Self-Assembling 1,4,5,8-Naphthalentetrahydro-1-carboxylic Diimide-Microwires for Optoelectronic Devices

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Abstract

The widespread use of organic electronic devices requires simple yet effective synthesis techniques to create materials with low-cost and high performance. We report the solution phase self-assembly of 1,4,5,8-naphthalenetetrahydro-1-carboxylic diimide (NDI) microwires from dimethylsulfoxide. These microwires were characterized by means of scanning electron microscopy, thermal analysis, and infrared and fluorescence spectroscopies. The microwires were also characterized for their electrical properties and were shown to exhibit an n-type semi-conductive property as well as photo-responsive changes in conductivity. The electron mobility within the NDI microwires was determined to be lower than previous literature reports, yet the combination of photo-responsive changes in electrical conductivity may hold promise of photo-sensors, organic light-emitting diodes, and other optoelectronic devices.

Keywords: 1,4,5,8-naphthalenetetrahydro-1-carboxylic diimide; NDI; Microwire; Optoelectronic; Mobility

Introduction

The last decade has seen immense interest in self-assembled supramolecular structures for organic electronic applications [1-7] and in particular aromatic diimides derivatives [8]. Thin films and other nanostructures of Perylene tetracarboxylic diimide (PTCDI) [9-11], and NDI [12-18] (Figure 1), along with their derivatives, have been well studied for a range of applications from organic field effect transistors (OFET) and organic light emitting devices (OLED) to organic photovoltaic’s (OPVs). Both PTCDI and NDI are well known for their interesting photo-luminescent and electronic properties. Recently, some attention has been paid to electronic devices built from these supramolecular assemblies because of the unique properties of such nanomaterials [16,19-21]. Previously, we reported the physical properties and electronic characteristics of a single unsubstituted PTCDI nanowire prepared from vapor deposition [18]. In our previous attempts, NDI nanowires prepared in the gas phase are not uniform or crystalline [22], and thus are not conductive or semi-conductive, which limits their applications. The electronic properties of a single NDI nanowire have not yet been reported. In this study, we report the self-assembly of crystalline NDI microwires through π-π stacking and hydrogen bonding from solution and the characterization of the physical and electronic properties of the structures.

Experimental Section

NDI was purchased from TCI Chemical and used as received. Anhydrous DMSO (99.7%) was purchased from Acros Organics and was used without further purification. NDI was dissolved in DMSO at various concentrations. NDI microwires were prepared from evaporation of DMSO in an Omni-Lab VAC 101965 glove box system under nitrogen, the atmosphere within a glove box was maintained under 0.2 ppm moisture content. Wires were self-assembled in glass vials through evaporation of DMSO with a starting volume of 5mL of NDI solution in a 20mL sample vial.

Fluorescence spectra were obtained with a Hitachi F-7000 fluorescence spectrometer. Attenuated total reflection infrared (ATR-IR) spectra and cross-polarized optical microscopy (CPOM) were obtained on a Smith Polarized IR microscope. Thermal analyses were obtained with a thermo-gravimetric/differential thermal analyzer (TG/DTA 6300, SII Nanotechnology Inc). Scanning electron microscopy (SEM) images were obtained using a Hitachi TM-1000 tabletop microscope. Elemental composition was found on a Zeiss Supra 50 VP equipped with an Oxford energy-dispersive X-ray spectroscopy (EDS). Photon sensing experiments were performed with a microwire resistor device mounted inside a electromagnetic shielding box which was then placed inside the chamber of the Hitachi F-7000 fluorescence spectrometer. The shielding box was left uncovered with the topside directly facing the Xe lamp of the fluorescence spectrometer. Current-Voltage (I-V) curves were measured on a Keithley 2636A dual channel system source meter before and after the device were exposed 355nm light from a Xe lamp. The two gold electrodes at the distance of 10μm from each other were patterned by a lift-off photolithography process. The two gold electrodes are suitable wire across the electrodes to ensure that the only conductive path was through the single mesowire. The two gold electrodes are used as a source and a drain, the SiO2 serves as a gate oxide, and the

Figure 1: Chemical structure of NDI.

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Received: January 23, 2014  Accepted: March 12, 2014  Published: March 16, 2014
p-type Si wafer is a gate electrode. Gate voltage experiments were performed using a -2V to +2V sweep under a 10V bias on a Keithley 2636A dual channel system source meter.

**Results and Discussion**

Evaporation of a 1.0×10⁻³M NDI in DMSO solution afforded self-assembled crystalline NDI microwires of several hundred microns in length (Figure 2). The size of NDI microwires was found to be kinetically controlled as a function of evaporation rate; slower evaporation rates led to much larger wires, but fast evaporation of solution led to aggregation on the surface and no well-defined nanostructure. Typical time frames for full evaporation of DMSO solution were between 48-72 hrs. Dilute solutions of 1×10⁻⁴, 1×10⁻⁵ and 1×10⁻⁶ M concentrations were also examined but were found not help the formation of microwires; lower concentration solutions were found to reduce or hinder wire formation. Higher concentrations than 1mM have not been investigated due to limited solubility of NDI in DMSO. Because wires at microscale are easy to handle than those at nanoscale, all the characterization of the NDI crystalline wires were conducted on NDI microwires that were prepared from evaporation of DMSO in a 1mM NDI solution. NDI has very low solubility in many common organic solvents and water. One caveat for self-assembly of this system is the highly hygroscopic nature of DMSO. If the same experimental methods are conducted outside an inert atmosphere, anhydrous DMSO absorbs atmospheric water vapor, precipitating the dissolved NDI out of solution rather than allowing NDI to self-assemble slowly. These microwires were characterized for composition, electrical and optical properties, as well as optical sensing applications.

X-ray diffraction (XRD) and transmission electron microscopy (TEM) are typically used to obtain the crystalline structures of the organic and inorganic materials. However, despite extended lengths, the diameter of our NDI nanowires is less than 50µm and therefore too small for single-crystal XRD. In another attempt, TEM electron diffraction showed no clear but a vague ring pattern (Figure 3) because the self-assembly of NDI assembly can be readily disintegrated under high electron beam voltage. The crystallinity of the 1D structures of triphenylene, however, can be determined from other techniques, such as polarized optical microscopy. Cross-polarized optical microscopy image and a polar plot of wire brightness as a function of angle show the NDI wires are crystalline (Figure 4) [23]. There are four repeats in a complete circle. The maximum or minimum brightness of the image repeats every 90°. When the long axis is parallel to the polarization light (0°), the brightness is the minimum. The brightness increases when the angle increases from 0o to 45o. The periodical change of the brightness vs. the angle shows that the NDI nanowires are birefringent single crystals [23], i.e. the crystal has two distinct indices of refraction and it splits one ray of light into two rays. The strong birefringence is associated with the plane-to-plane stacking (H-aggregation) [24] of NDI molecules in the nanowires.

ATR-IR spectroscopy, TG/DTA, and EDS were conducted to compare the physical properties of the self-assembling wires and the powdered NDI. Figures 5 and 6 show the similarity in IR spectra and TG/DTA results between the NDI powder and microwires. The similarity in NDI powder and microwires from both IR and TG/DTA does not provide information whether the structure of NDI nanowires is different from those in the powders because hydrogen bonding and the π-π interaction between NDI molecules exist in both NDI powders and wires. The useful information we draw from EDS (Figure 7) results is that DMSO...
molecules are not included in the NDI microwires since sulfur atoms are not observed.

Although the IR and TG/DTA techniques are not sensitive enough to distinguish the molecular environments of the NDI molecules in the forms of powders and microwires, the fluorescence spectrum of NDI microwires, on the other hand, showed significant differences from that of NDI powder as seen in figure 8. The NDI powder shows one emission peak at 446 nm, while NDI microwires show one peak at 476 nm. The redshift may be attributed to the formation of an ordered crystal network in the microwires. A weak emission peak at 580 nm in the microwires can be attributed to an excimer within the crystal structure of the NDI wires [25].

The conductance of the microwires was tested with the Keithley Model 2636A controller by applying conductive silver paste on each end of millimeter-long wires as the source and drain electrodes in a manner where one probe is grounded and the other was connected to a source measurement unit. Conductivity measurements have been successfully made across wires of lengths over 1 millimeter. Microwire devices show electrical current on a dielectric SiO₂ surface.

Gate voltage tests were made to measure the effect of an external magnetic field on the conductivity of the wire. Our NDI single microwire metal-oxide-semiconductor field-effect transistor (MOSFET) is of a depletion type, since the channel exists at zero gate-source voltage. To determine the output characteristics of the device, the drain-source voltage, \( V_{ds} \), was swept between -2V to +2 V, and the gate-source voltage, \( V_{gs} \), was kept constant throughout the sweep. The experimental output characteristics of the device (Figure 9 left) show that NDI wires behave like n-type transistor. At 0V bias, the electrical conductivity was determined to be \( 4 \times 10^{-7} \) S cm⁻¹. The conductivity of this wire has been shown to decrease with testing and time. This process is believed to be the result of degradation of the crystal structure within the wire, however whether this degradation is of chemical or physical nature will be the focus of future studies on long-term device stability.

The electron mobility was determined at to be on the order of \( 10^{-9} \) cm² V⁻¹ s⁻¹ based directly on the electrical conductivity given in equation 1. \( \mu_e \) is the electron mobility as a function of the elementary electron charge, \( e \), number density of electrons, \( n \), and the electrical conductivity, \( \sigma \). In the calculation of electron mobility, the number density of electrons was assumed to be 1.

\[
\mu_e = \frac{ne}{\sigma} \tag{1}
\]

When NDI wire devices were exposed to the excitation maxima \( \lambda_{ex} = 355 \) nm the current within the wire increased as shown in figure 9 right, suggesting the device can be used for photo-detectors.
ambient conditions

OLEDs, photovoltaics, and optoelectronic devices promise for a wide variety of applications such as photo-detectors, mobility, the photo-responsive conductivity increases could hold conductivity along the length of the wire. Despite the low electron characteristics and are photo-responsive, leading to increased manufacturing. Microwires of NDI show n-type semiconductive crystallization procedures, aiding throughput in potential future within allows for the production of multiple wires during single atmospheric conditions. These variables allow for a tunable dependent on the concentration of the solution, evaporation rates microwires through solvent evaporation. The size of NDI wires is 8.


phenomenon can be accounted for by the electronic transitions and hence photo-generated currents between excited molecules along the path of conduction [26].

Conclusions

Unsubstituted NDI has been shown to form self-assembled nano/microwires through solvent evaporation. The size of NDI wires is dependent on the concentration of the solution, evaporation rates and atmospheric conditions. These variables allow for a tunable system to tailor for specific applications. The process described within allows for the production of multiple wires during single crystallization procedures, aiding throughput in potential future manufacturing. Microwires of NDI show n-type semiconductive characteristics and are photo-responsive, leading to increased conductivity along the length of the wire. Despite the low electron mobility, the photo-responsive conductivity increases could hold promise for a wide variety of applications such as photo-detectors, OLEDs, photovoltaic’s, and optoelectronic devices.

Acknowledgement:

Support for this work was provided by the National Science Foundation (No. DMR-1104835).

References

