

8-hydroxyquinoline lithium nanoribbons: synthesis and the photoconductivity sensing

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Large-scale and high-purity 8-hydroxyquinoline lithium nanoribbons with average width of 125 nm, thickness of 25 nm, and length up to several hundreds of micrometers, were successfully synthesized via a facile solvothermal route. The room-temperature photoluminescence spectrum of the products showed a strong and stable blue emission centered at 470 nm under excitation at 325 nm. And the as-prepared nanoribbons exhibited photoresponse. As the light source was switched on and off, the currents could be reversibly switched between high and low value at the voltage of 0.01 V, which might be useful in the fabrication of photosensor and photoswitch microdevices or nanodevices in the future.

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1. Introduction

Since Tang and VanSlyke [1] firstly employed vacuum deposition for the formation of a thin film with two sublimed molecular layers sandwiched between the electrodes, and obtained bright green emission through the transparent anode based on tri(8-hydroxyquinoline)aluminum (AlQ_3) in 1987, AlQ_3 were studied extensively and have progressed remarkably in the past twenty years [2]. And AlQ_3 has become one of the most efficient electron transport and emitting materials for optoelectronic devices [3-6]. Furthermore, one-dimensional 8-quinolinol/metal-chelates nanomaterials have attracted a great deal of excitement owing to the excellent photoluminescence and electroluminescence performance [7-12].

However, it is still not satisfactory for the use of AlQ_3 in view of its monocolour emission-green electroluminescent material. It is desirable to obtain other 8-quinolinol/metal-chelates nanomaterials being capable of emitting blue in high intensity. 8-hydroxyquinoline lithium (LiQ) has been considered to be an excellent blue light-emitting material [13-15].

Herein, we prepared LiQ nanoribbons through a facile solvothermal method without surfactants or templates. The as-prepared nanoribbons had uniform morphology and excellent photoluminescence performance. A photoconduction device was fabricated based on LiQ and the photoconductive properties were studied.

2. Experimental details

All of the chemical reagents used were analytical grade and without further purification. In a typical synthesis, 1 mmol of lithium chloride and 1 mmol 8-hydroxyquinoline were dissolved into 40 mL methanol under stirring, which was transferred into a Teflon-lined autoclave of 60 mL capacity and heated to 140 °C for 8 h and cooled to room temperature naturally. Then ultrapure water was dropwise added into the resulting solution under violently stirring. The resulting suspension was separated centrifugally, washed with ultrapure water for several times, and then dried under vacuum at 60 °C for 12 h.

The morphology and size of the products were studied by a Hitachi S-4800 scanning electron microscope (SEM), JEOL-2010 transmission electron microscope (TEM). Fourier transform infrared (FTIR) spectrum was obtained with KBr pellets for solids on a Shimadzu FTIR-8400S spectrometer. Thermogravimetric analysis - differential thermal analysis (TGA-DTA) measure was performed in a SETARAM-TG92 to inspect the phase transition of the nanoribbons in the temperature range from room temperature to 600 °C at a heating rate of 10 °C min^{-1} .

The as-prepared samples were dispersed in ethanol (1×10^{-5} M) for photoluminescence excitation (PLE) and photoluminescence (PL) spectra measurement by a Hitachi-850 fluorescence spectrophotometer at room temperature. The photoconductivity measurements were tracked with a CHI 620B electrochemical workstation. Light was supplied with incandescence lamp (12 V, 10 W).

3. Results and discussion

Fig. 1 shows the XRD pattern of the sample. The peaks at $2\theta = 15.9^\circ$, 18.9° , 21.7° , and 24.7° are strong, which are in agreement with those reported in literatures and reveal that the chemical compound we got is really LiQ [16]. Elemental analysis (EA) is carried out with a Heraeus CHN-O Rapid instrument. The EA results of the sample show that the content (%) of C, N, and H is 69.55, 9.02, and 4.01, respectively. The values are consistent with the calculated values (C 71.59%; N 9.27%; H 3.97%) of LiQ.

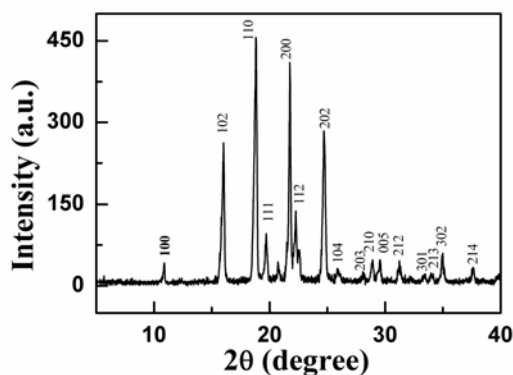


Fig. 1. XRD pattern of LiQ.

The FTIR spectrum is recorded to reveal the composition of the products as shown in Fig. 2. The vibrations at 1577 , 1369 , and 1327 cm^{-1} are assigned to the quinoline group of LiQ. The bands at 1503 and 1470 cm^{-1} should correspond to the vibrations of the pyridyl and phenyl groups in LiQ [17]. The band at 1107 cm^{-1} is attributed to a C-O stretching vibration. The peaks at 825 , 795 , and 748 cm^{-1} are associated with C-H deformation vibrations, and the peaks at 480 cm^{-1} are associated with the Li-O and Li-N stretching vibration [18, 19], which further support that the as-prepared products are pure LiQ.

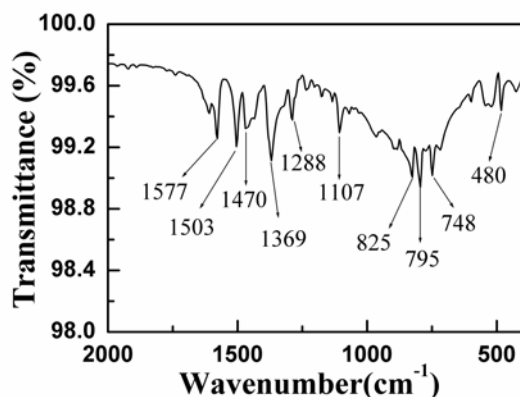


Fig. 2. FTIR spectrum of LiQ.

Fig. 3(a) displays a panoramic SEM image of the as-prepared products, which shows they are large-scale ribbon-like morphology with lengths up to tens of micrometers. The high magnification SEM image shown in Fig. 3(b) further reveals that the as-synthesized products are ribbon-like morphology with average width of 160 nm and thickness of 30 nm . The corresponding TEM image also confirms that the products are ribbon-like morphology as the inset of Fig. 3(a).

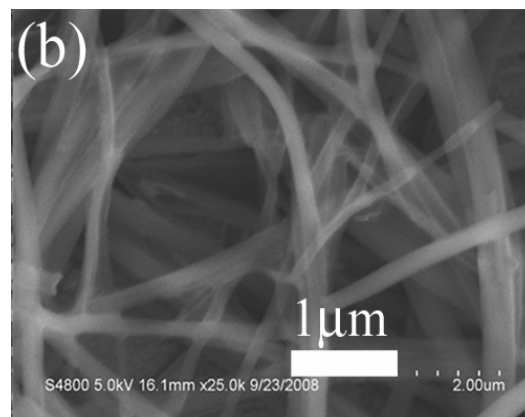
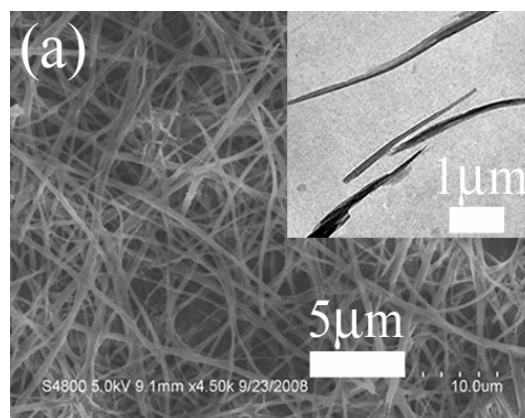


Fig. 3. SEM image of LiQ with ribbon-like morphology: (a) at low magnification, (b) at high magnification, and the inset is the corresponding TEM image.

Fig. 4 displays TGA-DTA curves of LiQ nanoribbons heated from room temperature to $600\text{ }^\circ\text{C}$ at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. The weight loss rate is 58% , which is ascribed to the sublimation of LiQ nanoribbons.

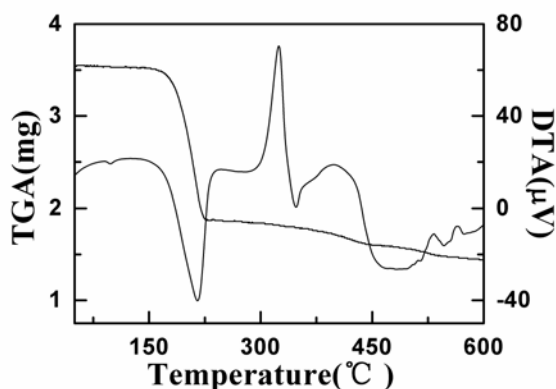


Fig. 4. TGA and DTA curves of LiQ nanoribbons.

The room temperature PLE and PL spectra of LiQ nanoribbons dispersed in ethanol (1×10^{-5} M) are acquired and shown in Fig. 4. The PLE spectrum (Fig. 5(a)) reveals that LiQ nanoribbons have excitation centers located at 325 nm under an emission of 470 nm. The PL spectrum excited at 325 nm (Fig. 5(b)) presents a strong emission centered at 470 nm.

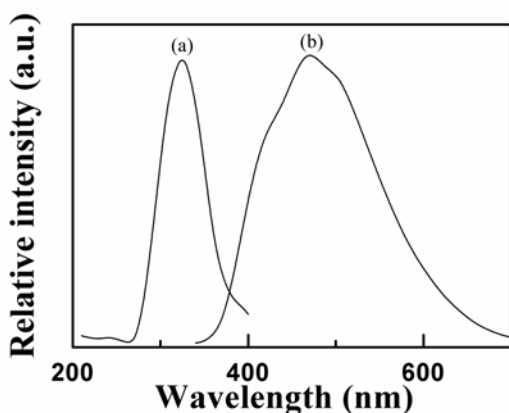


Fig. 5. Room temperature spectra of LiQ nanoribbons dispersed in ethanol (1×10^{-5} M): (a) PLE spectrum with the emission of 470 nm; (b) PL spectrum excited at 325 nm.

In order to measure the current signals through LiQ, indium tin oxide (ITO) coated glass with the electrode gap of $25 \mu\text{m}$ was employed as the substrate. A bundle of LiQ was dispersed and bridged over the electrodes with effective length of $28 \mu\text{m}$, as shown in the inset of Fig. 6. Gold gap electrodes were fabricated on the substrate by thermal evaporation with a micrometer-sized Au wire as the mask; by slightly moving the Au-wire mask, Au–Au gap electrodes were deposited [21]. The distance between the nanoribbons and light source was 10 cm.

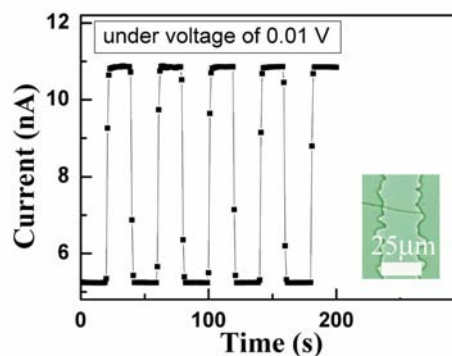


Fig. 6. Photoswitch characteristics of a bundle of LiQ ribbons during light switching on/off, and the image of a bundle of the products between two Au electrodes from an optical microscope (inset).

Fig. 6 shows the reversible photoconductive characteristics of LiQ during light switching on/off. A voltage of 0.01 V was applied across the two electrodes and the current recorded during the light was alternatively on and off at 20 s intervals. Obviously, the current through the LiQ promptly increased or decreased according to the illumination on/off, which shows high sensitivity. In these cases, the energy from the light excites the electrons in the semiconductor LiQ from the valence band into the conduction band, increasing the charge carrier concentration via direct electron-hole pair creation and thus enhancing the conductivity of the nanoribbons. After several tens of cycles and continuous operation about 1 h, the device displays high reproducibility and stability, and no degradation is observed.

4. Conclusions

In summary, Large-scale and high-purity LiQ nanoribbons with high intensity of blue-green photoluminescence were obtained by a facile solvothermal approach without any template or surfactant. The nanoribbons showed a strong blue emission. The photoswitchable conductivity of a bundle of LiQ nanoribbons exhibited the unique photoswitching response, which was fast and reversible under on/off light exposure conditions. The experimental results provide a foundation for the development of novel organic chelates nano-devices.

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