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Synthesis of Organic One-Dimensional Nanomaterials by Solid-Phase Reaction

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During the past decade, the synthesis and functionalization of one-dimensional (1D) nanomaterials has become one of the most highly energized research areas. Because of their low dimensionality and high aspect of ratio, 1D nanomaterials possess highly unusual physical properties. Great efforts have been placed on the synthesis of 1D nanomaterials, and various methods^{1–6} have been exploited. Most of studies concern metallic,⁷ semiconductor⁸ and other inorganic materials.⁹ In contrast to inorganic materials, organic materials have peculiar electronic and optical properties. They are readily synthesized, show remarkable improvements on stability, and can be polyfunctionalized to allow for tailoring their optical, electronic, and chemical properties. There are some preparation methods available^{10–12} for organic nanomaterials, such as reprecipitation,¹⁰ evaporation,¹¹ and microemulsion.¹² However, the preparation of organic 1D nanomaterials remains poorly studied, and only a few successful examples have been reported.¹³

In recent studies, we have developed a novel and generic technique to fabricate the anthracene (AN) nanowires and perylene (PY) nanorods on the basis of solid-phase organic reactions under controlled reaction temperature, time, and argon gas flow rate. Solid-phase reaction of 9-anthracenecarboxylic acid (ACA) with CaO at 340 °C for 2 h, placed at the center of a quartz tube that was inserted in a horizontal tube furnace, resulted in wool-like products that formed on the surface of the copper wafer placed at the downstream end of the quartz tube. The full characterization data of the products indicates the typical characteristics of AN. The SEM image (Figure 1A) reveals that the products consist of a large quantity of wirelike nanostructures with lengths in the range of several to tens of micrometers, while their diameters are in the range of tens of nanometers to several micrometers. The aspect of ratio of the corresponding nanowires lies in the range of about 50–100. Figure 1B shows that the diameter of AN nanowires is about 410 nm. The surfaces of AN nanowires are clean and smooth. The nanowires are rather straight and have a uniform diameter along the entire length. TEM observations reveal that the geometrical shape of the AN nanostructures is a wire (Figure 1C,D). The diameter and length of the AN nanowires is in the range of 40 nm to 1.5 μm and 9–20 μm . The X-ray diffraction (XRD) patterns of the AN nanowires show it to be a monoclinic crystalline system. The stronger diffraction peak of the nanowires at (200) indicates a preferential orientation along the *a* axis and a quasi-one-dimensional shape, which is demonstrated by the TEM and SEM.

The luminescence spectra of the AN nanowires during synthesis display differences from those of AN bulk crystals (Figure 2A) which demonstrates the characteristics of AN monomer emission bands at 420 and 445 nm (attributed to the 0–0 band by D₁ and D₂ bands, respectively) and the excimer bands at 486 and 530 nm

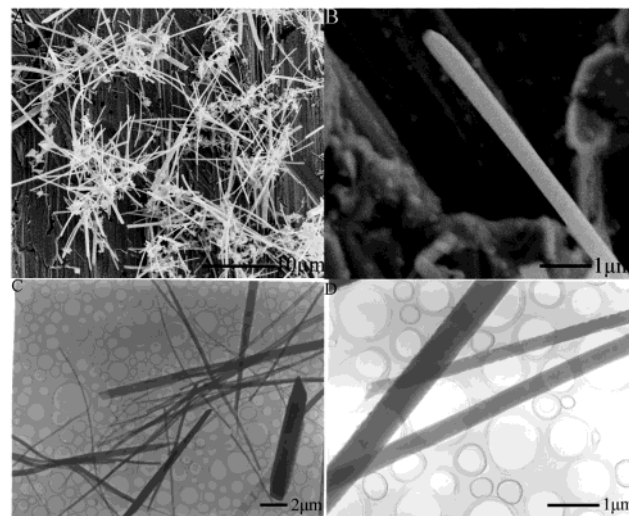


Figure 1. (A) Low magnification SEM image of the AN nanostructures to show the large quantity of nanowires. (B) SEM images of typical single AN nanowire. (C) Low magnification TEM image of the AN nanostructures to show the large quantity of nanowires. (D) TEM images of some typical AN nanowires.

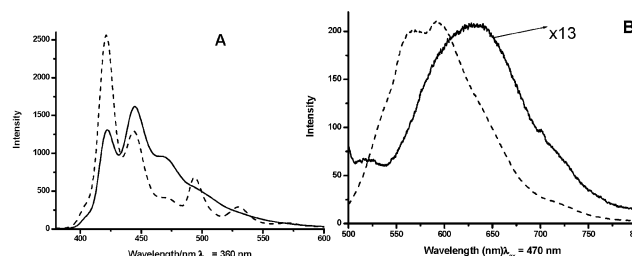


Figure 2. (A) The luminescence spectra of AN nanowires (solid line) and the bulk crystal of AN (dash line). (B) The luminescence spectra of PY nanorods (solid line) and the bulk crystal of PY (dash line).

(attributed to the AN formed by two AN molecules overlapped each other with one benzene ring^{14,15}). The (100) direction of the anthracene crystal is known to be responsible for the D₂ band in the luminescence spectrum, whereas those in the (001) direction are responsible for the D₁ band.¹⁶ However, the emission spectrum of AN nanowires show a sharp luminescence centered at 443 nm due to growth of orientation along the *a* axis. In the case of AN nanowires having larger diameters, the maximum peak position of the emission band is shifted to longer wavelength. Without the appearance of any broad band in the longer wavelength region (486 and 530 nm), it is suggested that there is scarcely any excimer^{17,18} in the AN nanowires. It is also completely different from AN nanoparticles in which there are dual emissions, the monomer bands

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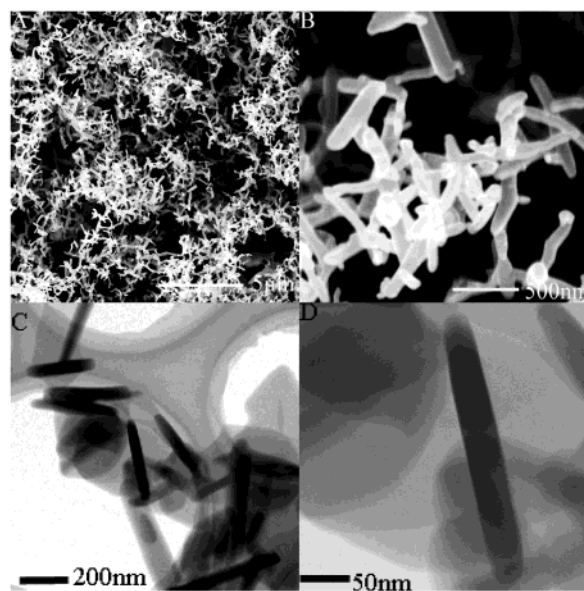


Figure 3. (A) Low magnification SEM image of the perylene nanosstructures to show the large quantity of nanorods. (B) Medium magnification SEM images of PY nanorods. (C) TEM images of the large quantity of PY nanorods. (D) TEM images of a typical PY nanorods.

at 400 and 420 nm and the red-shift bands at 450, 486, and 513 nm.¹⁹

The PY nanorods were synthesized by solid-phase reaction of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) with BaO at 280 °C for 2 h. The full characterizations of the product indicate it is comprised of PY molecule. SEM images reveal that the products consist of a large quantity of rodlike nanostructures with lengths in the range of hundreds nanometers to several micrometers, while their diameters are in the range of tens nanometers to hundreds nanometers (Figure 3A,B). The most of the PY nanorods have uniform diameter along their lengths, and the lengths are about 1 μm . The XRD patterns of the products display the PY nanorods to be α perylene crystal, which is demonstrated on fluorescence spectrum. TEM observations also reveal that the geometrical shape of the PY nanostructures is a rod (Figure 3C). The diameter and length of the PY nanorods lies in the range of 30–110 nm and 160–500 nm, respectively. Figure 3D shows that the typical diameter and length of PY nanorods is about 40 and 380 nm, respectively.

As described in the Figure 2B, only one excimer emission fluorescence (625 nm) is observed, which is different from the emission of PY bulk crystals demonstrating two kinds of excimer emission fluorescence at 566 nm (Y-type excimer) and 590 nm (E-type excimer), respectively. It suggests that the major build units of PY nanorods are the ideal dimeric α -phase PY packing configuration.^{20–22} In the α -phase PY crystal, the E-type excimer is interpreted as the stable one composed of card-packed dimeric units. In this excimer, the two PY molecules have a strong interaction in both the ground and excited states, enough to show the dimmer absorption to be different from the monomer absorption and the further red-shifted. It is also quite different from that of PY nanoparticles, which appear as the mixture emission of monomer, E-type and Y-type excimer emission.^{12,23}

In the present work, no droplet is found and no catalyst is used when the 1D organic nanoscale materials are synthesized at a proper synthesis temperature. Thus, the growth of the 1D organic nanoscale materials maybe governed by the vapor–solid (VS) process,^{24–26} which is proposed for the wirelike nanostructures of oxides. At the appropriate temperature, the chemical reaction of the solid phase

occurs, in which the melted organic reagents react with inorganic reactant. Then the products are evaporated at a higher temperature, directly depositing on a substrate at a lower region and growing into 1D organic nanomaterials. During the growth of the 1D organic nanomaterials, the temperature and the supersaturation ratio are the two dominant processing factors in controlling the morphology of the products.²⁷

We successfully obtained organic small molecular AN nanowires and PY nanorods using the solid-phase organic reaction thermal evaporation method. The AN and PY molecules display the dimension-dependent emission properties observed in the AN nanowires and PY nanorods. This approach is expected to form a new general route for the controlled morphosynthesis of organic molecular materials in restricted dimensions, with controlled size and shape, the solid-state physical properties of which are of great interest. As demonstrated above, the approach should have an outstanding potential in providing customized 1D nanomaterials for a broad range of applications in nanoscience.

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Supporting Information Available: Synthetic procedures, full characterization data, and XRD patterns of AN nanowires and PY nanorods and the chemical reaction equations of ACA and CaO, PTCDA and BaO. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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