



Short Communication

Sonochemical fabrication of 8-hydroxyquinoline aluminum (Alq₃) nanoflowers with high electrogenerated chemiluminescenceChang-Jie Mao^{a,b}, Dan-Chen Wang^a, Hong-Cheng Pan^a, Jun-Jie Zhu^{a,*}^a Key Laboratory of Analytical Chemistry for Life Science (MOE), School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, PR China^b Department of Chemistry, Anhui University, Hefei 230039, PR China

ARTICLE INFO

Article history:

Received 30 April 2010

Received in revised form 22 May 2010

Accepted 11 June 2010

Available online 30 June 2010

Keywords:

8-Hydroxyquinoline aluminum nanoflowers

Sonochemical

Electrogenerated chemiluminescence

ABSTRACT

Well-defined Alq₃ nanoflowers were fabricated via a facile and fast sonochemical route. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), field-emission scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to characterize the structure and shape of the as-prepared product. The results showed that the resulting Alq₃ was composed of nanobelts with thickness about 50 nm, average widths of 200 nm, and length up to 10 μm. The Alq₃ nanoflowers exhibited good electrogenerated chemiluminescence behavior.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The formation of ordered superstructures have attracted considerable attention because of their unique properties and potentially exciting applications [1,2]. Numerous synthetic methods have been developed for the fabrication. Recently, sonochemical method has become an important tool in the synthesis of self-assembled superstructures, such as V₂O₅ [3], SrMoO₄ [4] and BiOCl [5], because of fast and large-scale preparation. However, most research focused on the inorganic materials, and only limited kinds of organic materials have been obtained until now. Therefore, the preparation of ordered superstructures of organic materials is still a challenge. Recently, sonochemical method has been extensively used in the synthesis of various nanomaterials. When liquids are irradiated with ultrasonic irradiation, acoustic cavitation produces very high temperature (5000 K), high pressures (20 MPa) and cooling rates (107 K/s), which could provide a unique environment for chemical reactions and novel nanostructures under extreme conditions [6].

Electrogenerated chemiluminescence (ECL) is a useful technique for both fundamental study and analytical applications [7]. Since the discovery of ECL of silicon semiconductor nanocrystals in 2002 [8], much progress has been made in ECL research by using various nanoparticles [9–11]. Recently, the ECL biosensors based on nanoparticles are becoming an efficient approach for biological analysis including DNA probe and immunoassay. For example, CdSe nanoparticles could be used to develop an ECL immunosensor

for sensitive detection of human IgG [12]. Although the ECL behavior of semiconductors has been observed, much effort has been directed to develop new class of ECL systems for the improvement of the sensitivity and efficiency.

8-Hydroxyquinoline aluminum (Alq₃) has become one of the most successful electron transport and emitting material for organic light-emitting diodes (OLED) devices because of its good electronic conductivity and strong electroluminescence emission [13–17]. Because of their excellent optoelectronic properties, most research has focused on the physical and chemical properties, and find its potential application in nanodevices [18–26]. Alq₃ have a potential application in ECL system due to not only involving non-covalent intermolecular interactions such as π–π stacking, but also involving the interactions between inorganic elements and metal elements. It is necessary to explore these materials to achieve maximum ECL behavior. Recent reports showed that orientated self-assembled structures could help to enhance performance and novel application [27,28]. However, controlling the assembly of nanobelts into nanoflowers is still a challenge. Herein, large scale Alq₃ nanoflowers composed of the nanobelts were fabricated without surfactants or templates by a facile sonochemical route. The resulting Alq₃ nanoflowers exhibited good ECL behavior.

2. Experimental

2.1. Synthesis of Alq₃ nanoflowers

All reagents were analytical purity and used without further purification. In a typical procedure, 10 mmol of 8-hydroxyquinoline and

* Corresponding author. Tel./fax: +86 25 83594976.

E-mail address: jjzhu@nju.edu.cn (J.-J. Zhu).

10 mmol of AlCl_3 were dissolved in 40 mL of ethanol/water solution (50% v/v, 50 mL), respectively. The solution was mixed and the total volume of the solution was 80 mL. Then the mixture solution was exposed to high-intensity ultrasound irradiation under ambient air for 1 h. Ultrasound irradiation was accomplished with a high-intensity ultrasonic probe (Xinzhi Co., China, JY92-2D, 1 cm diameter; Tihorn, 20 kHz, 60 W/cm²) immersed directly in the solution at room temperature. The sonication was conducted without cooling so that the temperature of the reactant mixture increased gradually. Finally, the samples were collected by ultrafiltration membrane and characterized by XRD, XPS, TEM and SEM.

2.2. Electrogenerated chemiluminescence

A 0.50 wt% chitosan stock solution was prepared by dissolving chitosan flakes in hot (80–90 °C) aqueous solution with 0.05 M HCl. After the solution was cooled to room temperature, the pH was adjusted to 3.5–5.0 with NaOH solution. The chitosan solutions were filtered using a 0.45 μm Millex-HA syringe filter unit (Millipore) and stored in a refrigerator (4 °C) when not in use. The chitosan solution was colorless. Carbon nanotubes (CNTs) were chemically shortened by ultrasonic agitation in a mixture of sulfuric and nitric acid (3:1) for 4 h. The resulting CNTs were separated and washed repeatedly with distilled water by centrifugation until the pH was \sim 7. The purified CNTs were dissolved in chitosan solutions (0.50 mg mL⁻¹) under sonication for 15 min to give homogeneous black solution. After 0.0154 g of Alq_3 powder was put into 2 mL CNT-CHIT solution under sonication for 30 min, the Alq_3 NCs/CNT-CHIT solution was obtained.

The electrochemical measurements for ECL was carried out on a CHI 812 electrochemical working station (Shanghai CH Instruments Co., China) using a three-electrode system. The electrodes were a carbon paste working electrode modified with above composite materials, a saturated calomel reference electrode (SCE), and a Pt counter electrode. The ECL emission was detected with a Model MPI-A Electrochemiluminescence Analyzer (Xi'an Remax Electronic Science & Technology Co., Ltd., Xi'an, China) in pH 7.4 phosphate buffer solution (PBS) containing 0.1 M KCl and 0.1 M $\text{K}_2\text{S}_2\text{O}_8$ under cyclic voltammetry scan rate: 100 mV/s.

3. Results and discussion

3.1. Characterization of Alq_3 nanoflowers

The crystalline phase of the products was determined by XRD measurement. Fig. 1a shows the XRD pattern of the product, which was prepared by the initial concentrations with 10 mmol of 8-hydroxyquinoline and 10 mmol of AlCl_3 . The peaks are in agreement with the JCPDS No. 26-1550 and literature report [13,20,26]. The yield of the nanoflowers by this method is about 70%.

In order to further examine the chemical environment of the elements in the product, X-ray photoelectron spectroscopy (XPS) experiment was performed. In the Fig. 1b, the peak at 74 eV may result from the binding energy of Al 2p; whereas the shoulder peak located at 399 eV corresponded to the binding energy of N 1s. The atomic ratio of the Al:N calculated from the peak area was approximately 1:3.3, which was consistent with the given formula for Alq_3 within the experimental errors.

The morphology of the product was studied by SEM and TEM images. Fig. 2a shows that the typical SEM image. It can be obviously observed that belt-like nanostructures with width of 200 nm and length up to 2 μm are prepared on a large scale. Meanwhile, the nanobelts combined into the flower-like shape. The higher-magnification SEM images in Fig. 2b reveal that the Alq_3

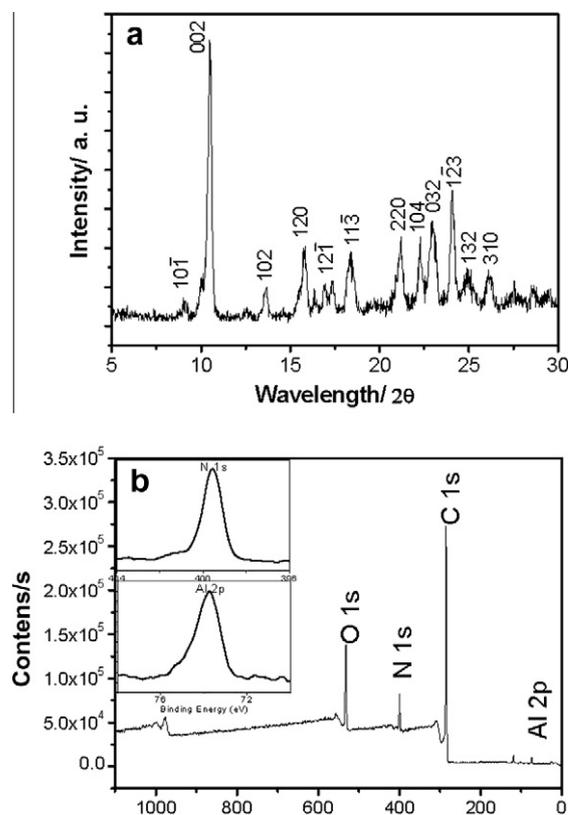


Fig. 1. (a) XRD pattern and (b) XPS of Alq_3 nanostructures. Inset: high-resolution XPS in the N 1s (top-left) Al 2p (bottom-left) region.

nanoflower is about 50 nm in thickness, 200 nm in width and several micrometers in length. A typical TEM image in Fig. 2c further confirms that the Alq_3 nanoflowers are indeed the self-assembled Alq_3 nanoflowers composed of the nanobelts, and the aspect ratios can reach up to tens. As shown in Fig. 2d, the width of these nanobelts is in the range of 50–200 nm and the length is tens of micrometers. Furthermore, it is found that the nanobelts are highly flexible.

In order to investigate the growth mechanism of the self-assembled Alq_3 nanoflowers superstructures, the evolution of morphology in the sonochemical process was studied. Fig. 3 shows the TEM images taken from the reaction mixture after the solution was exposed to high-intensity ultrasound irradiation at different reaction time. When the reaction time was shorter than 5 min, it was obvious that Alq_3 nanoparticles were observed in the initial reaction mixture as shown in Fig. 3a. As the reaction time was increased to 10 min, nanobelts predominated, and the percentage of initial nanoparticles was decreased as shown in Fig. 3b. Therefore, the small nanoparticles could serve as seeds for the growth of Alq_3 nanobelts. When the reaction time was prolonged to 30 min, the Alq_3 nanobelts aggregated together to form bundles (Fig. 3c). With the time increase, the bundles continued to grow and form flower-like bundles. After 30 min, the Alq_3 bundle with flower-like shape reached a stable state (Fig. 3d), and did not change with the increase of reaction time. When experiment was carried out in vigorous electric stirring for a comparison, irregular particles could be obtained in final products. The experimental result proved that high-intensity ultrasonic irradiation played an important role in the formation of Alq_3 nanoflowers.

On the basis of the above observation, a schematic illustration of the formation mechanism for the self-assembled Alq_3 nanoflowers was proposed as shown in Fig. 4. The sonochemical formation of self-assemble Alq_3 bundle might undergo three steps in

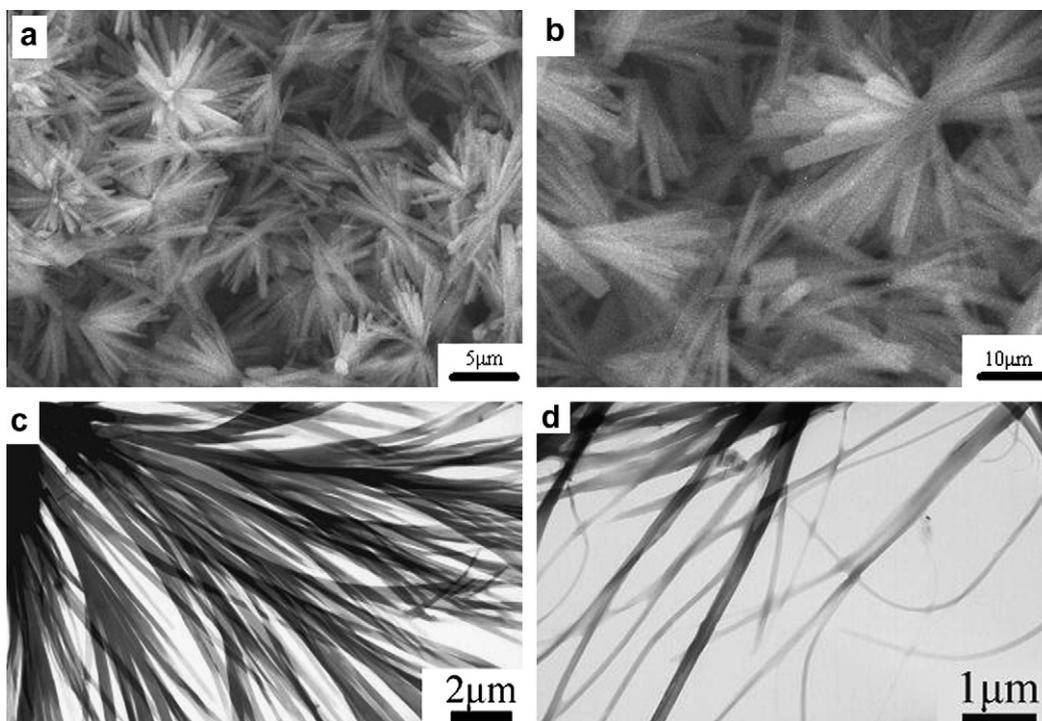


Fig. 2. SEM TEM images of the Alq₃ nanoflowers: (a) typical SEM image, (b) higher-magnification SEM image, (c) typical TEM image and (d) higher-magnification TEM image.

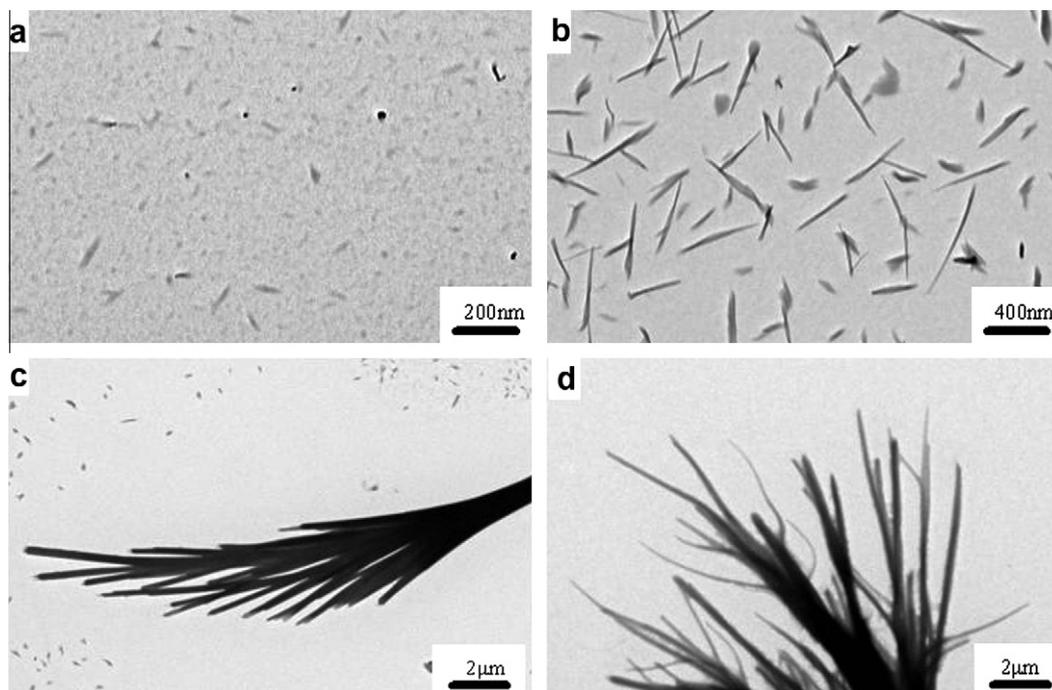


Fig. 3. TEM images of the sample collected at different reaction time of (a) 5, (b) 10, (c) 20 and (d) 30 min.

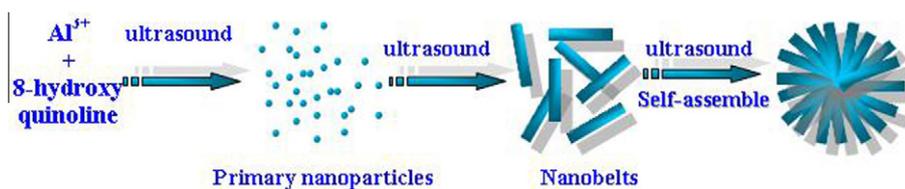


Fig. 4. Scheme of the growth mechanism of the Alq₃ nanoflowers.

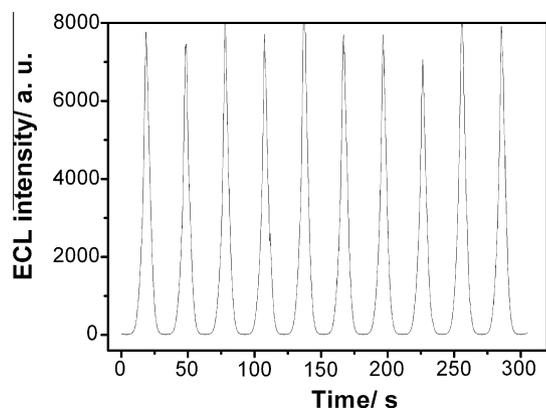


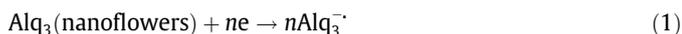
Fig. 5. ECL emission from the Alq₃ nanoflowers in 0.1 M PBS containing 0.1 M KCl and 0.1 M K₂S₂O₈ under cyclic voltammetry. Scan rate: 100 mV/s.

sequence: (1) acoustic cavitation formation of Alq₃ nanocrystals to produce primary nanoparticles; (2) under the microjets formed at the collapse of bubbles, these primary nanoparticles accompanying oriented attachment to form the nanobelts; and (3) the individual nanobelts were further attached to assemble into bundles, accompanying an Ostwald ripening process.

3.2. The behavior of electrogenerated chemiluminescence

The ECL behavior of the as-prepared Alq₃ nanoflowers was studied. The ECL emission under continuous potential scanning between 0 and −1.5 V for 10 cycles was shown in Fig. 5. The light emission of Alq₃ nanoflowers was stable and intense, which may be attributed to the Alq₃ nanoflowers and the addition of co-reactant. The results suggested that the Alq₃ nanoflowers had great potential applications in ECL biosensors and biolabeling.

ECL is generated by the relaxation of excited-state molecules that are produced through electron transfer annihilation of electro-generated anion and cation radicals [8]. In our case, ECL is produced upon concomitant reduction of Alq₃ and S₂O₈^{2−}. Upon the potential scan with negative direction, the Alq₃ nanocrystals were reduced to anion radicals (Alq₃^{•−}). Simultaneously, S₂O₈^{2−} as a co-reactant was oxidized to produce a strong oxidant SO₄^{•−}, then Alq₃^{•−} can react with SO₄^{•−} to emit light in aqueous solution. The proposed ECL mechanism is as follows:



4. Conclusions

In this paper, large scale 8-hydroxyquinoline aluminum bundles with nanoflowers were fabricated via a facile sonochemical route. The Alq₃ nanoflower is composed of nanobelts with thickness about 50 nm, average widths of 200 nm, and length up to 10 μm. ECL of the as-prepared Alq₃ nanoflowers was observed. The electrochemical data indicated that the superstructure had good ECL behavior. In particular, the relative strong ECL from the nanoflowers will provides new avenues in analytical systems and ECL biosensors.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant Nos. 20635020 and 20905001), China Postdoctoral Science Foundation funded project (20080441027) and Jiangsu Planned Projects for Postdoctoral Research Funds (0802008B).

References

- [1] A.P. Alivisatos, *Science* 271 (1996) 933.
- [2] J.T. Hu, T.W. Odom, C.M. Lieber, *Acc. Chem. Res.* 32 (1999) 435.
- [3] C.J. Mao, H.C. Pan, X.C. Wu, J.J. Zhu, H.Y. Chen, *J. Phys. Chem. B* 110 (2006) 14709.
- [4] C.J. Mao, J. Geng, X.C. Wu, J.J. Zhu, *J. Phys. Chem. C* 114 (2010) 1982.
- [5] Y.Q. Lei, G.H. Wang, S.Y. Song, W.Q. Fan, H.J. Zhang, *Cryst. Eng. Comm.* 11 (2009) 1857.
- [6] K.S. Suslick, *Science* 247 (1990) 1439.
- [7] A.J. Bard, J.D. Debad, J.K. Leland, G.B. Sigal, J.L. Wilbur, J.N. Wohlstatter, *Encyclopedia of Analytical Chemistry*, in: R.A. Huggins (Ed.), Meyers, Wiley, Chichester, UK, 2000, p. 9842.
- [8] Z. Ding, B.M. Quinn, S.K. Haram, L.E. Pell, B.A. Korgel, A.J. Bard, *Science* 296 (2002) 1293.
- [9] N. Myung, Y. Bae, A.J. Bard, *Nano Lett.* 3 (2003) 1053.
- [10] G.F. Jie, B. Liu, C.H. Pan, J.J. Zhu, H.Y. Chen, *Anal. Chem.* 79 (2007) 5574.
- [11] S.N. Ding, J.J. Xu, H.Y. Chen, *Chem. Commun.* (2006) 3631.
- [12] G.F. Jie, J.J. Zhang, D.C. Wang, C. Chen, H.Y. Chen, J.J. Zhu, *Anal. Chem.* 80 (2008) 4033.
- [13] M. Cölle, J. Gmeiner, W. Milius, H. Hillebrecht, W. Brütting, *Adv. Funct. Mater.* 13 (2003) 108.
- [14] W. Tang, S.A. Van Slyke, *J. Appl. Phys.* (1989) 3610.
- [15] H. Aziz, Z.D. Popovic, N.X. Hu, A.M. Hor, G. Xu, *Science* 283 (1999) 1900.
- [16] S. Barth, P. Muller, H. Riel, P.F. Seidler, W. Riess, H. Vestweber, H. Bassler, *J. Appl. Phys.* 89 (2001) 3711.
- [17] Z.L. Shen, P.E. Burrows, V. Bulovic, S.R. Forrest, M.E. Thompson, *Science* 276 (1997) 2009.
- [18] J.J. Chiu, C.C. Kei, T.P. Perng, W.S. Wang, *Adv. Mater.* 15 (2003) 1361.
- [19] J.J. Chiu, W.S. Wang, C.C. Kei, C.P. Cho, T.P. Perng, P.K. Wei, S.Y. Chiu, *Appl. Phys. Lett.* 83 (2003) 4607.
- [20] Y.S. Zhao, C. Di, W. Yang, G. Yu, Y. Liu, J. Yao, *Adv. Funct. Mater.* 16 (2006) 1985.
- [21] C.P. Cho, C.A. Wu, T.P. Perng, *Adv. Funct. Mater.* 16 (2006) 819.
- [22] C.P. Cho, C.Y. Yu, T.P. Perng, *Nanotechnology* 17 (2006) 5506.
- [23] J.S. Hu, H.X. Ji, A.M. Cao, Z.X. Huang, Y. Zhang, L.J. Wan, A.D. Xia, D.P. Yu, X.M. Meng, S.T. Lee, *Chem. Commun.* (2007) 3083.
- [24] W. Chen, Q. Peng, Y.D. Li, *Adv. Mater.* 20 (2008) 2474.
- [25] A.M. Collins, S.N. Olof, J.M. Mitchels, S. Mann, *J. Mater. Chem.* 19 (2009) 3950.
- [26] X.H. Wang, M.W. Shao, G. Shao, S.W. Wang, *J. Nanosci. Nanotechnol.* 9 (2009) 4079.
- [27] Y. Li, B. Tan, Y. Wu, *Nano Lett.* 8 (2008) 265.
- [28] C.K. Chan, H. Peng, G. Liu, K. Mcilwrath, X.F. Zhang, R.A. Huggins, Y. Cui, *Nat. Nanotechnol.* 3 (2008) 31.