanostructured PDA materials offer mechanical robustness, reversible chromatic responses, improved thermal stability, and faster responses to chemical stimuli.<sup>5-8</sup> Peng *et al.* recently demonstrated this further through introduction of secondary nanostructured materials such as carbon nanotubes, magnetic nanoparticles to fabricate multifunctional PDA composites with enhanced mechanical robustness and sensitivity.<sup>9,10</sup> To date, the efforts on structure manipulation of PDA materials are demonstrated only to vesicles, liposomes, thin films, and powders. Along with the line of tuning PDA material structures to enhance sensing response, here we report the synthesis of diacetylene nanowires and fabrication of nanowire papers with high surface area than bulk nanostructures. Subsequent polymerization induced by ultraviolet irradiation resulted in PDA nanowire and nanowire papers exhibit unusual chromatic changes in response to thermal and chemical stimuli.

Here we used 5,7-octadecadiynoic acid (ODDA, see ESI, Fig. S1†) as the structure directing agent for the synthesis of conjugated nanowires. ODDA has extended  $\pi$ -electron delocalization along its conjugated polymer backbones. Additionally, the acidic head group allows the formation of intermolecular hydrogen bonding with environmental water.<sup>11</sup> These weak non-covalent interactions enable formation of ordered packing of diacetylene network in aqueous solution.<sup>12</sup> Unfortunately, commercial ODDA is not soluble in water, which does not allow us to self-assemble them to form molecularly ordered packing through these non-covalent interactions. To overcome this problem, we dissolved ODDA in a NaOH aqueous solution (see detailed experiments in ESI†). Acid-base neutralization reaction resulted in base form of ODDA (ODDNa) that dissolves in the aqueous phase forming a homogeneous clear sol solution. Following 12–48 hours storing in the dark, an ODDNa gel was formed (see ESI, Fig. S2†). Our studies in controlled experiments indicated that both hydrogen bonding and  $\pi$ - $\pi$  stacking are essential for the self-assembly of stable solid gel networks. Due to these weak non-covalent interactions, the ODDNa gel is temperature sensitive (see ESI, Fig. S3†). Slight temperature increasing melts the gel into a clear sol solution, which self assembles back to a gel upon cooling. Water is necessary within the gel network for hydrogen bonding to form a stable self-assembled gel network (see ESI, Fig. S4†). More

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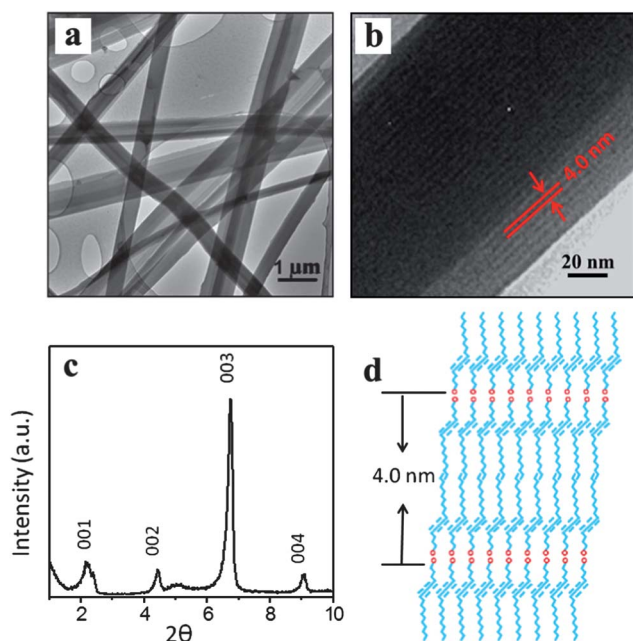
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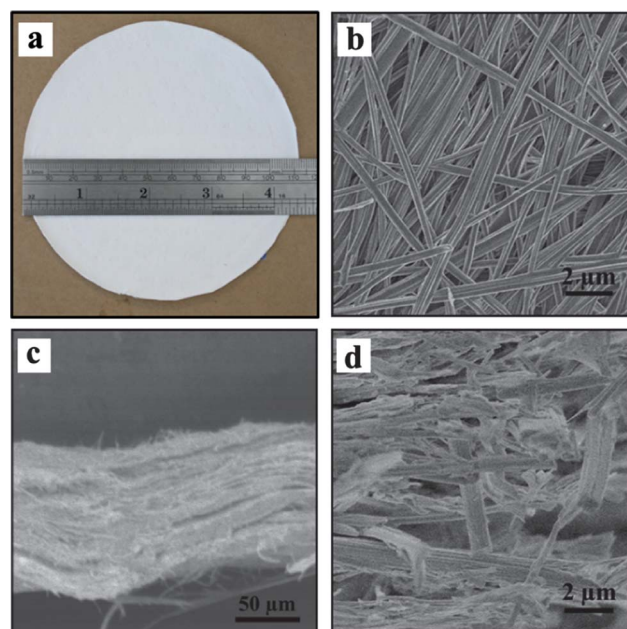
water is needed accommodate the hydrogen bonding when the amount of ODDA is increased, consistent with the previous observation.<sup>11</sup> Finally, our detailed experiments indicated that enough ODDNa is required to initiate non-covalent self-assembly to form stable solid gel network (see ESI, Fig. S5†).

XRD patterns show a lamellar mesostructure with an interlayer periodicity  $\sim 4.0$  nm (Fig. 1c) that is indexed from the (001) peak. TEM image (Fig. 1a) reveals that the single nanowire has uniform electron contrast through the whole length of the nanowires without apparent defects. High resolution TEM image further confirms the layer structure within individual nanowires, indexed from XRD. The measured  $d$ -spacing between each layer from TEM image (Fig. 1b) is  $\sim 4.0$  nm. This length scale covers from the hydrophilic head groups to the self-assembled alkane chains (Fig. 1d).

The ODDNa nanowire papers were fabricated at room temperature by filtering the gels on a Büchner funnel, similar to the processes for making nanofiber membranes.<sup>13–15</sup> Followed by drying in air, an ODDNa paper was peeled from regular Whatman filter paper as a freestanding membrane. Depending the size of the Büchner funnels, varied size of ODDNa papers can be made from several centimeters to tens of centimeters. Fig. 2a shows a  $\sim 4$  inch ODDNa paper after drying. All the preparation processes (filtering, drying, *etc.*) were conducted in dark by using aluminum foils to cover the solutions and filters to avoid light-induced polymerization. The ODDNa papers can be readily converted to acidic form (ODDA) by reacting with hydrochloric vapor in a 3 L glass desiccator with concentrated hydrochloric acid. SEM studies indicate the ODDNa nanowire paper are typically  $\sim 100$   $\mu\text{m}$  thick (Fig. 2c). A further decreasing of



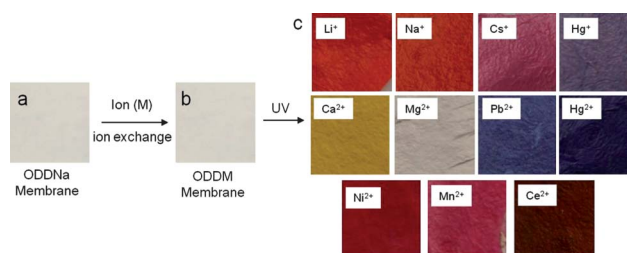
**Fig. 1** Structure of single ODDNa nanowires. (a) A representative low-resolution TEM image of the single ODDNa nanowires. (b) High-resolution TEM image of single ODDNa nanowires in (a), showing a layer structure with  $d$ -spacing of  $\sim 4.0$  nm between the nearest two layers. (c) XRD patterns of single ODDNa nanowires. (d) A schematic molecular packing of lamellar nanostructure. Here only the  $\pi$ - $\pi$  interactions between conjugated chains are displayed. The hydrophilic head groups are represented using circles.



**Fig. 2** Formation of freestanding ODDNa nanowire membranes. (a) An optical picture of freestanding ODDNa membrane covered with a ruler. (b) Plan-view SEM image of the ODDNa nanowire membrane in (a). (c) Cross-sectional SEM image of the ODDNa nanowire membrane in (a). (d) High resolution section of the cross-sectional SEM image in (c).

concentration of nanowire solution reduces paper thickness. The nanowires uniformly interweave within the paper, resulting in macropores for higher surface accessibility (Fig. 2b–d). The length of individual nanowires is more than 100  $\mu\text{m}$ . The interweaved long nanowire network offers mechanical strength so that the paper can be freely handled by hands and trimmed with scissors (see ESI, Fig. S6†). These nanowire papers can easily survive from bending and folding in all directions (see ESI, Fig. S7†), revealing the robust mechanical flexibility.

One of the important characteristics of the nanowire papers is that they change color when exposed to a broad variety of metal cations. As shown in Fig. 3, the paper shows gradual color changes from red to brown, to purple, and to purple blue for +1 cations of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Cs}^+$ , and  $\text{Hg}^+$ , respectively. For +2 cations, the colors corresponding

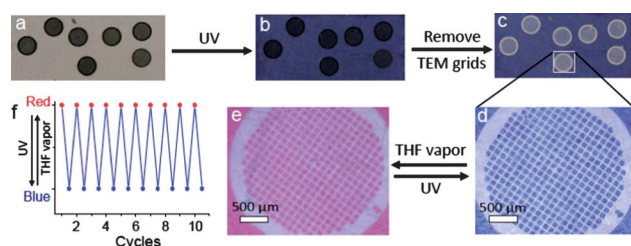


**Fig. 3** Metal ions induced color changing of PDDNa nanowire papers. (a) Optical pictures of 1 cm  $\times$  1 cm ODDNa nanowire paper. (b) The ODDM nanowire paper in (a) after metal ion (M) exchange through soaking in metal ion solutions for 2 min. Here M is used to represent metal ions regardless of the number of charges. (c) Optical pictures of individual polymerized PODDM nanowire papers after exposure to 256 nm UV irradiation for 10 min.

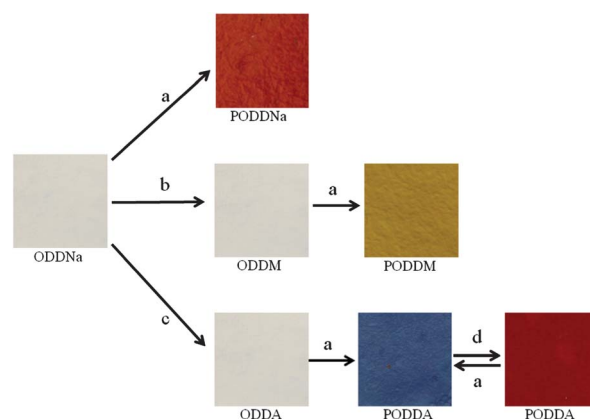
to each of the ion are dramatically different. We find that the base form (ODDNa) nanowire paper is not sensitive to different ions. After ion exchange, the ODDM nanowire papers remain white. The polymerized PODDNa papers display a red color and are not sensitive to varied ions either. PODDNa papers remain red after metal ion exchange. Variation of color only occurs after the ion-exchanged ODDM paper was polymerization by UV irradiation. This is quite different from previous work in which polymerized DA responds to external binding to the head groups.<sup>16</sup> In previous cases, binding causes configuration changes of polymerized backbones. In our case, binding of different charged metal ions occurs before polymerization. Ion binding pre-positions ODDNa conjugated molecular chains which encodes the molecular chain configuration or ordering to correspond to different metal ions (different charge and size). After UV-irradiation, the polyconjugated backbone expresses the pre-positioned or encoded molecular ordering by different ions and translates into variation of color that corresponds different ions.

After conversion into acidic form ODDA from basic form (ODDNa), ODDA nanowire paper can be polymerized by UV irradiation and displays rapid and reversible blue  $\leftrightarrow$  red chromatic changes induced by UV irradiation and solvatochromic transition of the papers (Fig. 4). This allows selected areas of polymerization on the paper. In our screening experiments to determine the UV light source, 256 nm UV light was found to be the most effective for polymerization of ODDA papers (see ESI, Fig. S8†). We have also optimized the irradiation time to be 20 seconds (see ESI, Fig. S9†). Starting with an ODDA paper, we used TEM grids as mask to cover some areas of the paper. Following UV irradiation, the covered areas remain as white (Fig. 4c and d). The uncovered areas were polymerized and turned into blue color (Fig. 4c). After the paper was exposed to THF, the blue patterned areas turned into red. Recovering of the blue patterned areas from the red ones occurred after irradiation with UV light. Fig. 4f shows ten cycles of reversible chromatic transition, which reveals the mechanical robustness for sensing application.

In summary, we developed a simple sol-gel process to synthesize semiconducting nanowires that are self-assembled through non-covalent interactions. The sol was formed through ODDA acid-base



**Fig. 4** Patterned polymerization induced by UV irradiation and solvatochromic transition of PODDNa nanowire papers. (a) Optical picture of PODDNa paper (white color) with TEM grids on top. (b) Optical image of patterned blue/white paper formed by UV irradiation for 20 seconds. (c) Specimen (b) after removal of TEM grids to show the blue/white patterns. (d) Magnified picture of one TEM grid patterned area in (c). (e) Patterned red/white paper after exposing paper (c) to THF vapor for 1 min. To show the reversible response from red (e)  $\rightarrow$  blue (d), the TEM grid was re-covered on the pattern so that the white-patterned areas were not irradiated by UV light. (f) Ten cycles of reversible chromatic transition between red and blue.



**Fig. 5** Flow chart of the color changes under different conditions. (a) UV radiation (256 nm) for 1 min. (b) Emersion in different metal-salt solution (0.1 M) for 2 min. (c) The ODDNa paper was changed to ODDA by exposure to HCl vapor after stored in a 3 L glass desiccator with 10 mL concentrated HCl (6 N) for 12 h. (d) THF vapor for 1 min.

neutralization reaction to form ODDNa in aqueous phase. Subsequent ODDNa self-assembly was induced by non-covalent self-assembly *via* hydrogen bonding and  $\pi$ - $\pi$  stacking of conjugated backbones, forming PDA nanowires. Filtration of the ODDNa gel leads to nanowire papers that possess flexible mechanical robustness for free folding and cutting like regular printer papers. The paper shows rapid sensitivity to different ions, solvents, and UV irradiation, as well as reversible blue  $\leftrightarrow$  red chromatic switching induced by UV irradiation and solvatochromic transition (Fig. 5).

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