doi:10.1246/cl.2010.114

Template-based In Situ Fabrication and Melamine Sensing of Bis(8-quinolinolato)zinc(II) Complex Nanorod Arrays

Xiang-Zi Li,[1,2] Rui Yu,[1] and Xian-Wen Wei*[1]
[1]*College of Chemistry and Materials Science, Key Laboratory of Functional Molecular Solids, Ministry of Education, Anhui Key Laboratory of Molecule-Based Materials, Anhui Normal University, Wuhu 241000, P. R. China*
[2]*Department of Chemistry, WanNan Medical College, Wuhu 241000, P. R. China*

(Received October 5, 2009; CL-090891; E-mail: xwwei@mail.ahnu.edu.cn)

Parallel polycrystalline bis(8-quinolinolato)zinc(II) complex nanorod arrays, with diameters in the range of 250–320 nm and length of 25 µm, are in situ fabricated by liquid–liquid interfacial precipitation in the pores of porous anodic aluminum oxide membrane. The prepared nanorods show an enhanced photoluminescence emission compared to submicron particles and can be used as a good melamine probe for easy and highly sensitive detection.

Since tris(8-quinolinolato)aluminum complex was first reported,[1] metal–8-quinolinolato (MQ_n, M: metal) complex nanowires and nanorods have been investigated extensively due to their unique properties and applications in the field of organic light-emitting devices[2,3] and photoluminescence (PL) sensing for protein[4] and glucose.[5] There have been various approaches to prepare nanowires of CdQCl,[5] AlQ_3,[6–8] GaQ_3[9] and nanorods of AlQ_3,[10–12] ZnQ_2,[4] CdQ_2,[13] such as sonochemical,[4,5,11] sublimation,[6–9] surfactant-assisted,[10,12] and solvothermal routes.[13,14] However, work on the hard template, in situ fabrication of one-dimensional (1D) MQ_n nanostructures is rare, and it is still a challenge to prepare parallel and uniform 1D MQ_n arrays with larger aspect ratios. As is known to all, hard-template-mediated preparation, initiated by Martin,[15] has proven to be a more simple and promising route to prepare ordered arrays of nanostructures. Particularly, anodic aluminum oxide (AAO) membrane is considered as an attractive template material for fabricating 1D nanostuctures,[16–19] because its pore density and aspect ratio are high, the pore distribution is uniform, and the shape and size of prepared 1D nanomaterials can be easily controlled.

Herein we present a simple and mild method to fabricate ZnQ_2 nanorod arrays embedded in AAO templates with a high filling rate and uniform growth. The synthesis technique is based on the in situ reaction of Zn^{2+} and 8-quinolinol through liquid–liquid interfacial precipitation into the pores of AAO membrane without heat and any surfactants, and the prepared nanorods are polycrystalline and show an enhanced photoluminescence compared to that of submicron particles. Moreover, the ZnQ_2 nanorods can be developed into a fluorescence sensor for melamine.

The AAO membranes (Anodisc®) were purchased from Whatman Co., the quoted pore diameter of which was ca. 200 nm. In general synthesis, the AAO membranes were put into the middle of two silica half cells.[16] The same volumes of 0.10 M $Zn(CH_3COO)_2$ and 0.05 M 8-quinolinol in ethanol were added into each cell, respectively. The reaction remained for 48 h at ambient temperature. Zn^{2+} and 8-quinolinol would enter the pores of the AAO membranes and form nanorods. The resulting ZnQ_2/AAO composite was polished with sand paper and washed several times with deionized water, then it was dipped into 2 M NaOH for 4 min to partly remove AAO membrane and for 24 h to remove the membrane substrate completely. Finally, the product was rinsed with deionized water 10 times. For melamine sensing, the ZnQ_2 nanorods were dispersed into deionized water by ultrasonication and separated into several equal portions (4 mL) to get nearly the same disperse concentration, then 0.2 mL of aqueous melamine solution with different concentration (100–600 ng mL^{-1}) was injected into each portion, and their PL properties were checked. All the reagents used in the experiment were of AR purity.

The morphology of the products was examined by field emission scanning electron microscopy (FE-SEM, S4800). Figure 1a shows a typical cross-section image of the nanorod arrays, the products are composed of parallel, smooth, and uniform nanorods with length up to 25 µm, and the nanorod arrays are of high-density with a high filling rate from top-view image (Figure 1b). After the AAO being removed completely, separate nanorods can be obtained (Figures 1c and 1d) with some shorter length (15 µm) due to treatments of ultrasonic and rinsing, and their diameters are in a range of 250–320 nm with the aspect ratio over 80. The transmission electron microscopy (TEM, Hitachi H800) image of the products shown in Figure 2a confirmed that the nanorods have similar sizes as shown by SEM. The corresponding selected-area electron diffraction (SAED) pattern (insert of Figure 2a) shows the nanorods are polycrystalline.

X-ray powder diffraction (XRD, SHIMADZU 6000) pattern of the products shown in Figure 2b could be indexed to polycrystalline ZnQ_2[4] (JCPDS No. 48-2116), which is in accordance with the SAED result. From which the grain size of nanorods

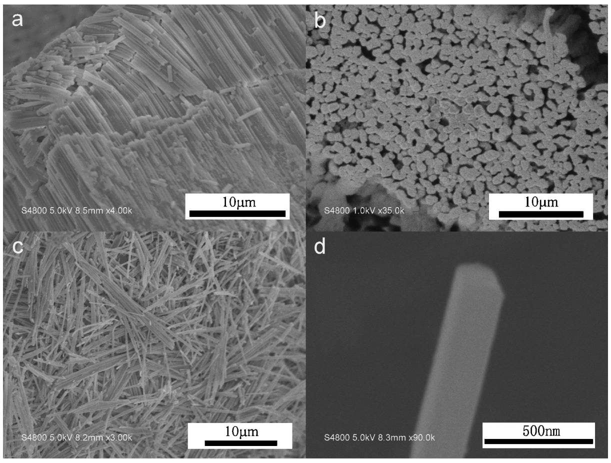

Figure 1. FE-SEM images of the prepared nanorod arrays (a), (b) and separate nanorods (c), (d).

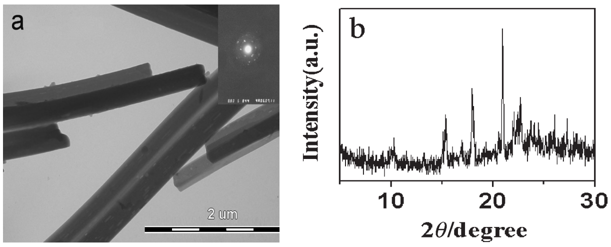

Figure 2. TEM image (a) and XRD pattern (b) of ZnQ_2 nanorods, insert is SAED pattern.

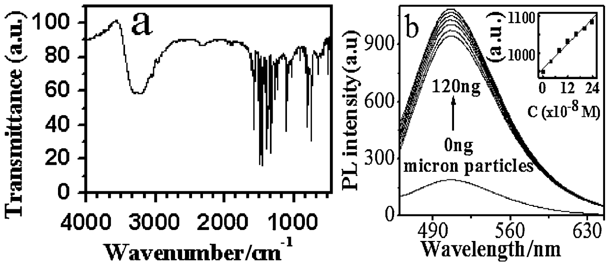

Figure 3. (a) IR spectrum of ZnQ_2 nanorods, (b) PL spectra of ZnQ_2 submicron particles, and nanorods mixed with different concentration of aqueous melamine solution. Insert is the linearity curve of PL intensities vs. the concentrations of melamine mixed with ZnQ_2 nanorods.

calculated by the Scherrer formula is about 46 nm. Additionally, the product was also identified with Fourier transform infrared spectroscopy (FTIR Prestige-21, KBr pellets). As indicated in Figure 3a, the vibrations at 1605, 1576, 1425, 1389, 1371, and 1329 cm^{-1} are assigned to the quinoline group of ZnQ_2. The bands at 1500 and 1469 cm^{-1} should correspond to both the pyridyl and phenyl groups in ZnQ_2. The peaks at 744, 641, and 502 cm^{-1} are associated with in-plane ring deformation.

PL measurements were performed with an F-4500 spectrofluorometer at room temperature. Figure 3b represents PL spectra of ZnQ_2 nanorods and irregular submicron particles dispersed in deionized water, irradiated with excitation wavelength at 438 nm. The emission ranges from 460 to 645 nm, and the maximum peaks are all located around 505 nm. Compared to ZnQ_2 in dichloromethane,[20] ZnQ_2 nanorods present a spectral blue shift for the π–π interactions between pairs of quinolinolato ligands from neighboring ZnQ_2 molecules, but there is no obvious emission shift relative to submicron particles since the interactions in the molecular crystal ZnQ_2 are not very strong.[13] ZnQ_2 nanorods present higher PL emission intensity relative to irregular submicron particles, which could be attributed to their larger specific surface and smaller grain size than that of submicron particles enhancing the absorption of light and the emission of PL.[21] As shown in Figure 3b, ZnQ_2 nanorods display increase of PL intensities in the presence of melamine, which could be attributed to activation of surface states of ZnQ_2 nanorods by melamine binding, and the PL intensity increases linearly with the increasing concentration of melamine over a range from 3.96×10^{-8} to 2.38×10^{-7} M (insert of Figure 3b), then levels off as the melamine concentration increases. The ZnQ_2 nanorods show a good fluorescence sensor for traces of melamine, and the detection limit is similar to that of electrochemical determination.[22] Contrarily, micron particles hardly have a good melamine sensing. The melamine concentration dependence of the PL intensity can be described by a Langmuir-type binding model, resembling the emission enhancement behavior of ZnQ_2 nanorods by protein binding[4] and zinc ions on the quantum dots.[23]

In summary, bis(8-quinolinolato)zinc(II) complex nanorod arrays are obtained in situ by liquid–liquid interfacial precipitation of $Zn(CH_3COO)_2$ and 8-quinolinol in ethanol in the presence of AAO membranes. The bis(8-quinolinolato)zinc nanorods with big aspect ratios are polycrystalline in structure and have evidently enhanced PL emission and a good melamine sensing with low detection limit compared to that of submicron particles. The method is simple, efficient, and inexpensive and may be extended to prepare other organic complexes nanorod arrays.

This work is supported by Science and Technological Fund of Anhui Province for Outstanding Youth (No. 08040106906), the National Natural Science Foundation (Nos. 20671002 and 20490217), the State Education Ministry (EYTP, SRF for ROCS, SRFDP 20070370001) of P. R. China, the Education Department (No. 2006KJ006TD) of Anhui Province, and Wannan Medical College (No. WK200802).

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