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Shape-Controlled Micro/Nanostructures of 9,10-Diphenylanthracene (DPA) and Their Application in Light-Emitting Devices

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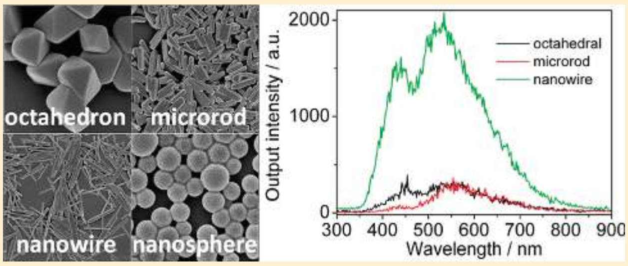
ABSTRACT: Two novel shapes of 9,10-diphenylanthracene (DPA) micro/nanostructures: octahedron and sphere together with microrod and nanowire have been synthesized via a surfactant-assisted self-assembling process. These micro/nanostructures have been characterized by UV—vis, fluorescence spectra, X-ray diffraction (XRD), field emission scanning electron microscope (FESEM), and transmission electron microscope (TEM). Our results indicated that the absorption and emission spectra of as-prepared particles were slightly blue-shift when the shape of DPA particles changed from octahedron to microrod and finally to nanowire. This result could be explained by the different growth directions of DPA micro/nanostructures. To study the relationship between shape and devices' performance, the heterojunction light emitting diode (LED) devices of quartz/ITO/organic particles/*n*-SiC/Ti(10 nm)/Au(120 nm) have been prepared. The testing results showed that the different shapes of DPA micro/nanostructures did affect the performance of diodes and the nanowire was the best shape for the heterojunction light emitting diode (LED) devices.

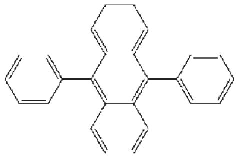


1. INTRODUCTION

The assembly of organic small molecules into micro/nanostructures, whose properties are beyond those of their bulk components, have attracted extensive attention not only in fundamental science but also in potential technological applications.[1−6] Many reports have demonstrated that the properties of these micro/nanostructures can be easily tailored by molecular design, chemical modification of their structures, doping treatment, or chemical conversion. Especially, the shape control, size management, and surface modification of organic micro/nanostructures have provided a powerful platform to tune their optical and electronic properties.[7]

Because 9,10-diphenylanthrance (DPA, Scheme 1) is a highly fluorescent molecule and has been widely used in organic optoelectronics, the investigation of the shape-dependent properties of DPA micro/nanostructures might be helpful in enhancing the devices' performance and in preparing other polycyclic aromatic micro/nanomaterials, whose structures are similar to DPA molecules. Recently, Lee et al. have reported that DPA molecules readily self-assembled into nanoribbons and nanorods by varying the solubility of DPA molecules in the preparation solution.[3a] To achieve a detailed understanding of the shape-dependent property of DPA micro/nanostructures and explore the relationship between shape and the performance of organic light-emitting diodes (OLED), we reinvestigated the DPA system and obtained two new shapes of DPA micro/nanostructures: octahedron and sphere. In addition, the performance of OLEDs based on various shapes of DPA micro/nanostructures such as octahedron, microrod, nanowire, and nanospheres has been tested and compared in this work. Our results show that the different shapes of DPA micro/nanostructures do affect the performance of diodes and the nanowire is the best shape for heterojunction light emitting diode (LED) devices.

Scheme 1. Structure of 9,10-Diphenylanthracene



2. EXPERIMENTAL SECTION

Materials. 9,10-Diphenylanthracene (DPA) and tetrahydrofuran (THF) were purchased from Alfa Aesar company (Germany)

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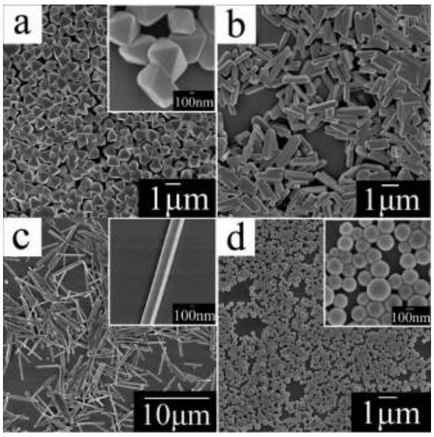

Figure 1. FESEM images of different morphologies of DPA particles: (a) microoctahedrons, the insert is the magnified area; (b) microrods; (c) nanowires, the insert shows a typical nanowire; (d) nanospheres, the insert is a magnified area.

and VWR Singapore PTE Ltd. (France), respectively. Poly(ethylene glycol)-block-poly(propyleneglycol)-block-poly(ethylene glycol) (P123), cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), and polyvinylpyrrolidone (PVP40T, wt 40 000) were purchased from Aldrich Company (Germany). All chemicals were used directly without further purification. Ultrapure water was obtained from the Millipore S. A. 67120 apparatus (France) with a resistivity of 18.2 MΩ cm.

Methods. The octahedral DPA microcrystals were prepared by adding 1 mL of 0.5 mM DPA/THF solution into 5 mL water containing P123 (1 mg/mL) with a strong stirring. After stirring for 5 min, the solution was kept undisturbed overnight at room temperature before characterization. If the surfactant P123 was replaced by CTAB and SDA and other conditions kept same, nanowires rather than octahedrons were produced.

DPA microrods: 0.5 mL of 1 mM DPA/THF solution was diluted by 0.25 mL THF and was then injected into 5.25 mL P123 (1 mg/mL) aqueous solution. After stirring for 5 min, the obtained solution was aged overnight to give DPA microrods.

DPA nanowires: 0.5 mL of 1 mM DPA/THF solution was added to 5.5 mL P123 aqueous solution with strong stirring for 5 min. The as-prepared solution was left standing overnight before purification.

DPA nanospheres: 0.5 mL of 1 mM DPA/THF solution was injected into 5.5 mL PVP (0.5 mg/mL) aqueous solution. After stirring for 5 min, the obtained solution was aged overnight to form DPA nanospheres.

The preparation of SEM samples: A drop (30 μL) of the solution was put on a silica wafer and dried over 12 h. The as-prepared samples were then coated with platinum in an ion coater for 40 s.

Characterization. The sizes and shapes of the micro/nanostructures were observed on a FESEM (JSM-6340F, JEOL) at an accelerating voltage of 5 kV. The samples were also studied by TEM (JEM 2010F) to further confirm their morphologies. The X-ray diffraction (XRD) patterns were performed on a Bruker D8 X-ray diffractometer with Cu Kα radiation. The operating 2θ angle ranges from 5 to 90°. The cell data were obtained using a *JADE* software to simulate XRD patterns. The UV−vis absorption and fluorescence spectra of DPA nanostructures were recorded on Shimadzu UV-2501 and RF-5301 spectrophotometer, respectively. The FTIR spectra (KBr pellets) were performed on PerkinElmer spectrum GX.

Fabrication and Testing of Devices. The heterojunction LED was fabricated according to our previous procedure.[8] Briefly, on a clean *n*-SiC substrate, a Ti/Au contact (size of about 2 × 2 mm^2, ∼10 nm thick for Ti, and ∼120 nm thick for Au) was deposited by using electron beam evaporation at room temperature. Various DPA micro/nanostructures were drop-coated on the other side of *n*-SiC substrate. The top of the organic layers was covered by the ITO electrode, which was used as DPA micro/nanostructures' contact. The spectra were measured by connecting the cathode and anode of a constant voltage source to the ITO and Ti(10 nm)/Au(120 nm) metal contacts, respectively. Light was collected from the surface of the ITO glass by an optical fiber.

3. RESULTS AND DISCUSSION

Figure 1 shows the typical SEM images of the DPA nano/microstructures with different morphologies, which were prepared by the surfactant-assisted precipitation method via changing the ratio of DPA, water, surfactants, and organic solvents. As shown in part a of Figure 1, repeatable microoctahedrons were observed when 1 mL 0.5 mM DPA/THF solution was dropped into 5 mL P123 water solution (the ratio of THF/P123 is 1:5) with a strong stirring. The average size of as-prepared microoctahedrons is about 700 nm. When the ratio of THF/P123 increased to 1:7, microrods with the diameter in the range of 500−600 nm and the length between 1 and 2 μm were formed after 12 h (part b of Figure 1). When the ratio of THF/P123 was further increased into 1:11, the nanowires (diameter: 100−300 nm and length 2−4 μm) were obtained (part c of Figure 1). The insert in part c of Figure 1 shows a typical nanowire with the smooth and clean surface. In addition, the other ratios of THF and P123 solution were also performed. When the ratio is less than 1:5, the irregular structures including microoctahedrons and rods were formed, while the ratio is larger than 1:11, only the nanowires can be observed (Figure S1 of the Supporting Information). It is very clear that the ratio of THF/P123 does change the shape of DPA micro/nanostructures from microoctahedrons to microrods and then to nanowires.

The effect of surfactants on the aggregation behavior of DPA molecules was also investigated. When P123 surfactant was replaced by PVP, a large quantity of nanospheres with the size in the range of 100−250 nm were obtained. Unlike P123 surfactant, where the shapes changed as a function of the ratios of THF/P123, spherical shapes were retained when PVP surfactant was used at various THF/PVP ratios, ranging from 1:5 to 1:11. Further investigations with other surfactants such as CTAB and SDS only gave microrods (Figure S2 of the Supporting Information).

The micro/nanostructures were further examined by TEM and SAED patterns as shown as in Figure 2. The TEM results confirm the observed morphologies by SEM. The typical SAED patterns of microoctahedrons and nanowires (parts b and d of Figure 2) show that these as-prepared micro/nanostructures are crystalline. These as-prepared DPA micro/nanostructures were further characterized by powder XRD (Figure 3). Except the nanospherical shape, which is amorphous and has no XRD peaks in the experimental conditions, all other resulting shapes displayed the sharp peaks in XRD spectra. The further analysis of the XRD patterns shows that all crystalline shapes can be indexed into C2/*c* space group with the similar lattice constants (a = 10.683 Å, b = 13.552 Å, c = 12.257 Å, and β = 90.54°) as reported.[9]

Such formation of diverse shapes of DPA molecules could be explained by two different factors: (a) THF has a big effect on the

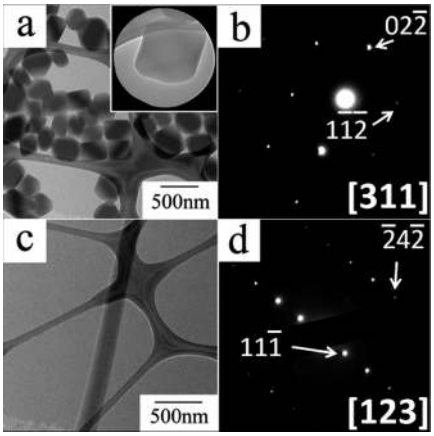

Figure 2. TEM images of micro/nanostructures (a) microoctahedron using P123 as surfactant, insert displays an octahedron; (b) the corresponding SAED pattern of the typical octahedron, the crystal structure viewed along the [311] direction; (c) nanowire using P123 as the surfactant; (d) the SAED pattern of the typical nanowire and the crystal structure viewed along the [123] direction.

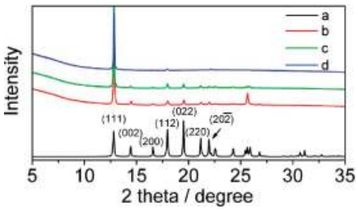

Figure 3. XRD patterns of DPA: (a) the simulation from single crystal's structure, (b) microoctahedrons, (c) microrods, and (d) nanowires. Note that nanospherical particles are amorphous and no peaks were observed under the same experimental conditions.

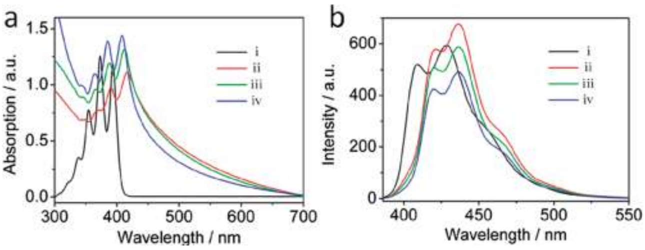

Figure 4. UV–vis (a) and fluorescence (b) spectra of DPA: (i) molecules in THF, (ii) microoctahedrons in aqueous solution, (iii) microrods in aqueous solution, and (iv) nanowires in aqueous solution.

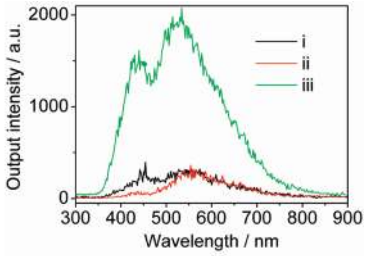

Figure 5. EL spectra of DPA micro/nanostructures/*n*-SiC heterojunction LED biased at 20 V: (i) microoctahedrons, (ii) microrods, and (iii) nanowires.

solubility of DPA molecules, which is a very important factor during the dynamic growth (size, direction, and shape) of DPA particles,[3a] and (b) the interaction between surfactants and DPA molecules plays another key role during the growth of DPA particles. The surfactants such as P123, CTAB, and SDS have a weak dipolar–dipolar interaction with DPA molecules, which has less effect on the self-assembly of DPA molecules. In these conditions, DPA molecules can form crystalline structures more easily. However, the self-aggregation might be disturbed and amorphous particles are formed if the surfactant (e.g., PVP) has a strong interaction ($\pi\cdots\pi$ attractions) with DPA molecules. Currently, the behavior of surfactants is still in debate.

The UV–vis absorption spectroscopy of DPA molecules in THF solution exhibits the maximum absorption (λ_{max}) at 393 nm and other peaks at 354 and 373 nm ($\pi-\pi^*$ transition, part a of Figure 4). When the DPA nanostructures were formed, all UV–vis absorptions are red-shifted with a broad tail absorption (scattering) in a longer wavelength (part a of Figure 4). The emission spectra of DPA molecules and particles have a similar trend as observed in UV–vis absorptions. Interestingly, when the shape of DPA particles changed from octahedron to microrod and finally to nanowire, that is, the length of particles increases, the UV–vis absorption and emission spectra are slightly blue-shift, which might be attributed to the different growth directions of crystalline DPA structures. Although the UV–vis absorption of DPA nanospherical particles undergo a slightly red-shift (6 nm different with molecules' absorption, Figure S3 of the Supporting Information), the fluorescence was obviously quenched (Figure S3 of the Supporting Information). These results might be explained by their amorphous structures and the attached PVP surfactants.

To avoid the effect of surfactants, all samples are washed three times by methanol/water (1:1) solution and checked by FTIR to confirm no surfactants' existence (Figure S4 of the Supporting Information). Figure 5 shows EL spectra from the heterojunction LED of different micro/nanostructures under a forward bias of 20 V. The spectra were measured by connecting the cathode and anode of a constant voltage source to the ITO and Ti/Au metal contacts of the heterojunction respectively. Light was collected from the surface of the ITO glass by an optical fiber to a PMT detector (Figure S5 of the Supporting Information). It is found that the emission spectrum of nanowire-based LEDs can be fitted by two Gaussian curves with peak wavelength at ~445 and 525 nm. However, the EL spectra from microoctahedrons and microrods show a broad emission bandwidth with fwhm equal to ~110 nm at the same bias and the emission peak is centered at a wavelength of ~550 nm. It was noted that no emission was observed from the heterojunction LED under a reverse bias, which suggested that a heterojunction is formed between the *p*-organic nanostructure and *n*-SiC. These EL spectra also show that the emission intensities in microoctahedrons, microrods, and nanowires are highly different. The emission intensity of microoctahedrons and microrods is approximately 6 times less than that of nanowires. The different electrical conductivities of these nanostructures may cause different efficiencies of external injection of carriers under a same forward bias. These results demonstrated that the nanowire is the best shape for heterojunction light emitting diode (LED) devices.

4. CONCLUSIONS

In summary, four different shapes of DPA particles have been successfully prepared by a surfactant-assisted reprecipitation method. The as-prepared shapes show different UV−vis absorptions and emissions phenomena. Further study about the effect of different shapes on OLED application indicates that the nanowire is the best shape that gives the best performance for such devices.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. SEM images of DPA particles prepared from THF/P123 (THF/P123 = 1:3 and 1:15) water solution; SEM images of DPA prepared from different surfactants; UV−vis absorption and fluorescence spectra of DPA nanospheres; FTIR spectra of different shapes of DPA particles after washing; and the lighting images of different shapes of DPA particles on OLED. This material is available free of charge via the Internet at http://pubs.acs.org.

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