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Preparation, characterization, and photoswitching/light-emitting behaviors of coronene nanowires†‡

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Coronene nanowires were prepared through the reprecipitation method. The as-prepared one-dimensional (1D) nanostructures were characterized by UV-vis, fluorescence spectra, X-ray diffraction (XRD), optical microscopy, field emission scanning electron microscopy (FESEM), and transmission electron microscopy (TEM). We found that coronene nanowires in aqueous solution emitted strong green light instead of blue light for coronene molecules in THF solution. Moreover, the thin film of coronene nanowires on rGO/SiO₂/Si electrode produced a strong photocurrent response upon irradiation. In addition, a heterojunction light emitting diode (LED) device with the structure of quartz/ITO/p-coronene nanowires/n-SiC/Ti (10 nm)/Au (120 nm) has been fabricated. The strong electroluminescence (EL) emission centered at ~430 nm was detected with a forward bias at 20 V. Our result showed that the use of organic nanowires as the p-type hole injection layer could produce diodes with performance better than those with only inorganic thin-film structures.

Introduction

Organic nanowires and nanorods have attracted particular attention during the past decades not only because they can act as active elements in nanoelectronics,¹ but also because they have the potential applications in biosystems.² The properties of organic nanowires and nanorods can be easily tailored by chemical modification of their structures, doping treatment or chemical conversion.³ Besides these, their optical behaviours can be affected by the aggregating effect, surface effect, or the increasing intermolecular interactions induced by the change of lattice.⁴ Currently, the self-assembly and applications of small organic molecules have been significantly focused due to their diversity, tailorability, and multifunctionality. Particularly, polycyclic aromatic materials with strong $\pi\cdots\pi$ stacking interactions, which can form columnar mesophases or 1D structures, are receiving continuous attention.⁵

The tunable optical and electronic properties have been realized through the shape control (*e.g.* nanoribbons, nanotubes, and nanowires)^{6–9} or size control^{10,11} or surface modification of organic nanostructures.¹² Compared to inorganic nanoparticles, organic nanostructures, as next generation electronic materials, have more flexibility in their synthesis and chemical modification to enhance their performance for prospective applications in various semiconductor devices.

Although several efforts have been made to synthesize new coronene derivatives and to control their self-assembly by utilizing various noncovalent interactions such as H-bonding,

$\pi\cdots\pi$ stacking and solvophobic interactions,¹³ the 1D self-assembly of a commercially available polycyclic aromatic hydrocarbon, coronene (Scheme 1), is unexploited. Clearly, systematic study of the parent molecule might be instructive to design and fabricate its derivatives.

Herein, we employ coronene as a model compound to fabricate its corresponding nanowires by the reprecipitation method. The as-prepared coronene nanowires were observed to exhibit strong green fluorescence in aqueous solution instead of blue fluorescence for coronene molecules in THF solution. The photoswitching and light-emitting behaviors were also studied in this research.

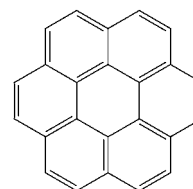
Experimental

Materials

Coronene, poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (P123), and anhydrous THF were bought from USA Lab, Aldrich Company (Germany) and VWR Singapore Pte Ltd (France), respectively. All chemicals were used directly without further purification. Ultrapure water in the experiment was produced by Millipore S. A. 67120 apparatus (France) with a resistivity of 18.2 M Ω cm.

Methods

The coronene nanowires were prepared as follows: 1 mL of 0.5 mM coronene solution in THF was injected into 5 mL water containing P123 (1 mg mL⁻¹) or other surfactants such as sodium



Scheme 1 The structure of coronene.

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dodecyl sulfate (SDS, 0.5 mg mL⁻¹) and cetyltrimethylammonium bromide (CTAB, 0.5 mg mL⁻¹). After stirring for 5 min, the nanowires were aged overnight at room temperature before characterization. In a typical preparation, a drop (20 μL) of the solution was put on a silicon wafer and dried over 12 h. The as-prepared samples were coated with platinum in an ion coater for 30 s before the SEM investigation.

The sizes and shapes of the nanowires were observed on a FESEM (JSM-6340F, JEOL) at an accelerating voltage of 5 kV. The samples were also studied by a TEM (JEM 2010F). The X-ray diffraction (XRD) patterns were measured on a Siemens D5005 X-ray diffractometer with Cu K α radiation. The operating 2 θ angle ranges from 5° to 85°. The cell data were obtained using JADE software to simulate XRD patterns.

The UV-vis absorption and fluorescence spectra of coronene nanowires were recorded on Shimadzu UV-2501 and RF-5301 spectrophotometer, respectively. Optical image was recorded by the Nikon intersilight C-HGF1 microscopy.

The photoswitching device was fabricated with reduced graphene oxide (rGO) as the electrode¹⁴ and the performance were measured by the electrochemical workstation (CHI 600C, CH Instrument Inc., USA). The typical device's fabrication was as follows. First, the graphene oxide (GO, 0.2 mg mL⁻¹ GO solution) was spin-coated (by 4000 rpm) onto a pre-cleaned hydrophilic SiO₂/Si wafer to form a GO-film on the SiO₂/Si substrate. Then, the as-prepared GO film was reduced to rGO by thermal annealing at 1000 °C for 2 h in Ar/H₂ (v/v = 1 : 1), which was used as the rGO-film/SiO₂/Si electrode. After that, the organic nanowires dispersed in pure water were drop-cast onto the above-prepared electrode, followed by the annealing at 150 °C for 1 h in an inert argon atmosphere. The photocurrent measurements were conducted in a three-electrode electrochemical cell with the coronene nanowires/rGO/SiO₂/Si electrode as the working electrode, a standard saturated Ag/AgCl as the reference electrode, and a Pt wire as the counter electrode. In this experiment, the potential is set at -0.5 V and the electrolyte is 0.5 M Na₂SO₄ aqueous solution. A 150 W halogen lamp was employed as the illumination source. The area of the immersed working electrode was kept at 0.5 cm². The thickness of thin film is 700 nm \pm 50 nm, which was measured on Alpha-Step IQ Surface Profiler.

The typical fabrication method of the heterojunction LED was shown as follows: The HF-cleaned n-SiC substrate was coated with a metal contact (size of about 2 \times 2 mm²), which consisted of a layer of \sim 10 nm thick Ti film and a layer of \sim 120 nm thick Au film, by using electron beam evaporation at room temperature. Coronene nanowires were drop-cast on the opposite side surface of metal-electrode-deposited n-SiC substrate. The top of the coronene nanowires was covered by the ITO coated quartz substrate, which was used as p-coronene nanowire contact. The EL spectra of the heterojunction LED were measured by connecting the anode and cathode of a rectangle pulse voltage source (with repetition rate and pulse width of 7.5 Hz and 80 ms, respectively) to the ITO coated quartz substrate and Ti (10 nm)/Au (120 nm) metal contact on the n-SiC, respectively. Light was collected from the uncoated side of the quartz substrate by an objective lens.

Results and discussion

Coronene nanowires have been prepared by reprecipitation in aqueous solution. Fig. 1a presents the typical SEM morphologies of coronene nanowires with diameters in the range of 100–500 nm and lengths of a few micrometres to 150 μm. Fig. 1b shows the magnified image of a typical single nanowire with a 250 nm diameter. It is clear that the surface of as-prepared nanowire is smooth and clean. The similar self-assembly behaviours of coronene were also observed in aqueous solution containing different surfactants such as CTAB and SDS solution (see ESI†, Fig. S1 and S2). Note that the charges of surfactants (CTAB: positive, SDS: negative, and P123: neutral) did not affect the aggregation of coronene molecules to form nanowires.

The coronene nanowires were further characterized by TEM (Fig. 1c) and selected area electron diffraction (SAED) patterns, which proved that all of these nanowires were single crystals (Fig. 1d). The polarized optical microscopy (POM) images of self-assembled coronene nanowires indicated that not only these nanowires were crystalline in nature but also they could be easily obtained in a large amount (Fig. 1e). Coronene nanowires have been characterized and confirmed by X-ray

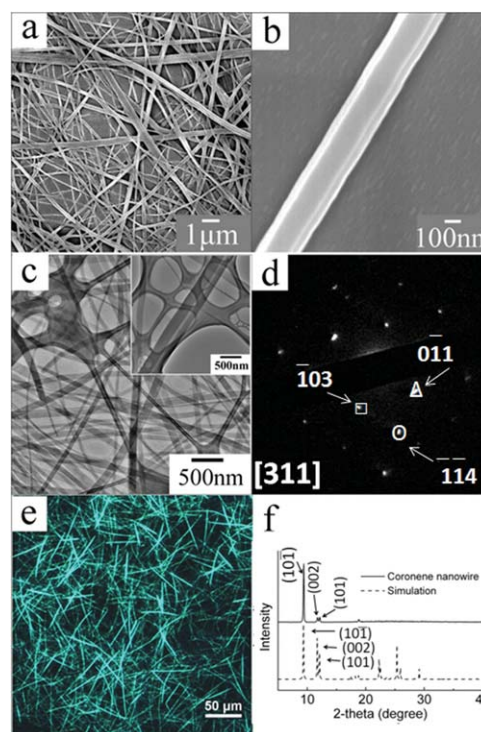


Fig. 1 (a) FESEM image of self-assembled 1D coronene nanowires using P123 as surfactants; (b) the magnification of single coronene nanowire; (c) TEM image of coronene nanowires, the inset shows a typical single nanowire; (d) the corresponding SAED pattern of the typical nanowire. The crystal structure of coronene nanowires viewed along the [311] direction. The square, triangle and circle represent (103), (011), (114), respectively; (e) the POM image of coronene nanowires excited at 365 nm; (f) the XRD patterns of coronene nanowires (solid line) and simulation from single crystal's structure (dash line).

diffraction (XRD), with the results shown in Fig. 1f. The XRD pattern of coronene nanowires was indexed in space group $P2_1/n$ as previously reported results with 'standard' lattice constants ($a = 10.122 \text{ \AA}$, $b = 4.694 \text{ \AA}$, $c = 15.718 \text{ \AA}$, and $\beta = 106.02^\circ$).¹⁵ The sharp diffraction peak at $2\theta = 9.34$ resulted from the ordered packing of coronene molecules. These distinct peaks ($2\theta = 9.34^\circ$, 11.66° , 12.06° , and 18.72°) also confirmed the high crystallinity of samples.

Coronene molecules in THF solution exhibited the absorption maximum (λ_{max}) at 301 nm and other peaks at 290, 323, 340 nm ($\pi-\pi^*$ transition) (Fig. 2a). When excited at 340 nm, the strong emission peaks at 425, 432, 443, 453, 472, and 482 nm were observed, which presented a blue fluorescence (inset in Fig. 2a). These results suggested that the coronene molecules were in monomeric form.¹⁶ However, when coronene nanowires were formed in aqueous solution, the absorption intensity decreased and a red-shift peak at 357 nm was observed, which was indicative of the formation of J-type aggregation structures through $\pi-\pi$ stacking and hydrophobic interaction.¹⁷ Interestingly, the fluorescence spectrum of coronene nanowires in aqueous

solution exhibited emission bands at 472, 500 nm (510, 530 nm, shoulder peaks) and emitted bright green light (inset in Fig. 2a). The red-shift emission is due to the aggregation of coronene molecules. Such aggregation can enhance the intermolecular interactions among coronene molecules, which were beneficial to the formation of excimers and led to the red-shift emissions of coronene nanowires. It should be noted that the quantum yield of coronene nanowires ($\Phi_f = 0.04$ using 9,10-diphenylanthracene ($\Phi_f = 0.95$ in ethanol) as standard¹⁸) was 4 times higher than that of coronene molecules in THF solution ($\Phi_f = 0.01$) with the excitation wavelength at 340 nm. The UV-vis spectrum of coronene nanowire thin film displayed the several broad absorption peaks at 321, 338 and 358 nm (Fig. 2b). The absorption spectra of coronene molecules in solution, nanowires in solution and nanowires in thin film are all different and the bathochromic shift of the low-energy region is expected to be similar to the previous observations of absorption from aggregate states in other organic molecular crystals such as tetracene,¹⁹ α -perylene²⁰ and 1,3-diphenyl-5-(2-anthyl)-2-pyrazoline.²¹ Considering our experimental results, we do believe that coronene molecules in aqueous solution and thin film could form J-type aggregation according to Kasha's rule.²² The aggregation of coronene molecules allows the intermolecular electronic interactions to extend over a larger number of molecules and the coupling of the electronic transitions caused the difference among the absorption spectra of coronene molecules in solution, nanowires in solution and nanowires in thin film.

To probe the photoswitching behavior of the coronene nanowires, a photoelectrochemical cell consisting of a coronene nanowires/rGO/SiO₂/Si electrode, a Pt-wire counter electrode and a Ag/AgCl (saturated KCl solution) reference electrode was constructed. The generation of photocurrent, in the presence of 0.5 M Na₂SO₄ solution as the supporting electrolyte, was recorded on an electrochemical workstation. Visible light ($\lambda > 400 \text{ nm}$) was obtained from a 350 W xenon lamp with a filter. A steady anodic photocurrent of $1.64 \mu\text{A cm}^{-2}$ was generated when the coronene nanowires/rGO/SiO₂/Si electrode was subjected to be excited with visible light (Fig. 3). Note that no photocurrent

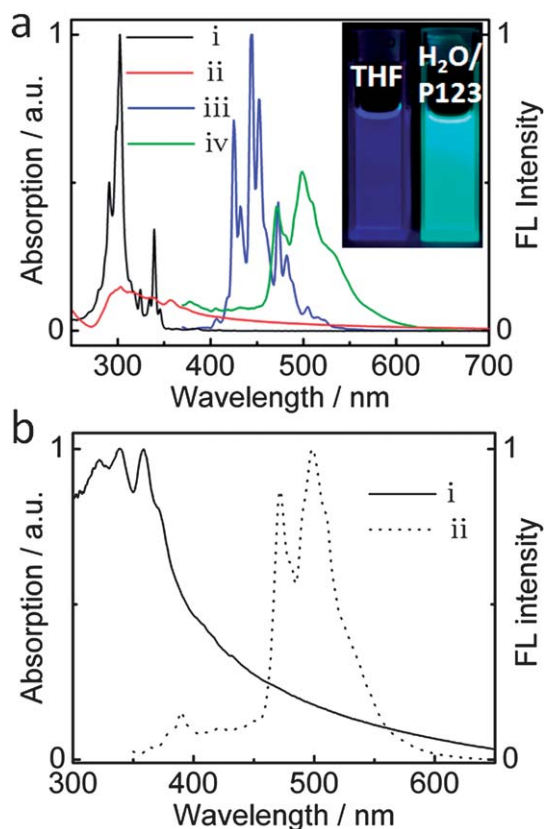


Fig. 2 (a) UV-vis absorption and fluorescence spectra: (i) and (ii) are the UV-vis absorptions of coronene molecules in THF (black line, i) and coronene nanowires in aqueous solution (red line, ii), respectively. (iii) and (iv) are emission spectra of coronene molecules in THF (blue line, iii) and coronene nanowires in aqueous solution (excited at 340 nm, green line, iv). Inset shows visual fluorescent color of coronene in THF and nanowires in aqueous solution. (b) Solid-state UV-vis spectrum of coronene nanowire thin film (solid line, i), and the corresponding emission spectrum (dotted line, ii) at an excitation wavelength of 340 nm.

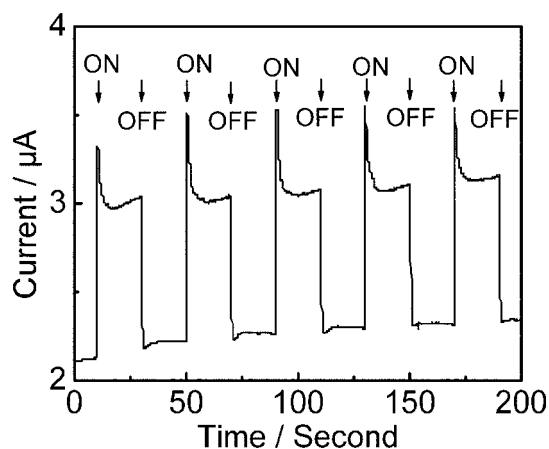


Fig. 3 Time dependence of the generated photocurrent of coronene nanowires on the rGO surface upon the irradiation of 120 mW cm^{-2} white light in $0.5 \text{ M Na}_2\text{SO}_4$ solution.

was observed from pure rGO film under the same experimental conditions. The on–off cycles of illumination confirmed the reproducibility of the photocurrent response of coronene nanowires.

To expand the applications of these nanowires, a heterojunction LED was fabricated. Fig. 4 plots the current–voltage (I – V) curve of the LEDs and the inset of Fig. 4 shows the schematic diagram of the proposed p-organic nanowires/n-SiC LED. The heterojunction LEDs had a turn-on voltage of ~ 8.7 V. When the forward bias was applied to about 16.6 V, the current reached up to ~ 2 mA, while only a small reverse leakage current of 20 μ A was observed at -20 V. Hence, it was evident that the current–voltage curve showed a rectifying behaviour and the use of organic nanowires as the p-type hole injection layer could produce diodes with performance better than those with inorganic thin-film structures.

Fig. 5 shows the EL spectra of the coronene nanowires/n-SiC heterojunction LED biased at different forward voltages. The EL spectra show broad emission spectra with FWHM equal to ~ 90 nm at 20 V. However, no light emission was observed from the heterojunction LED under the reverse bias. The inset displays a colour photo of the LED taken at forward bias at 20 V. Note that only the region on the with metal contact in the LED gives the intense light emission. It should also be mentioned that the emitted light could be clearly seen by a naked eye in normal office light environment. In addition, we should point that the 4H–SiC samples in our experimental condition exhibit no measurable light emission under either optical or electrical excitation, which is similar to the reported results.²³ Therefore, we can confirm that the EL spectrum is only from coronene nanowires.

Conclusion

In summary, coronene nanowires have been successfully prepared by reprecipitation method. The as-prepared nanowires show strong green fluorescence in aqueous solution instead of blue emission for coronene molecules in THF solution. This

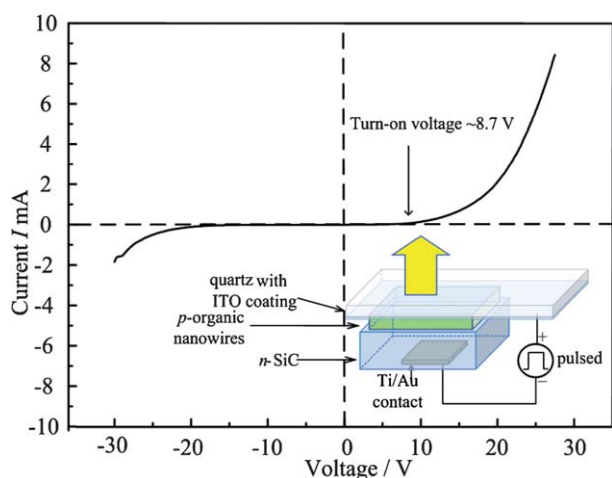


Fig. 4 Current–voltage (I – V) curve of the heterojunction LED. The inset is the schematic diagram of the proposed p-organic coronene nanowires/n-SiC heterojunction LED.

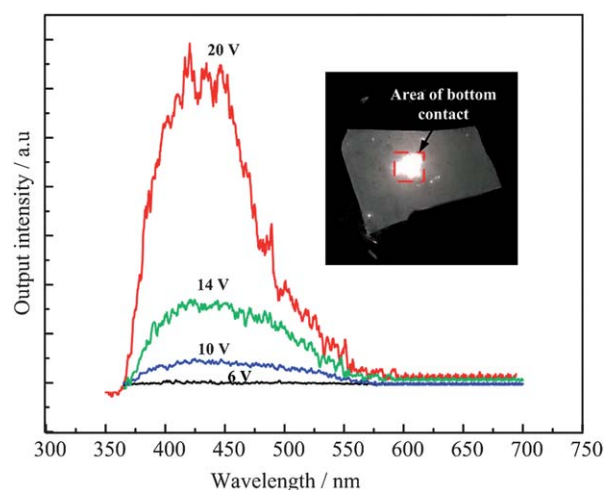


Fig. 5 EL spectrum of the p-organic nanowires/n-SiC heterojunction LED biased at different forward voltages.

material not only shows strong photoswitching behavior, but also has a good performance in the heterojunction LED.

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