J|A|C|S COMMUNICATIONS

Published on Web 02/18/2009

Vertical Organic Nanowire Arrays: Controlled Synthesis and Chemical Sensors

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Vertical arrangement of nanowire materials has been found to be advantageous for applications such as solar cells,[1] batteries,[2] electrochemical sensors,[3] field emitters,[4] light emitting diodes,[5] and transistors[6] and has led to the discoveries of nanolasers[7] and nanopiezotronics.[8] So far, the predominating body of work has focused on inorganic materials. Organic nanowires can bring new opportunities since they are composed of molecular building blocks with relatively weaker interactions, thus allowing highly flexible structural tunability. Organic nanostructures have emerged to play increasingly important roles in miniaturized optoelectronic devices.[9] Here we report the direct growth of vertically aligned organic nanowires of 1,5-diaminoanthraquinone (DAAQ) on solid surfaces. The crystal lattice and parameters of the nanowires and their growth direction were determined by extensive electron diffraction studies. The fluorescence of DAAQ nanowires can be quenched when exposed to acidic vapor and recovered by basic vapor. The ease of the oriented vertical growth should allow the direct integration of these nanowires into photonic sensing devices.

DAAQ (Figure 1, inset) belongs to a class of quinoid compounds that have been used in the dye industry for over a century.[10] Vertical

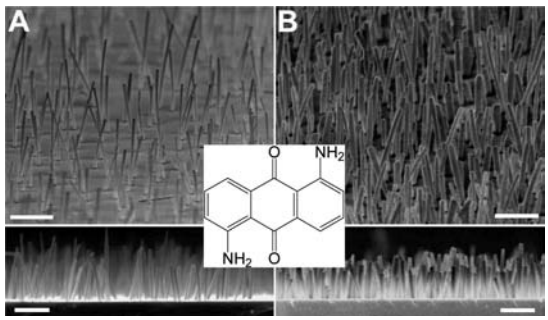

Figure 1. SEM images (top: 40° tilted view; bottom: cross-sectional view) showing the vertically aligned DAAQ nanowire arrays prepared at (A) 160 °C, for 5 min and (B) 180 °C, for 5 min. All scale bars are 1 μm. The inset shows the molecular structure of the DAAQ molecule.

arrays of DAAQ nanowires on solid substrates were prepared by a physical vapor transport method.[11] In a typical synthesis, a thin coating of DAAQ was made on the inner wall of a round bottle flask by spreading an ethanol solution. This ensured uniform heating over the entire sample area in the subsequent sublimation steps. Then the flask was heated to a predetermined temperature of 150−200 °C to vaporize the powders. The vapor of DAAQ can be transported downstream by air, nitrogen, or diffusion under vacuum to deposit on a solid substrate (e.g., Si, glass, Au, Al, Fe, Cu foils, or W needle) placed downstream. Figure 1 shows the typical scanning electron microscope (SEM) images of the vertically aligned nanowire arrays prepared on Si wafers. The length and diameter of the nanowires were controlled by the growth conditions. For example, the diameter can be tuned from 80 to over 500 nm by the evaporation temperature, while the length can be tuned from 500 nm to over 10 μm by the deposition time (see Figure S1 for more).

Figure 2A is a transmission electron microscope (TEM) image showing the smooth surface and uniform width of a typical nanowire

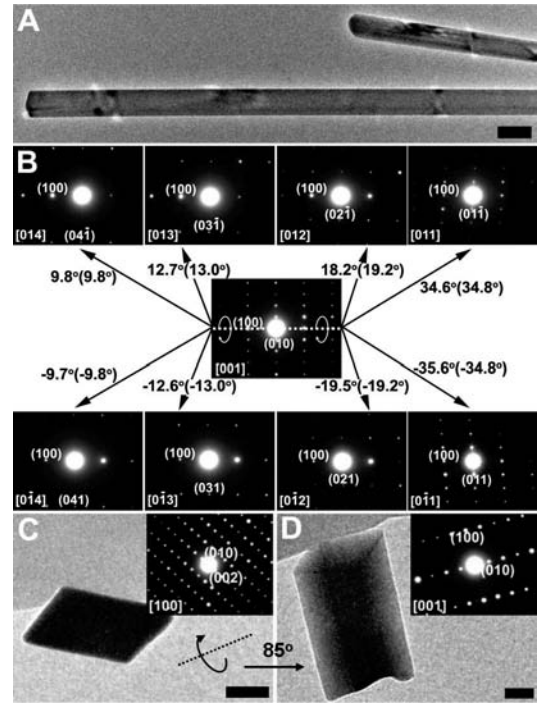

Figure 2. (A) TEM image of the DAAQ nanowires. Scale bar is 200 nm. (B) A set of electron diffraction patterns of the same nanowire acquired while rotating the nanowire along its [100] axis. For example, a 34.6° of axial rotation switched the pattern from along [001] to [011] zone axes, while a 35.6° rotation in the opposite direction switched it to one along the [0−11] zone axis. The angles in parentheses are theoretical values calculated from the reconstructed unit cell. (C) Cross-sectional and (D) tilted TEM views of a single DAAQ seed grown on SiO_x coated copper grid. Scale bars are 50 nm. Insets: electron diffraction patterns taken from the seeds.

product. To determine the crystal structure and the growth direction of the DAAQ nanowires, we collected the orientation dependent electron diffraction patterns from a few single nanowires. Figure 2B shows a set of patterns obtained by continuously rotating a single nanowire along its axis. These patterns allowed reconstruction of the reciprocal lattice for determining the lattice type and parameters (see Supporting Information).[12] The reciprocal lattice parameters derived from the reconstruction are $a^* = 0.265$ Å^{-1}, $b^* = 0.103$ Å^{-1}, $c^* = 0.067$ Å^{-1}, $\alpha^* = \gamma^* = 90°$, $\beta^* = 97.6°$, which correspond to a monoclinic lattice with $a = 3.78$ Å, $b = 9.73$ Å, $c = 15.01$ Å, $\beta = 82.4°$. The reconstructed unit cell was validated by the good agreement

10.1021/ja809360v CCC: $40.75

between the experimental tilting angles among the zone axis and those recalculated (in parentheses) based on the unit cell parameters corresponding to the diffraction patterns in Figure 2B. The nanowire axis was found to be along the [100] direction, which is the same direction pointing from the transmitted spot to the (100) spot in the diffraction patterns (Figure 2B). In addition, the XRD pattern of DAAQ nanowires also showed a preferred orientation of the (100) plane (Figure S2). The XRD pattern of the nanowires matched the powder pattern except for the relative peak intensities, suggesting that DAAQ did not undergo phase transition or chemical reaction during the vapor transport.

Since the organic nanowires were made without catalysts or liquid droplets as is needed in the vapor−liquid−solid synthesis for many inorganic nanowires, the growth should be controlled by a vapor−solid condensation process. To observe the early stage of nanowire growth, the deposition was stopped within seconds. SEM observation of the substrates revealed that DAAQ first deposited as well-separated nanoparticles of ∼100 nm in diameter (Figure S3) with a density comparable to that of the final nanowire arrays. This indicates that the nanowires were grown on these seed nanoparticles. Crystallographic studies on such nanoparticles grown on SiO_x coated copper grids were carried out in TEM by electron diffraction. When viewed from the bottom, the cross section of the nanoparticles was perpendicular to the electron beam. The electron diffraction pattern could be indexed along the [100] zone axis (Figure 2C). When tilted off to nearly 90°, the electron diffraction pattern (Figure 2D) again shows the (100) spot, which confirms that the growth direction was along the [100] direction. Since vertical nanowires were obtained on many different substrates, it implies that the vapor may have condensed to form similarly oriented seeds on those surfaces as well.

The intramolecular charge transfer between the neighboring amine and carbonyl groups is responsible for the color and fluorescence of DAAQ. In an ethanol solution, the molecules exhibit two resolved absorption bands at 275 and 490 nm, respectively (Figure 3A, red line).

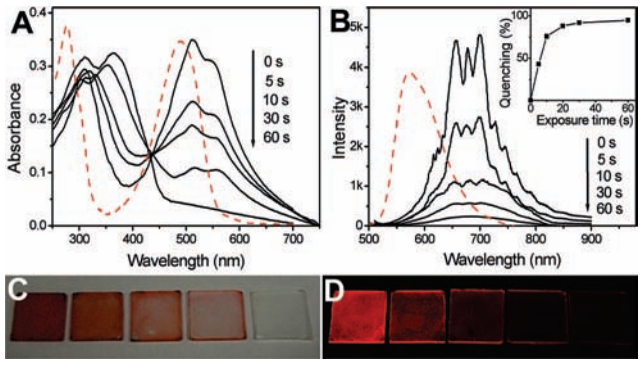

Figure 3. Time dependent absorption (A) and PL (B) spectra of the DAAQ nanowire arrays on exposure to the HCl vapor (*ca.* 5 ppm in air). The red dashed lines are the spectra of diluted DAAQ solution in ethanol. The inset in (B) shows the PL intensity at 675 nm over time. (C and D) Photographs showing samples exposed to HCl for 0, 5, 10, 30, and 60 s, respectively. (C) was taken under bright field illumination, and (D) was taken under dark field excitation by blue light (460−490 nm). The blue background color in (D) was removed to better match the observation by eye. The color changes observed in (C, D) were consistent with the changes in the spectra in (A, B).

The UV band is attributed to the $\pi \rightarrow \pi^*$ type $2^1B_u \leftarrow X^1A_g$ transition, while the visible band is assigned as the $1^1B_u \leftarrow X^1A_g$ transition, which is also $\pi \rightarrow \pi^*$ type and has a predominant intramolecular charge transfer character.[13] Both bands exhibited a red shift in the nanowires due to the molecular aggregation. Since the charge transfer can be interrupted if the N atoms are protonated, we carried out acid sensing experiments based on the changes in color and fluorescence on exposure to ∼5 ppm of HCl vapor in air. Figure 3A shows the absorption spectra of the nanowire arrays after being exposed to HCl for different lengths of time. The visible band rapidly decreased accompanied by apparent bleaching of the red color of the sample (Figure 3C). The photoluminescence (PL) spectrum of free DAAQ molecules in ethanol shows an approximately symmetric peak centered at 575 nm, whereas the nanowire arrays displays a super broadband emission from 500 to 900 nm (Figure 3B). On exposure to HCl, the PL intensity rapidly decreased, reaching over 90% quenching after only 30 s. Fluorescence quenching can be seen by eye when the samples were illuminated with blue light (460−490 nm) (Figure 3D). In a control experiment, DAAQ powders composed of micron sized particles did not show an apparent response even after 30 min of exposure (Figure S4).

Both the absorption and PL can be recovered in air to ∼95% of their original intensity in ∼2 h. However, they can be rapidly reset by basic vapors (e.g., NH_3) within 2 s. This also provides a mechanism for detecting basic vapors. The basic vapor deprotonated the amine groups and helped to restore the intramolecular charge transfer, leading to the recovery of color and fluorescence (Figure S5). The nanowires were exposed to cycles of acid and base vapors. A good consistency in the bleaching and quenching efficiencies (Figure S6) was observed.

In summary, vertical organic nanowire arrays of DAAQ dye molecules were prepared by a facile physical vapor transport method. The crystal structure and growth direction of the nanowires were determined by TEM and electron diffraction. These fluorescent nanowires were sensitive to acidic and basic vapors. The ease of oriented vertical growth should make it possible to directly integrate these nanowires into photonic sensing devices.[14]

Acknowledgment. The work was supported by a seed grant from the NU-NSEC (NSF EEC-0647560) and an ACS-PRF grant (48678-G10). TEM work was performed in the EPIC facility of the NUANCE center at Northwestern.

Supporting Information Available: Materials and methods; More SEM images of the nanowires; XRD patterns of the nanowires and bulk DAAQ; SEM images of the nucleation stage; Sensing performance of DAAQ powder; Pictures showing color and fluorescence changes of the nanowires on exposure to HCL and NH_3; PL quenching−recovery circles. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA809360V