Surfactant-assisted Hydrothermal Route to Organometallic Tris(8-hydroxyquinoline)aluminum Nanorod Bundles

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A new surfactant-assisted hydrothermal route was presented to prepare organometallic tris(8-hydroxyquinoline)aluminum nanorod bundles on a large scale. In this hydrothermal system, sodium dodecylbenzenesulfonate (Chemical formula: $C_{12}H_{25}$–C_6H_4–SO_3Na, SDBS) played key roles in controlling the morphology and quality of the resultant products. The as-prepared nanorod bundles showed enhanced PL emission compared to submicron particles prepared by the same hydrothermal method.

Recently, one-dimensional (1-D) conducting polymer and small-molecular-weight organic semiconductor nanomaterials have attracted much attention because of their unique physical properties and potential application in fabricating nanodevices.[1–3] However, the preparation methods of 1-D organic nanomaterials is not diversiform compared with those of 1-D inorganic nanomaterials because of their thermal instability and weak mechanical properties.[4] Until now, there have been some reports on 1-D organic nanomaterials prepared by several methodologies, such as template,[5] reprecipitation,[6] solid-phase reaction,[7] vapor deposition technique,[3] and so on. Hydrothermal method has been successfully used to prepare a lot of insoluble 1-D inorganic nanomaterials.[8] Because many organic materials are also insoluble in water and hydrothermal method is facile and mild, it is feasible and significant to explore this method to prepare 1-D organic functional nanomaterials.

Since a strong electroluminescence at a low driving voltage was first reported in 1987,[9] tris(8-hydroxyquinoline)aluminum (AlQ_3) has played an important role in organic light-emitting diodes (OLEDs). Its physical properties, such as electroluminescence, photoluminescence, and field emission, have been extensively studied.[10–12] Many efforts have been made to this organometallic semiconductor because it offers possibility of flexible displays, owning low purification cost and more versatile color specificity, in comparison with inorganic III–IV semiconductors.[13] Up to now, nanostructured AlQ_3, such as nanoparticles,[14] nanorods,[15] nanowires, and nanobelts,[10,13] has been reported. However, most of the preparation methods of AlQ_3 nanostructures are based on vapor deposition. Herein, we present a novel hydrothermal route to 1-D amorphous AlQ_3 nanorod-assembled bundles. Further, these amorphous AlQ_3 nanorod bundles show an enhanced photoluminescence compared to submicron particles prepared by the same hydrothermal method.

In a typical process, 1 mmol of aluminum nitrate and 3 mmol of 8-hydroxyquinoline were dissolved into 45 mL of distilled water under stirring. Then, 1 mmol of SDBS were added into the solution. Agitating for several minutes, the solution was poured into stainless steel autoclave with a Teflon liner of 60 mL capability and heated at 120 °C for 12 h. After autoclave was cooled to room temperature, the resulting floater was separated centrifugally and washed with distilled water for several times. Then, the products were dried under vacuum at 60 °C for 4 h.

The X-ray diffraction (XRD) pattern (not shown here) study of the sample shows that it is amorphous structure. The element analysis data of the products shows the weight percent of Al:C:H:N is 5.72, 71.32, 3.85, and 8.34, respectively. The results of elemental analyses are close to theoretical weight percent of Al:C:H:N in pure $Al(C_9H_6ON)_3$ with 5.87, 70.57, 3.95, and 9.15, respectively. The weight loss of the products was studied and shown in Figure S1.[17] The thermogravimetric curve shows that this compound does not contain crystal water and is stable up to 307 °C. On the basis of the results of element and thermogravimetric analysis, the sample can be identified as $Al(C_9H_6ON)_3$. Figure S2[17] represents Fourier transform infrared spectra of as-prepared products, the sample prepared in the absence of SDBS, and pure AlQ_3. All vibration modes in figure S2b and S2c are in agreement with those of pure AlQ_3 (Figure S2a) and reported in literatures,[12,16] which further supported the as-prepared products were pure AlQ_3.

The morphology of the products was examined by electronic microscopic techniques. Figure 1 displays field-emission scanning electron microscopy (FE-SEM) images of the products. It shows clearly that the products are nanorod bundles. To individual nanorod, it is quite uniform in both radial and axial direction. The diameters and lengths of the nanorods range from 80 to 120 nm and 1 to 2 µm, respectively. Because AlQ_3 are soluble in absolute ethanol, the products were dispersed in distilled water by ultrasonic means and then a few drops were deposited onto the carbon-coated copper grids for TEM characterization. Figure 2 shows the transmission electron microscopy (TEM) images of the products prepared in the presence and absence of SDBS, respectively. Although the products were dispersed by ultrasonication for several minutes, they still retained the morphology of nanorod bundles, which further validated the result of FE-SEM observation. The electron diffraction recorded on the single nanorod bundles shows no spot or ring, indicating its amorphous structure, which is in accordance with the result of XRD analysis.

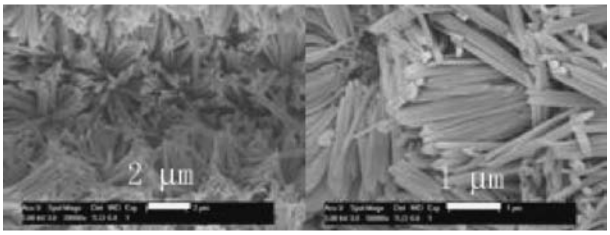

Figure 1. Top view of the FE-SEM image of the products (left); Side view of the FE-SEM image of the products (right).

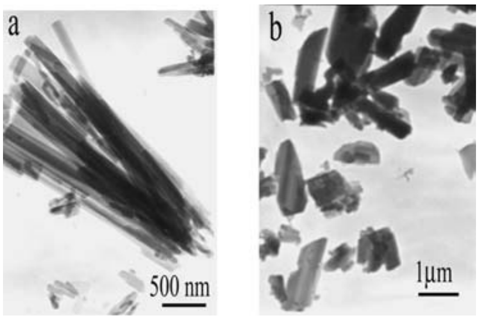

Figure 2. TEM image of the sample prepared hydrothermally in the presence of SDBS (a) and in the absence of SDBS (b).

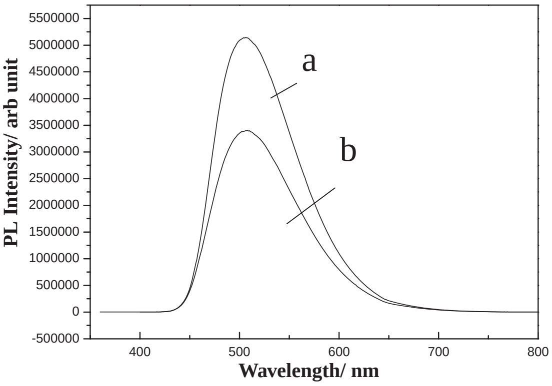

Figure 3. PL spectra of AlQ_3 nanorod bundles (a) and submicron particles (b) excitated at 250 nm at room temperature.

In this hydrothermal system, SDBS played a key role in controlling the formation of nanorod bundles. On one side, it could combine with Al^{3+} and controlled the concentration of free Al^{3+} in solution, adjusting the nucleation and growth rate of AlQ_3, which benefited the formation of nanorod bundles. On the other hand, surfactant SDBS might be acted as soft template to control the morphology of the resulting products. In the absence of SDBS, the default experiment showed that the products were irregular submicron particles (see Figure 2b). In addition, reaction time and temperature also influence the quality of the final products. If reaction time is less than 6 h or more than 18 h, AlQ_3 nanorod bundles cannot be obtained. When reaction temperature is more than 140 °C, the products contain the carbonized substance. The optimum conditions for preparing AlQ_3 nanorod bundles are 100–140 °C for 8–16 h.

PL measurements were performed on a Fluorolog-3-Tau steady-state spectrofluorometer at room temperature using as-prepared solid powder as samples. Figure 3 represents PL spectra of AlQ_3 nanorod bundles and irregular submicron particles with excitation wavelength at 250 nm, respectively. Both PL spectra show a strong green visible light luminescence ranging from 450 to 700 nm with the maximum intensity centered at about 509 nm. Previous study showed amorphous AlQ_3 nanoparticles prepared by vapor condensation exhibited the maximum intensity at about 538 nm.[14] Hence, the PL spectra of AlQ_3 nanorod bundles and irregular submicron particles prepared by hydrothermal route show obvious blue shift contrasted with amorphous nanoparticles prepared by vapor condensation. Although the exact reason of the blue shift is not clear at present, we think it is probably caused by different shape and preparation method of samples. Compared to irregular submicron particles, AlQ_3 nanorod bundles exhibits stronger emission, which could be attributed to their larger specific surface than submicron particles enhancing the optical absorption.

In conclusion, tris(8-hydroxyquinoline)aluminum nanorod bundles have been successfully prepared by a new surfactant-assisted hydrothermal route on a large scale. The as-prepared amorphous tris(8-hydroxyquinoline)aluminum nanorod bundles showed good thermal stability on certain extent. Its PL emission was evidently enhanced than submicron particles prepared by the same hydrothermal route. This kind of surfactant-assisted hydrothermal method can be extended to prepare other functional 1-D organometallic nanomaterials.

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