Excitation-wavelength-dependent photoluminescence of a pyromellitic diimide nanowire network†

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Nanowires from deposition of pyromellitic diimide (PMDI) from the gas phase and their unique excitation-wavelength-dependent photoluminescence were demonstrated. The luminescence peaks of the PMDI nanowires red-shifted as the excitation wavelength increased. The relationship between the luminescence peak and the excitation wavelength is nearly linear in a broad range of excitation.

The observation of excitation-wavelength-dependent photoluminescence (EWDP) from nanostructures of metal oxides and semiconductors has attracted attention because of the nanostructures’ unique luminescent behavior and potential applications in photoluminescence, solar energy conversion, optoelectronic and chemical sensor devices. Examples of these nanostructures are nanocollodions,1 nanowires of ZnO,2 porous silicon,3 anodized alumina membranes,4 etc. In general, the emission peaks of these nanostructures shift toward longer wavelength when the excitation wavelength increases. Several mechanisms have been proposed to explain the EWDP phenomenon, such as incomplete solvation of the excited state of the species,1 size distribution for the nanocrystallites,3 level splitting by doped ions,4 etc. All of these involve the existence of a size or change distribution of molecules or the nanostructures. It has also been suggested1 that the presence of the heterogeneous, energetically different molecules or nanostructures alone is not enough for a system to exhibit EWDP behavior. Another common requirement is that the species should be excited selectively and there is no energy transfer between the energetically different species. These may be the reasons why EWDP behavior has been observed from only a few nanostructures so far. In this work, we report the EWDP phenomenon of a pyromellitic diimide (PMDI) nanowire network, which is the EWDP behavior observed in an organic material nanostructure.

![Pyromellitic diimide](image)

During the past decade, considerable attention has been focused on self-assembled or supramolecular electronics that are based on polycyclic aromatic hydrocarbons.5 The need for higher quantum efficiency and ease of fabrication in nanoelectronics drives the search for new materials. Polycyclic aromatic hydrocarbons have been a subject of great interest as potential candidates for self-assembly into nanostructures having semiconducting and photoluminescence properties.

Most of the self-assembling processes of small organic molecules to form nanostructures have been carried out in solution. Many polycyclic aromatic hydrocarbons, however, have a very low solubility in any solvent due to the high lattice energy. The traditional approach is to modify the polycyclic aromatic hydrocarbons with side chains to increase the solubility.5 Recently, alternative approaches, such as reprecipitation,6 thermal evaporation,7 microemulsion,8 laser ablation9 et al. have been applied to assemble polycyclic aromatic hydrocarbons into nanostructures without modifying the molecules.

The assembly of polycyclic aromatic hydrocarbons through the thermal evaporation and deposition method is in its infancy and only a few studies have been reported. In our previous work, we reported10 the formation of perylenediimide (PTCDI) and naphthalenediimide (NPDI) nanostructures in the gas phase with a thermal evaporation method. Here, we applied the same method to grow a PMDI nanowire network. Briefly, 5 mg of PMDI powder was placed in a 50 mL quartz tube. The tube was heated in a vacuum to 500 °C for 1 h. The tube was allowed to cool to room temperature. PMDI nanowires that were self-assembled on glass substrates were collected for analysis.

Fig. 1, left, shows a scanning electron microscopy (SEM) image of the nanowire network of PMDI. The PMDI nanowires have a dimension of ~60–500 nm, and a length greater than 10 μm. Transmission electron microscopy (TEM) experiments indicated that the PMDI nanowires (Fig. 1 right) have an amorphous structure. The surface of the nanowires is rough. Small grains, with diameter of 10–20 nm, were widely distributed on the nanowire surfaces. No electron diffraction pattern (figure not shown) of the PMDI nanowires was observed. More TEM images with different sizes and morphologies of PMDI nanowires are shown in the ESI.†

The PMDI nanowires were further studied by attenuated total reflectance infrared (ATR-IR), photoluminescence, and UV-visible spectroscopy. The ATR-IR experiment showed that the nanowires are comprised of the diimides, but not decomposed chemicals. Fig. 2 shows the PMDI nanowire network has two photoluminescent peaks (Fig. 2a and c). When the network was excited at 360 nm, two photoluminescent peaks at 477 and 564 nm were observed.

Since the PMDI powder does not show fluorescence in the visible range, the photoluminescence from the PMDI nanowire network may be attributed to the band gap of the
nanostructures. Various mechanisms, such as the quantum size effect,\textsuperscript{3} have been proposed to explain the photoluminescence properties of nanostructures.\textsuperscript{11,12} According to these mechanisms, nanostructures with different morphologies, shapes, and sizes have a photoluminescent wavelength, which varies over a wide spectral range from the infrared to the UV. However, since the band gap between the levels of free electrons and holes of organic nanostructures is generally greater than the intramolecular band gap (around 4 eV in PMDI), it is not clear at this stage why the emission can occur in the visible range.

The unique property of this nanowire network is its EWDP behavior. When the nanowire network was excited at various wavelengths from short to long with an interval of 20 nm, the photoluminescence peaks showed a synchronous red-shift with an interval of 20 nm. The shift of the first photoluminescence peaks exhibited in a wide range from 438 to 794 nm with the excitation wavelength from 320 to 680 nm. The PMDI in solutions has a weak fluorescence, but EWDP behavior was not observed (see ESI).

Although the photoluminescence phenomenon of nanostructures is not fully understood, it is generally recognized\textsuperscript{1–4} that the EWDP phenomenon is due to the size distribution of nanostructures, which can also be used to explain the EWDP behavior of the PMDI nanowire network. The TEM images have shown the existence of a size distribution of the PMDI nanowires. It is expected that nanowires of different sizes can be excited only at different wavelengths. This has been confirmed from the excitation spectra of the PMDI nanowire network (Fig. 3), which showed that the photoluminescence at various wavelengths originated from the excitation of different sized nanowires. Beside the size distribution, the observation of EWDP from the PMDI nanowire network is also attributed to the separation of the nanowires so the energy transfer between a structure with a higher vibrational level and a structure with a lower vibrational level of the excited states is inefficient.

PMDI powder does not show adsorption between 300 and 1000 nm. On the other hand, the PMDI nanowire network has a broad absorption spectrum from 300 to 1000 nm, suggesting broad energy levels or band gaps. This result further confirmed the existence of a size distribution of the nanowires. From the molecular level, the band gap differences may originate from the intermolecular potentials and the hydrogen bonding between the PMDI molecules.

This photoluminescence of PMDI nanowires, to the best of our knowledge, is the first EWDP phenomenon observed for a nanostructure of an organic material. It should be noted that the photoluminescence of PMDI nanowires is extremely weak, especially at longer excitation wavelengths (Fig. 2). The fact that the EWDP phenomenon has not been observed from other organic nanostructures, such as the PTCDI nanowires, may be due to the fluorescence of organic molecules themselves, which overlapped the weak photoluminescence of the nanostructures. The PMDI nanowires might be, so far, the only nanostructure to demonstrate a nearly straight line between the luminescence peak and the excitation wavelength in a broad range (greater than 300 nm) of excitation. This linear relationship is different from other EWDP behaviors reported\textsuperscript{1,13} and will be further investigated in the future. For instance, it is possible that the EWDP effect is caused from excitons as the PMDI molecules pack, or a charge transfer.
state. Another possibility is a combination of a broad range of excitonic and solvation effects between clusters of PMDI molecules leading to a broad range of localized singlet energies, which depends directly on the short range packing of the PMDI clusters.

In summary, we reported the EWDP behavior of a PMDI nanowire network. The luminescence peak shifts towards red linearly as the excitation wavelength increases. This observation has been attributed to the presence of energetically different forms of the nanowires. Potential applications of these nanowires include in optoelectronics and light emitting devices. Our results continue to demonstrate the uniqueness of the nanostructures obtained by the simple yet effective self-assembly technique from a gas phase deposition method.

Notes and references