2,4,5-Triphenylimidazole Nanowires with Fluorescence Narrowing Spectra Prepared through the Adsorbent-Assisted Physical Vapor Deposition Method

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The single crystalline nanowires have been fabricated from a small organic functional molecule, 2,4,5-triphenylimidazole (TPI), through an adsorbent-assisted physical vapor deposition (PVD) method. The introduction of the absorbents can significantly improve the dimensional uniformity of the as-prepared TPI nanowires. The TPI nanowires displayed interesting size-dependent optical properties, that is, the absorption spectra of the wires exhibit an obvious blue shift with the decrease of diameter, and simultaneously, the vibrational fine structures of the emission spectra emerge and become more pronounced with the diameter decreasing from 500 to 40 nm even at room temperature, which are usually observed only under cryogenic conditions. The emergence and enhancement of the vibrational structures are contributed to the increase of the long-range order and the degree of orientation with the decrease of diameter. The strategy described here should give a useful enlightenment for the fabrication of wirelike nanostructures from small organic molecules.

Introduction

During the past decades, one-dimensional (1D) nanomaterials have attracted extensive attention because of their unique properties and prospective applications in nanoscaled devices,[1−4] and yet most of the research works have been focused on inorganics[1−5] and polymers.[6−8] Recently, organic nanomaterials based on low-molecular-weight compounds have attracted more and more attention[9−15] because their electronic and optical properties are fundamentally different from those of inorganic ones.[16,17] There have been some reports on organic nanoparticles prepared with various methods, such as reprecipitation,[9−11] microemulsion,[12,13] thermal evaporation,[14] laser ablation,[15] and so forth. However, 1D nanomaterials fabricated from small organic molecules are much less investigated, and although a handful of approaches have been reported,[18−20] the control of monodispersity of the products remains the main problem all the time. Therefore, the development of a facile, mild, and widely applied method for the preparation of organic 1D nanostructures with high monodispersity is of great scientific and technical significance.

Vapor deposition (VD) is a facile and feasible method for preparing nanomaterials and has achieved great success in fabricating inorganic 1D nanostructures,[4,21,22] polymeric thin films,[23] and inorganic−polymer nanocomposites,[24] but the monodispersity of the products is hard to control[18] when small organic molecules are selected as deposition sources. It is known that for the VD method, the degree of saturation

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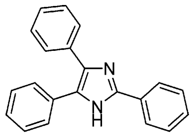
Chart 1. Chemical Structure of the TPI Molecule



is the predominant factor in controlling the morphology and dispersity of the products.[25]

Herein, we developed a new strategy, adsorbent-assisted physical vapor deposition (PVD), to improve the dimensional uniformity of organic nanowires. Adsorbents such as neutral aluminum oxide or silica gel used widely in column chromatography were introduced into our PVD method to control the degree of saturation considering that there should exist an adsorption−desorption equilibrium between the adsorbents and the organic sources. Through this method, the single crystalline nanowires were prepared from 2,4,5-triphenylimidazole (TPI), a small organic functional compound with fine photoluminescent[26] and chemiluminescent properties.[27] The adsorbents are proved to be indispensable in improving the uniformity of the as-fabricated TPI nanowires. The TPI nanowires show very interesting size-dependent optical properties. The absorption spectra of the wires exhibit an obvious blue shift with the decrease of the wire diameter. The emission spectra of the nanowires measured at room temperature are remarkably narrowed, and the vibrational fine structures become more pronounced with the diameter decreasing from 500 to 40 nm, which are usually observed only under cryogenic conditions.

Experimental Section

The model compound used in our work, TPI (Chart 1) was purchased from Sigma-Aldrich (No. T8320-8) and was used without further treatment.

The TPI nanowires were fabricated with the adsorbent-assisted PVD method. In a typical preparation, neutral aluminum oxide (or silica gel) and TPI were mixed uniformly with certain w/w ratios through grinding, which were subsequently put into a quartz boat. The quartz boat loaded with the mixture was then put into the center of a quartz tube which was inserted into a horizontal tube furnace. Cooling water flows inside the cover caps to achieve a reasonable temperature gradient in the tube. The protection of nitrogen was adopted during the process of VD to prevent the TPI from being oxidized. The flowing rate of nitrogen was kept at 100 sccm. Various substrates were put along the downstream side of the flowing nitrogen to collect the products. The kind of substrates did not influence the growth of TPI. The instrument is displayed in Figure 1. To prepare TPI nanowires, the furnace was heated to the sublimation temperature. After being heated, the TPI source was physically deposited onto the substrates and some wool-like products were obtained.

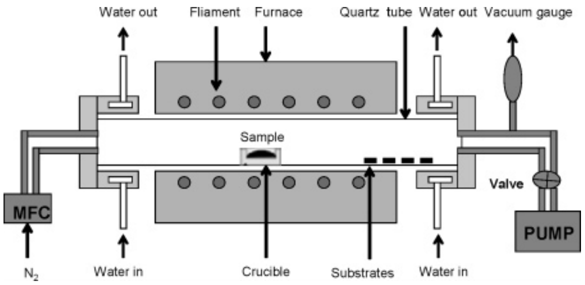


Figure 1. Instrument used for the preparation of the TPI nanowires.

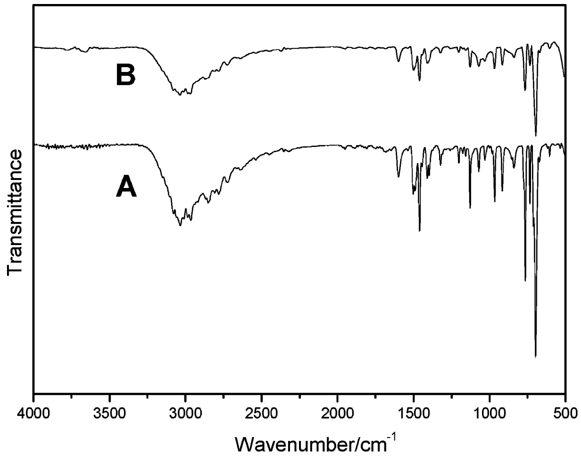


Figure 2. FT-IR spectra of (A) TPI powder and (B) TPI nanowires.

The as-prepared nanowires were characterized by field emission scanning electron microscopy (FE-SEM, Hitachi S-4300), transmission electron microscopy (TEM, JEOL JEM-2010), X-ray diffraction (XRD, Japan Rigaku D/max-2500 rotation anode X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation (λ = 1.5418 Å)), Fourier transform infrared (FT-IR) spectra (Bruker Tensor 27), electrospray ionization mass spectroscopy (ESI-MS) spectra (Shimadzu LCMS-2010), UV−visible absorbance spectra (Shimadzu UV-1601PC), fluorescence emission spectra (Hitachi F-4500), and fluorescent anisotropy (Edinburgh, FLS 920). The weight loss speeds of TPI and TPI mixed with adsorbents were measured using thermal gravity analysis (TGA, PE TGA-7) in a nitrogen atmosphere with a heating rate of 2 °C/min. The molecular geometries of TPI supramolecular structures in the nanowires were drawn, and the minimum energy configuration was optimized using the semi-empirical AM1 (Austin Model 1) method as implemented in the AMPAC program package.

Results and Discussion

The FT-IR spectrum (Figure 2) and the ESI-MS spectrum (See Supporting Information) of the as-prepared nanowires are consistent with those of the TPI powder, which proves that the TPI has not undergone decomposition or other chemical reactions during the VD process.

The length and diameter of the as-prepared TPI nanowires are dependent largely on the preparation conditions such as deposition time and temperature. Longer wires can be obtained by prolonging the deposition time. For example, if the deposition temperature is fixed at 230 °C and the w/w ratio of neutral aluminum oxide to TPI is fixed at 500:1, when 30, 60, 120, and 240 s are adopted, the lengths of the nanowires prepared finally are 1, 10, 25, and 100 μm, respectively. Moreover, TPI nanowires with larger diameters can be prepared by applying higher temperature. For example, if the deposition time is fixed at 30 s and the w/w ratio of aluminum oxide to TPI is fixed at 500:1, when TPI is deposited at 200, 210, 220, and 230 °C, nanowires with diameters of 40, 120, 300, and 500 nm, respectively, are obtained.

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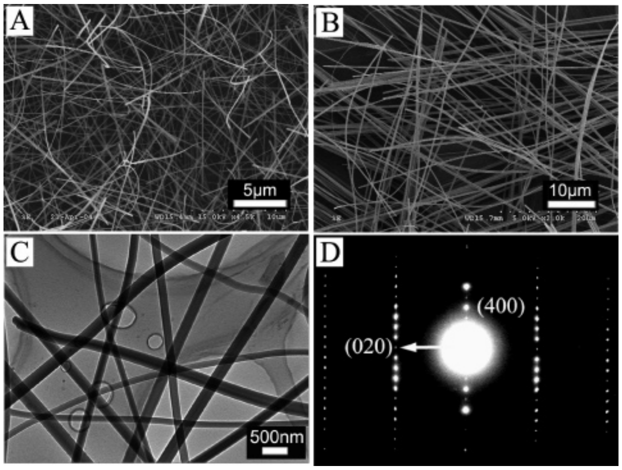

Figure 3. FE-SEM images of the TPI nanowires with (A) diameter of 120 nm and length of 10 μm and (B) diameter of 300 nm and length of 100 μm. (C) TEM images of some typical TPI nanowires. (D) SAED pattern of the TPI nanowire with the main diffraction spots indexed; the arrow indicates the direction of the wire.

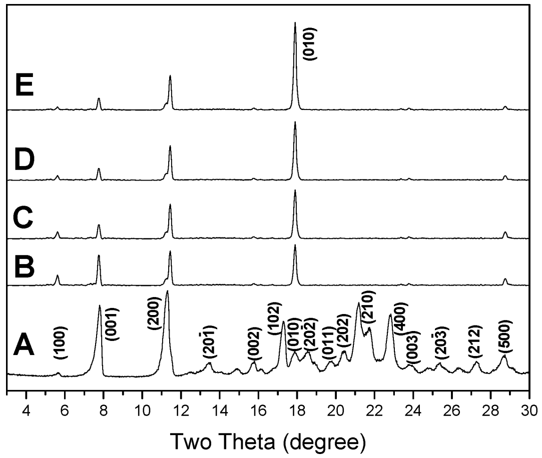

Figure 4. XRD spectra of (A) the TPI powder and TPI nanowires with diameters of (B) 500, (C) 300, (D) 120, and (E) 40 nm. The (200) peaks were normalized in the spectra of the nanowire samples.

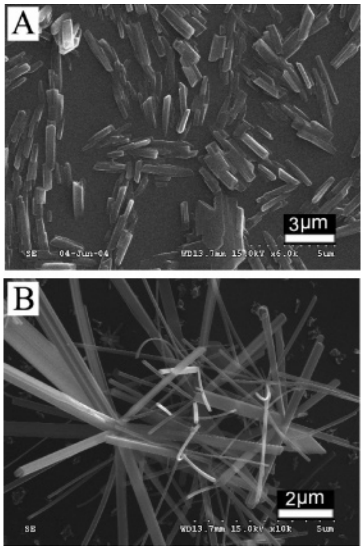

Figure 5. Products obtained by depositing TPI free of absorbent at 220 °C for (A) 30 s and (B) 60 s, respectively.

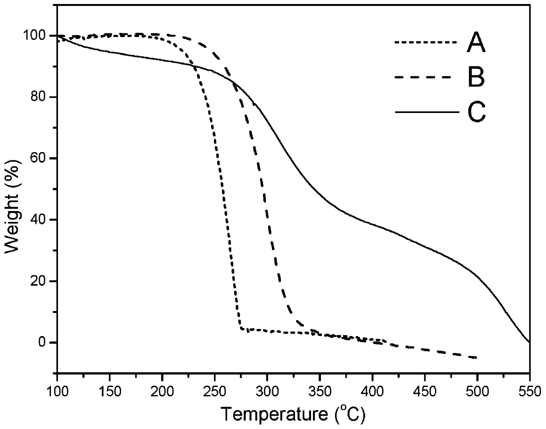

Figure 6. TGA plots of (A) the pure TPI powder, (B) the mixture of TPI with silica gel, and (C) the mixture of TPI with neutral aluminum oxide.

Figure 3A,B illustrates the typical FE-SEM images of the TPI nanowires deposited onto silicon wafers with different deposition times and at different temperatures. These images indicate that each of the nanowires obtained here has a smooth surface and uniform diameter all through the entire length. The TEM images prove that the geometrical shape of the TPI nanostructures is a solid wire (Figure 3C). The selected-area electron diffraction (SAED) pattern displayed in Figure 3D reveals that the as-prepared nanowires had single crystalline structures and grew along the *b* axis of the TPI crystal. This can also be proved by the contrast between the XRD pattern of TPI nanowires and that of the TPI powder displayed in Figure 4, which indicates the preferential orientation of the (010) lattice plane in the nanowires. Moreover, it is noticeable that the degree of the preferential orientation was obviously strengthened with the decrease of diameter from 500 to 40 nm.

The adsorbents are proved to play an important role in improving the uniformity of the TPI nanowires. When TPI powder is loaded into the quartz boat without any adsorbent, only some rodlike structures with very large diameters and poor monodispersity can be obtained (Figure 5), while if the adsorbent is replaced by inorganic salts without an adsorption property such as sodium chloride and potassium chloride powder, the uniformity can be improved only to a limited extent. Furthermore, the uniformity of the nanowires improves with the increase of the w/w ratio of adsorbent to TPI when the ratio is lower than 500:1, while it remains approximately the same when the ratio is increased further. The contrast indicates that although the dispersion also contributes to the uniformity of the nanowires, the role of the adsorption is more decisive.

The effect of the absorbents was further investigated with TGA measured in a nitrogen atmosphere. Figure 6 reveals the TGA plots of TPI powder and the mixture of TPI with the adsorbents, in which the weights of TPI are normalized as 100% for all the three samples. It can be observed from the slopes of the plots that the introduction of both neutral aluminum oxide and silica gel can slow the weight loss process of TPI remarkably in the adopted temperature arrange (200−230 °C), through which the degree of TPI vapor saturation is controlled readily. To satisfy the requirement of sample quantity, the w/w ratio of the adsorbent to TPI adopted in the TGA measurements was 10:1 rather than 500:1. It is reasonable that the weight loss speed should be even slower when the ratio was 500:1, as is the case in our

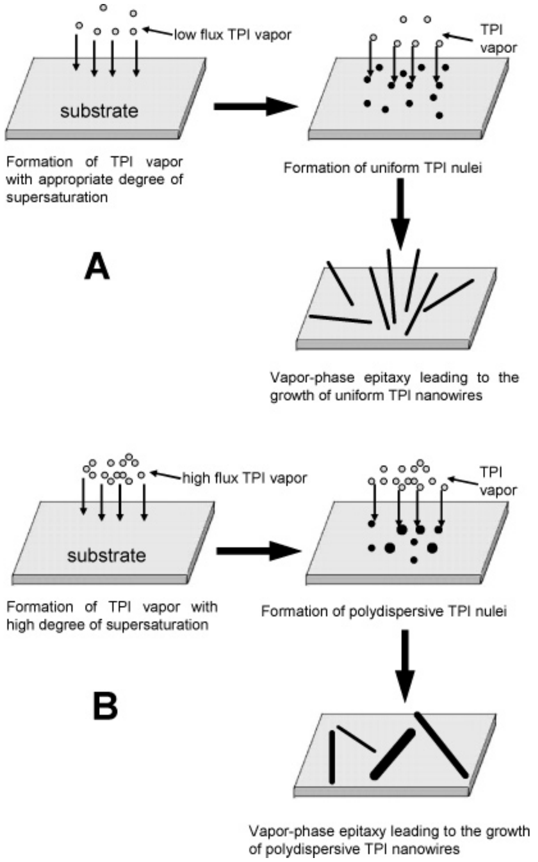

Figure 7. Schematic illustration of the growth mechanism of the as-deposited TPI nanowires (A) with and (B) without the assistance of adsorbents.

VD process. The plots of TPI mixed with sodium chloride and potassium chloride with a w/w ratio of 10:1 are almost the same as curve A.

The growth of the nanowires here is considered to be controlled by a vapor−solid process because no catalyst is adopted and no droplet is found at the top of the wires.[28] When the sources of the TPI/adsorbents mixture are heated to the deposition temperatures, the TPI will sublime to bring an appropriate degree of TPI vapor saturation via the adsorption−desorption equilibrium, which in turn results in the formation of small TPI crystal nuclei with relatively better uniformity on the substrates. The subsequent TPI vapor can be adsorbed onto the nuclei through the intermolecular interactions such as hydrogen bond, $\pi-\pi$ stacking, van der Waals contact, and so forth, leading to the uniform growth of TPI in one dimension by the mechanism of “vapor-phase epitaxy”. The vapor-phase epitaxy mechanism can also be testified by the fact that longer wires can be prepared by prolonging the deposition time. The mechanism is presented schematically in Figure 7A. Comparatively, when the TPI sources are free of adsorbents, as illustrated in Figure 7B, a high flux of TPI vapor can result in some large nuclei on the substrates during the initial stages, which can induce the growth of wires with larger diameter, and, therefore, the polydispersive products as shown in Figure 5 are obtained.

The optical properties of the TPI nanowires are dependent primarily on the diameter while insensitive to the length.

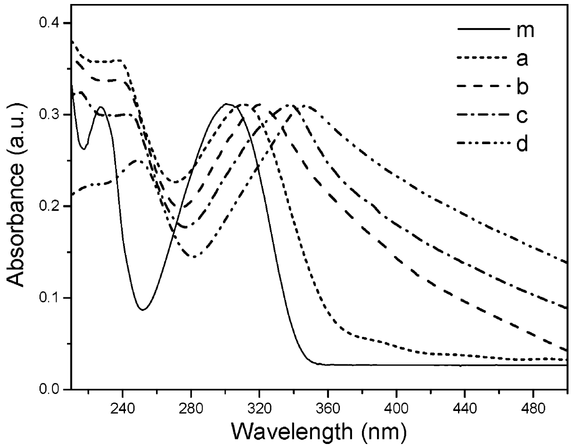

Figure 8. UV−visible absorption spectra of TPI nanowires with different diameters deposited onto quartz wafers: (a) 40, (b) 120, (c) 300, and (d) 500 nm. (m) The spectrum of TPI monomers.

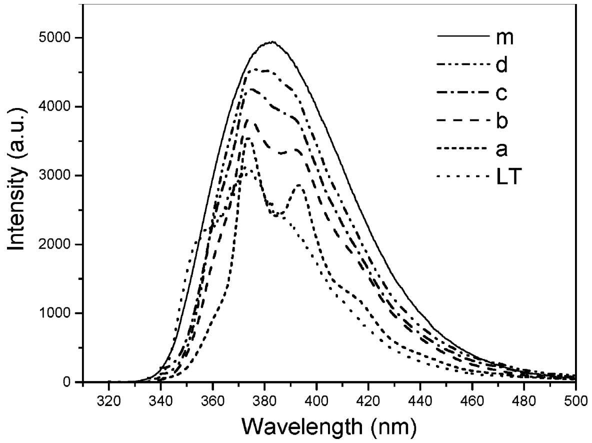

Figure 9. Fluorescence emission spectra of TPI nanowires with different diameters deposited onto quartz wafers: (a) 40, (b) 120, (c) 300, and (d) 500 nm. (m) The spectrum of TPI monomers measured at room temperature and (LT) low-temperature (77 K) fluorescence spectrum of the TPI monomer. All the emission spectra were excited at 310 nm (4.00 eV).

Figure 8 displays the UV−visible absorption spectra of TPI nanowires with different diameters deposited onto quartz wafers. The monomer in ethanol exhibits two resolved absorption bands at 227 nm (5.46 eV) and 302 nm (4.10 eV) attributed to the transition of phenyl rings and the $S_0 \rightarrow S_1$ transition, respectively. For the nanowire samples, both the bands exhibit obvious blue shift as the diameter decreases from 500 to 40 nm, and simultaneously a new band gradually emerges and becomes predominant in the region of 325−350 nm, which also shows a blue shift with the decrease of the diameter. As the diameter decreases, the increase of the surface area causes lattice softening, and, therefore, the Coulombic interaction energies between molecules become smaller, which results in the wider band gaps.[10]

A more significant phenomenon was displayed by the fluorescence emission spectra shown in Figure 9. The spectrum of the TPI monomer measured at ambient temperature shows an approximately symmetric peak centered at 383 nm (3.24 eV), whereas the vibronic levels are well resolved in the low-temperature spectrum measured at 77 K. It is interesting to note that the narrowing spectra can also be observed in our nanowire samples even at room temperature and became more pronounced with the decrease of diameter.

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The emergence and enhancement of the vibrational structures must be pertinent to the arranged mode of the TPI molecules in the as-prepared nanowires. The molecular packing arrangement with minimum potential energy in the nanowires was optimized with the AM1 method on the basis of the XRD and SAED results (see Supporting Information). The nanowires were stacked through $\pi-\pi$ interactions, and van der Waals contacts from the hydrogen bond chains formed between the N−H group at one TPI molecule and the pyridine-type N atom at the neighboring one. In an amorphous environment, the emission band broadening results mainly from the fact that the molecules each have somewhat different energy levels. In our single crystalline nanowires, however, the molecules are confined distinctly in the lattice with a specific geometric configuration and high degree of orientation, which can be further testified by the fluorescence anisotropy (See Supporting Information). In this case, many molecules share the same energy level, so the degree of freedom of their vibrations is drastically reduced.[29] The local environment of the molecules in the nanowires does not change in time during the emission process, and only those molecules that have energy levels corresponding with the excitation wavelength can be excited, which results in the emergence of the vibrational fine structures.[29]

Moreover, the vibrational structures become more and more resolved with the diameter decreasing from 500 to 40 nm, as is assigned to the increase of the long-range order[30] and the degree of orientation[31,32] with the decrease of the wire diameter, which was further testified to by the XRD patterns shown in Figure 2. When the diameter decreases to 40 nm, almost all the molecules adopt the same configuration, so the vibrational structures of the emission spectra become well-resolved just like that of the single molecules.[31−33]

Conclusion

In summary, the single crystalline nanowires were successfully fabricated from a small organic functional molecule, TPI, with the adsorbent-assisted PVD method. The adsorbents were proved to be effective in improving the uniformity of the TPI nanowires. An interesting size-dependent absorption spectrum and an evident narrowing of the emission spectra were observed in the nanowires at room temperature, which may be helpful for the development of homogeneous light emitting devices and to improve the resolution of fluorescence analysis without resorting to low temperature. The strategy described here should give a useful enlightenment for the fabrication of wirelike nanostructures from small organic molecules with tunable sizes and a wide range of applications.

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Supporting Information Available: The ESI-MS mass spectra of TPI powder and TPI nanowires, packing arrangement of TPI molecules in the nanowires, and fluorescence spectra and corresponding polarization spectrum of nanowrires with a diameter of 120 nm and length of 10 μm (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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