Facile solution synthesis of hexagonal Alq_3 nanorods and their field emission properties†

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A facile self-assembly growth route assisted by surfactant has been developed to synthesize tris(8-hydroxyquinoline)aluminium (Alq_3) nanorods with regular hexagonal shape and good crystallinity, which exhibit field-emission characteristics with a very low turn-on field of *ca.* 3.1 V μm^{-1} and a high field-enhancement factor of *ca.* 1300.

Organic nanomaterials have attracted tremendous interests for application in functional nanoscale electronic and optoelectronic devices, the crystallinity and molecular arrangement of which have a great influence on the performance of these devices.[1–4] However, compared with the overwhelming majority of inorganic nanomaterials, only a few successful preparations of organic one-dimensional (1D) nanomaterials such as nanowires and nanotubes are reported.[3,5–7] Recently, some macrocycle compounds,[8] discotic π-conjugated molecule,[9] oligomer,[10,11] block copolymer,[12] and amphiphilic molecular[13] 1D nanostructures have also been fabricated *via* supramolecular self-assembly routes. These organic 1D nanostructures generally lack good monodispersity and crystallinity. To our best knowledge, few organic nanorods with regular shape, uniform size and good crystallinity have been synthesized until now, especially *via* facile solution routes.

Since the first efficient low-voltage-driven organic light-emitting diodes (OLEDs) based on tris(8-hydroxyquinoline)aluminium (Alq_3) were reported by Tang and VanSlyke,[14] Alq_3 has become a important prototypical electron transport and emitting material for OLED devices because of its excellent stability and electroluminescence properties. Most research efforts devoted to this material have focused on device optimization for high luminescence, long term stability, and fast response times,[15–17] as well as determination of the polymorphism and crystal structure of Alq_3.[18,19] Recently, Wang and co-workers reported the synthesis of amorphous Alq_3 nanowires through a physical vapor deposition approach.[2] Herein, we, for the first time, report the preparation of crystalline Alq_3 nanorods through a facile self-assembly growth method assisted by surfactant in solution. The prepared nanorods had regular hexagonal geometry, good crystallinity, and good field-emission performance.

Alq_3 nanorods were prepared by a facile solution phase route (see ESI†). Briefly, a stock solution containing 2.5 mmol L^{-1} tris(8-hydroxyquinoline)aluminium in $CHCl_3$–C_2H_5OH (1 : 1, v/v) was prepared. Then, 100 μL of this stock Alq_3 solution was quickly injected into 5 mL of an aqueous solution of 0.45 mmol L^{-1} cetyltrimethylammonium bromide (CTAB) while stirring (*ca.* 600 rpm) at room temperature (25 °C). The mixture was continuously stirred for another 2 h. Fig. 1(a) shows a low magnification SEM image of the sample. It can be obviously seen that rod-shaped nanostructures have been successfully prepared on a large scale. The rods have a length of 5.0 ± 0.5 μm and width of 400 ± 20 nm. The high-magnification SEM images as shown in Fig. 1(b) and (c) reveal the nanorods have highly regular hexagonal prism geometric shape and smooth surfaces. Each rod has a hexagonal cross-section and six regular facets. A TEM image of the sample in Fig. 1(d) further confirms the whole nanorod has uniform structure. The sharp spots in the corresponding selected area electron diffraction (SAED) pattern (inset in Fig. 1(d)) show the nanorods are single crystalline. Significantly, the same SAED pattern can be obtained along the length direction of nanorods, indicating the nanorods have the identical crystal structure throughout. The energy dispersive X-ray (EDX) spectrum of the nanorod (see ESI†) shows obvious peaks of the elements C, N, O

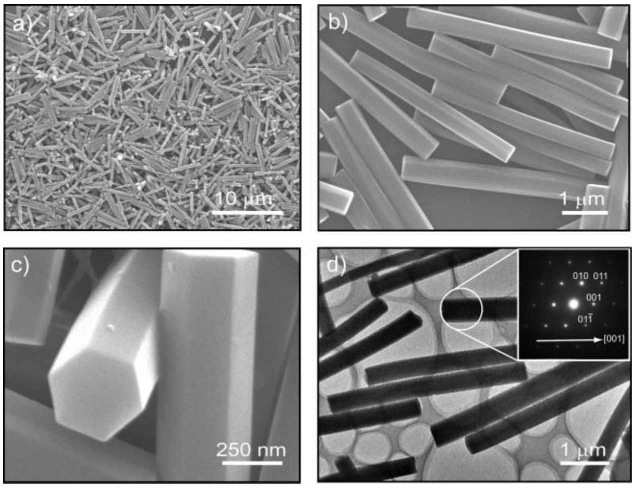

Fig. 1 Low (a) and high (b, c) magnification SEM images, and TEM image (d) of Alq_3 nanorods. The inset is the corresponding SAED pattern taken from the circled area.

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and Al which constitute the Alq$_3$ molecules ($C_{27}H_{18}AlN_3O_3$). The minor peak of Cu arises from the copper grid for TEM characterization. Therefore, the result implies the prepared nanorods are composed of Alq$_3$ molecules.

FTIR and Raman spectra were recorded to reveal the composition and the phase of prepared Alq$_3$ nanorods. For reference, the FTIR spectrum of Alq$_3$ starting powders was also measured as shown in Fig. 2(a). The FTIR spectrum of Alq$_3$ nanorods is very similar to that of the starting powders, indicating the high purity of sample and no change of chemical bonding. The IR peak at 419 cm^{-1} can be assigned to the Al–N stretching vibration, while the peaks at 523, 549 and 749 cm^{-1} can be assigned to Al–O stretching vibrations in the Alq$_3$ molecule. These vibration modes are in good agreement with those reported for α-phase Alq$_3$.[20] In the Raman spectrum of Alq$_3$ nanorods as shown in Fig. 2(b), three high-energy peaks at 504.6, 526.5 and 541.7 cm^{-1} have been previously attributed to the skeletal in-plane bending of the ligand.[21] Three vibration peaks at 117.0, 155.4 and 167.3 cm^{-1} are considered as the characteristic Raman fingerprints of the α polymorph.[18] Since the low-energy modes are highly sensitive to molecular packing, FTIR and Raman results thus suggest the prepared Alq$_3$ nanorods are composed of α-phase Alq$_3$.

X-Ray diffraction (XRD) experiments was performed to further investigate the crystal structure of the Alq$_3$ nanorods. The XRD patterns of the Alq$_3$ nanorods and starting powders are presented in Fig. 3. Comparison of the two curves shows that all the peaks in the latter can be accounted for by the former, confirming the nanorods consisted of pure Alq$_3$. However, in the present experiment, the starting Alq$_3$ molecules were self-assembled into a well-defined 1D nanostructure. To further ascertain the crystal structure and molecular self-assembly mode, we used the published crystal structures of Alq$_3$ and its solvent clathrates to simulate the theoretical XRD patterns. We found that all of the peaks in the XRD pattern of the nanorods could be indexed well by the simulated pattern of α-phase Alq$_3$ obtained by Masciocchi and co-workers (CCDC Refcode: QATMON01),[18] as shown in Fig. 3. Furthermore, the pattern of the nanorods is distinctively different from those simulated from other known Alq$_3$ phases, such as the β, γ and δ phases. The XRD pattern therefore supports that the Alq$_3$ nanorods have the α-phase structure (triclinic space group $P\bar{1}$, $a = 6.2586$, $b = 12.914$, $c = 14.743(2)$ Å, $\alpha = 109.66$, $\beta = 89.66$, $\gamma = 97.68°$). This result is consistent with the above IR and Raman analysis. However, Fig. 3 also shows the relative peak intensities in the XRD pattern of nanorods are remarkably different from those of the starting material, revealing orientated growth in the nanorods. After the determination of the crystal structure of the nanorods, the SAED pattern in Fig. 1(d) could be easily indexed according to the interplanar spacing of α-Alq$_3$. The result reveals that the Alq$_3$ nanorods grow along the [001] direction, that is, the crystallographic *c*-axis direction.

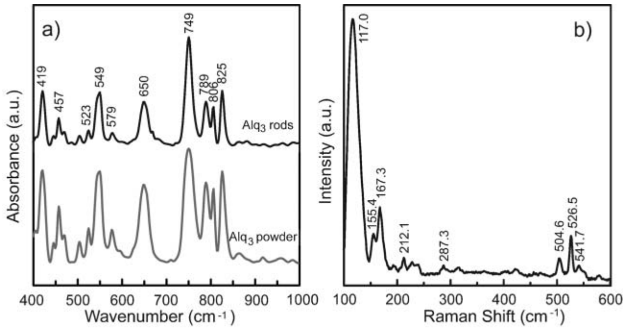

Fig. 2 (a) FTIR spectra of Alq$_3$ nanorods and Alq$_3$ starting powders. (b) Raman spectrum of Alq$_3$ nanorods.

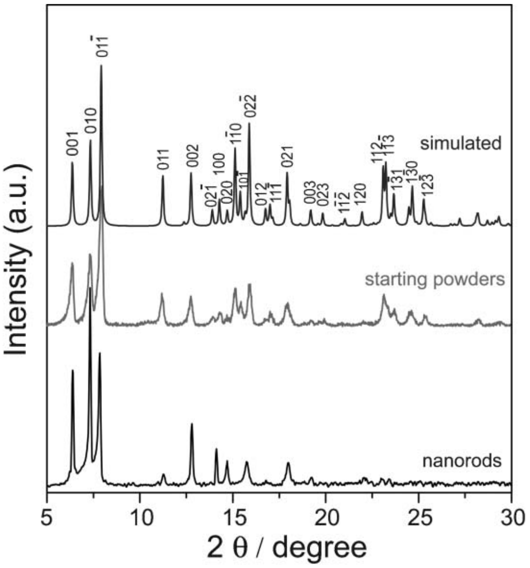

Fig. 3 XRD patterns of Alq$_3$ nanorods, Alq$_3$ starting powders, and simulated pattern from the published crystal structure data of α-Alq$_3$ (CCDC, Refcode QATMON01).

In further experiments, it was found that the presence of surfactant was essential to form Alq$_3$ nanorods. In the absence of surfactant, the two solutions to be mixed were immiscible and were present as two separate phases even with vigorous stirring, which resulted in that Alq$_3$ molecules could not effectively aggregate and assemble, and thus irregular spherical aggregates instead of uniform nanorods were obtained. It has been reported that CTAB not only could assume the role of a surface-active stabilizer, but also can form rodlike CTAB micelles either at concentrations above the second CMC of CTAB or by inducing interactions with other molecules. These rodlike micelles could be used as templates to synthesize one-dimensional inorganic or organic nanomaterials.[5,6,22] It can be therefore presumed that, in the present case, CTAB not only stabilizes the formed nanorods, but also contributes to the self-assembly of Alq$_3$ molecules into uniform rod-like structures in poor-soluble solution. However, the concentration of surfactant seems not to have a great influence on the morphologies of nanorods. At concentrations in the range of 0.5 to about 3 mM, nanorods with similar diameters and lengths are obtained. The delicate role of surfactant in the system needs to be further investigated.

The field-emission property of Alq$_3$ nanorods was measured using a two-parallel-plate configuration. Fig. 4 presents the field-emission characteristics by the typical curve of current density *J vs.* applied electrical field *E*. Alq$_3$ nanorods exhibit a turn-on field of 3.1 V μm^{-1} and a maximum current density of about 1.38 mA cm^{-2} at an applied field of 5.7 V μm^{-1}. The turn-on field is lower than that of other organic or inorganic nanomaterials,[2,23–25] but

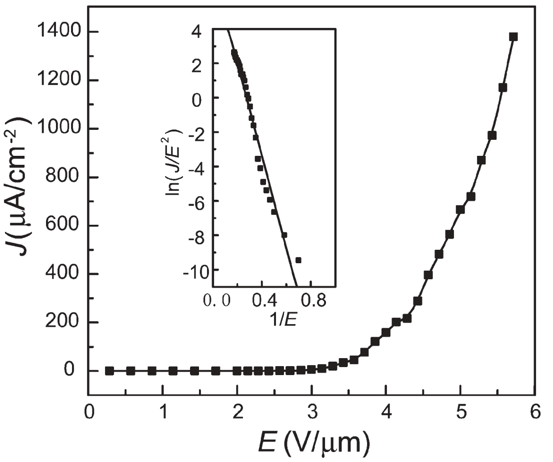

Fig. 4 Field emission J–E curve of the Alq_3 nanorods and the corresponding FN plot (inset).

comparable to that of organic charge-transfer complex nanowires.[3] The field-emission characteristic is further analyzed using the Fowler–Nordheim (FN) model described by eqn (1):[2]

$$\ln\left(\frac{J}{E^2}\right)=\ln\left(\frac{A\beta^2}{\phi}\right)+\left(\frac{-B\phi^{3/2}}{\beta}\right)\frac{1}{E} \qquad (1)$$

where A and B are constants ($A = 1.54 \times 10^{-6}$ A eV V^{-2} and $B = 6.83 \times 10^3$ V μm^{-1} eV$^{-3/2}$), J is current density, E is electric field, ϕ is the work function of the emitting sample, and β is field enhancement factor. The FN plot of Alq_3 nanorods shows a straight line with a slope of about -27 at high applied field as shown in the inset of Fig. 4. Assuming a work function of $\phi = 3.0$ eV for Alq_3,[2] the field-emission enhancement factor is estimated to be *ca.* 1300 based on eqn (1), which may be ascribed to the higher carrier mobility or conductivity expected in the crystalline Alq_3 nanorods.

In summary, a facile self-assembly route assisted by surfactant has been developed to synthesize Alq_3 nanorods with regular hexagonal shape and good crystallinity. FTIR, Raman spectral and XRD experiments show that the prepared nanorods have the α-phase crystal structure. Selected area electron diffraction (SAED) and structural analysis show the nanorods grow along the crystallographic c axis. The field-emission characteristics of the nanorods exhibit a very low turn-on field of *ca.* 3.1 V μm^{-1} and a high field-enhancement factor of *ca.* 1300.

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