Blue Luminescence from a Thin Film of the AlQ_3/SiO_2 Organic–Inorganic Hybrid Material

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We report an effective method to the high quality fabrication of the AlQ_3/SiO_2 organic–inorganic hybrid film with a blue luminescent under a UV light excitation. The high quality AlQ_3/SiO_2 film preparation makes the hybrid material a key step forward to the applications in OLEDs.

Organic light emission diodes (OLEDs), because of its high luminancent efficiency, low-power consumption, and wide range of emissive colors, has become to be one of the most promising techniques for next generation flat-panel display.[1–3] Some small screen full-color OLEDs have been in commercial applications now. But there are still some hindrances for the practical use of the large screen OLEDs. The difficulties in big size luminescent film fabrication may be one of the key issues. Most small molecule organic films have to be vacuum deposited,[4] and this technique is confined to a small screen fabrication owing to the limitation of equipments. While sol–gel approach, owing to its convenience for operation and low cost, has been proven to be suitable for large area optical film fabrication. So it calls for a solution processible method for OLEDs materials to achieve the big screen application.

Tris(8-quinolinolato)aluminum (AlQ_3), a stable metal chelate, stands as one of the most important organic materials used in OLEDs.[1,5,6] After about 20 years of intense research, it still to be one of the most common light emission and electron-transport materials among a class of low molecular weight materials for OLEDs. Much work has been done on the luminescent properties of AlQ_3, its luminescence can be blue- or red-shifted through the substitution on 8-hydroxyquinoline (HQ) ligand,[7–10] while rare cases concerned with the processiblity, and AlQ_3 still has to be sublimed to yield optical films. No report can be found for the blue emission AlQ_3 film fabrication via a conventional sol–gel approach. As a matter of fact, both blue emission and low cost chemical processing for the high quality thin film are essential for the wide application of the materials to full-color display.

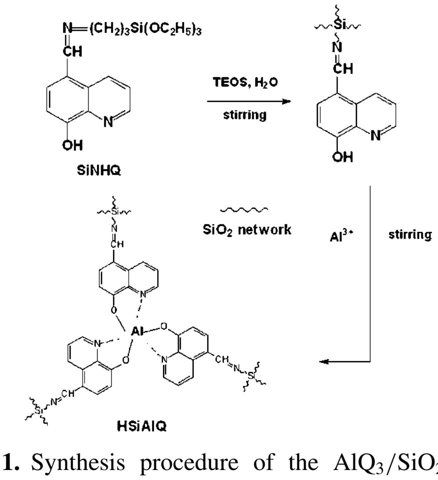
We have designed and synthesized a covalently bonded AlQ_3/SiO_2 organic–inorganic hybrid material by sol–gel approach in powder form with a strong blue luminescence.[11] Compared to some AlQ_3-containing polymer materials, this sol–gel route for covalently bonded organic–inorganic hybrid material is easy to achieve and cost-effective. Great differences in luminescent behaviours between a covalent-bonding hybrid material and a physically mixing sample were demonstrated in our previous work, showing the apparent and essential advantages of the covalently bonded organic–inorganic material over pure AlQ_3. Although there has been significant research activities aimed at developing hybrid materials,[12–14] few of these efforts have actually focused on film preparation which is suitable for the final application for flat-panel display. While in OLEDs applications, blue luminescent films combining with color conversion matrix (CCM) scheme seems to be one of the best options to achieve large area full-color display. So to apply this novel hybrid material in OLEDs fabrication, herein we report the high quality film preparation of the hybrid system with blue emission.

The synthetic procedure of the hybrid material was reported in our previous work, the typical sol making procedure is as follows (see Scheme 1): the silylated ligand SiNHQ was dissolved in ethanol, and tetraethoxysilane (TEOS) was added with a molar ratio 1:50 (SiNHQ:TEOS). The mixture was vigorously stirred for 12 h, then the aluninum nitrate solution was added to form a homogenous solution at once, and a blue emission is visible under UV light, which indicates the in situ formation of the aluminum complex. The mixture was stirred at room temperature for another 2 days and then ready for film preparation.

The films were fabricated by either spin-coating or dip-coating techniques. In spin coating, the hybrid sol dropped through a syringe filter to the substrate on the spin coater to yield clean films. The film thickness ranges from 100 to 700 nm depending on the viscosity of the sol and the sol–gel operation parameters. The freshly made films had been aged at 70 °C for one week to complete the hydrolysis and condensation and then ready for characterizations. There was an obviously visible blue luminescence from the film under a UV lamp irradiation (Figure 1).

In the UV–vis absorption spectra (Figure S1), the film shows a good transparency in visible light region, and the absorption band at 370 nm indicates the complexation of the ligands to Al^{3+}. In addition, comparing the absorption spectra and its emission spectra, there is no self-absorption effect, which make it competent for OLEDs application.

From the photoluminescent spectra (Figure 2) of the $AlQ_3/$



Scheme 1. Synthesis procedure of the AlQ_3/SiO_2 organic–inorganic hybrid sol.

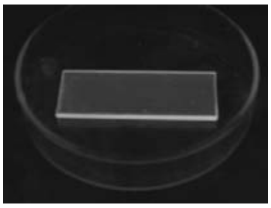


Figure 1. Visible blue luminescence from the hybrid film under an irradiation at 365 nm.

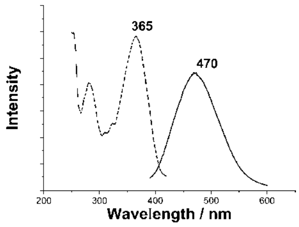


Figure 2. Photoluminescence (solid line) and excitation (dashed line) spectra of the hybrid film.

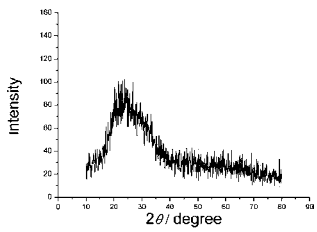
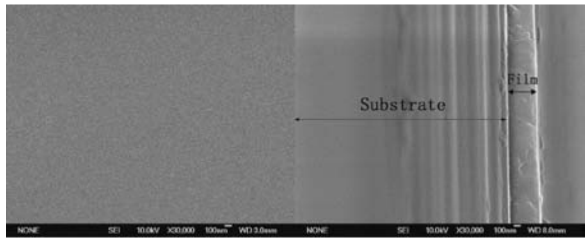


Figure 3. X-ray diffraction (XRD) pattern of the hybrid film.

SiO_2 hybrid film, a blue emission at 470 nm can be clearly observed when excited at 365 nm, which is slightly blue-shifted from the corresponding emission (476 nm) of the powder materials we have reported previously. The change of the emission wavelength might be resulted from the change of molecular packing status of the chromophores.[7] In the case of a film, during the aging stage, the shrinkage in sol–gel body caused by the condensation of TEOS was restrained to some extent by the interactions between the hybrid material and the film substrate. The packing density in a film will be lower than that in a powder material, which reduces the intermolecular interaction and causes the emission blue shift.

The room-temperature X-ray diffraction pattern of the hybrid film is depicted in Figure 3. We can see a broadly scattered peak around 23.1°, which represents a typical amorphous SiO_2 phase, indicating that no crystallization occurs during the heating stage, so the hybrid film shows good thermal stability towards environmental temperature change.

The surface and cross section scanning electron micrographs (SEM) images for the hybrid films are shown in Figure 4. Before SEM measurements, the films were dried for 1 week in air atmosphere. The surface image demonstrates a smooth and microstructurally homogeneous film, with no aggregation or phase separation. No cracks or pores can be found in the film. The cross section image shows that the film is flat and uniform in thickness. It can be concluded that it is the strong covalent bonding between the organic and inorganic phases that makes the well distribution of the organic moiety into the SiO_2 matrix on molecular level and yields a homogeneous film. All these shows that the hybrid films prepared by this route are of high quality and suitable for optical applications.



a b

Figure 4. SEM images on surface (a) and cross section (b) of the hybrid film.

In conclusion, we have explored an effective method to a fine film fabrication of the AlQ_3/SiO_2 organic–inorganic hybrid system, and the strong luminescent can be clearly observed under a UV light excitation. The high quality AlQ_3/SiO_2 film preparation makes, as we believe, the hybrid material a key step forward to the OLEDs applications.

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