

Electrochemical fabrication of arrayed alumina nanowires showing strong blue emission

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Abstract. Arrayed alumina nanowires having controlled uniform diameters of 30–90 nm and lengths of 2–10 μm have been fabricated electrochemically with a high yield using two-step anodized aluminum oxide membranes as templates. The observed photoluminescence of the arrayed alumina nanowires arising from the emission of F^+ and F centers is strong and blue-shifted compared with that of porous alumina membranes due to the structural difference of Al_2O_3 . Our synthesized alumina nanowires are also found to be chemically more stable than the templates.

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1 Introduction

The spectroscopic, electronic, and chemical properties of nanocrystalline metal and semiconductors are of great interest in both basic and applied researches [1–5]. Attentions have been paid to prepare nanotubes and nanowires of metallic oxides because of their possible applications in electrochemical processes and catalysis [6–10]. While bulk aluminum oxide is used as adsorbents, catalysts, and catalyst supports in many chemical processes [11–13], porous alumina membranes (PAMs) have been used as templates to fabricate arrayed nanowires via electrodeposition [14,15]. Various methods have been reported to synthesize nanometer-sized alumina of diverse geometries such as nanocrystals, nanotubes, nanowires, and nanopillar arrays [9–11,16–18]. Generally, the syntheses of nanostructured alumina are based on surfactants templating in aqueous and nonaqueous solvents to disperse reactants [6,12]. Products, however, are disorderly and show broad size distributions. Thus, the electrochemical fabrication of nanostructured alumina using PAMs as templates is indispensable to obtain final products of nanotubes and nanowires having arrayed morphology.

The photoluminescence of PAMs is reported to occur in the wavelength range of 400–600 nm [19–23]. Initially, the nature of this emission is known to originate from oxygen vacancies with a trapped electron (F^+ centers) in PAMs. The photoluminescence is observed to shift to the blue with the increase of the annealing temperature and with the gradual release of the internal stress from the volume expansion of aluminum during electrolysis [19,20].

Thus, the broad blue luminescence is then suggested to have two different kinds of blue emission bands brought by two different defect centers of F^+ and F centers (oxygen vacancies with two trapped electrons) [21–23]. The blue shift of the photoluminescence in certain PAMs has been attributed to the increased contribution of F^+ luminescence [21,22].

However, we will show in this paper that the blue-shifted photoluminescence of our fabricated arrayed Al_2O_3 nanowires is due to the structural difference of host alumina rather than the relatively increased contribution of F^+ defects. This paper also presents that arrayed alumina nanowires having controlled uniform diameters and lengths can be fabricated electrochemically with a high yield using two-step anodized ordered PAMs as templates.

2 Experimental

PAMs employed as templates were fabricated through a typical two-step anodizing electrochemical procedure with high-purity (99.999%) aluminium sheets, which had been already degreased and electropolished in a mixed solution of 100-mL 65% $\text{HClO}_4(\text{aq})$ and 400-mL ethanol for 3 min. The first anodization with a pair of graphite cathodes lasted for 12 h under a constant anodizing voltage of 40 V in an aqueous solution of 0.3-M oxalic acid at 15 °C. The porous oxide layer was completely removed for 12 h in a 1:1 mixture of 6.0% $\text{H}_3\text{PO}_4(\text{aq})$ and 1.8% $\text{H}_2\text{CrO}_4(\text{aq})$ at 65 °C. The second anodization was carried out for 90 min under the same electrochemical conditions as those in the first anodization. For the synthesis of alumina nanowires,

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the bottom of the highly ordered PAM was first removed electrochemically by controlling the reversed voltage in an electrolytic aqueous solution containing appropriately concentrated KCl. The resultant was then supplied with the anodic voltage of 40 V for 30–150 min in deionized water at 70 °C using a platinum cathode. The specimen was rinsed with water and dried at 50 °C. Arrayed alumina nanowires were isolated by dissolving PAM templates selectively using an aqueous solution of 1.0-M NaOH for 30 min.

Dried PAMs and alumina nanowires were characterized with a field-emission scanning electron microscope (FESEM) of JEOL (JSM-6700F). Colloidal solutions containing dispersed alumina nanowires were dropped to amorphously carbon-coated copper grids to examine using a transmission electron microscope (TEM) of JEOL (JEM-2000). Photoluminescence spectra were monitored with a CCD of Princeton Instruments (ICCD576G) following excitation at 355 nm using a Q-switched Nd:YAG laser of Quantel (Brilliant). Reflectance spectra were measured using a UV/vis reflectance spectrometer of Stellar-Net (EPP2000C UV-VIS).

3 Results and discussion

The FESEM images of Figure 1 show that arrayed alumina nanowires electrochemically prepared using PAMs as templates are well isolated from PAMs to show uniform diameters of 70 nm and uniform lengths of 3 μm . The diameters can be controlled in the range of 30–90 nm by varying the pore diameters of templates while the lengths can be modified in the range of 2–10 μm by changing template thickness and electrolysis time. Fabricated alumina nanowires are densely arrayed to be nearly parallel with each other and each of most nanowires is surrounded by six other nanowires. Thus, Figure 1 suggests that the simple chemical etching of embedded nanowires grown electrochemically in PAMs can produce well-arrayed alumina nanowires with a high yield. Our time-dependent FESEM images have indicated that alumina nanowires grow from the barrier-removed spots of the aluminum anode during electrolysis.

The TEM images of Figure 2 show that individual alumina nanowires can also be suspended in water and isolated by dissolving PAM templates selectively in 1.0-M NaOH(aq). This suggests that alumina nanowires are chemically more stable than PAM templates and that the structure of nanowires is quite different from that of PAMs. Isolated alumina nanowires are straight indeed (top of Fig. 2) and the surface of an isolated nanowire is quite coarse (bottom of Fig. 2). The latter indicates that alumina nanowires are also dissolved substantially during the etching of PAM templates with NaOH.

The emission spectra of arrayed alumina nanowires and PAM presented in the top of Figure 3 show that the emission of the nanowires having the maximum at 442 nm is strong and shifted to the blue compared with that of the membrane having the maximum at 446 nm. The strong photoluminescence of alumina in the range of

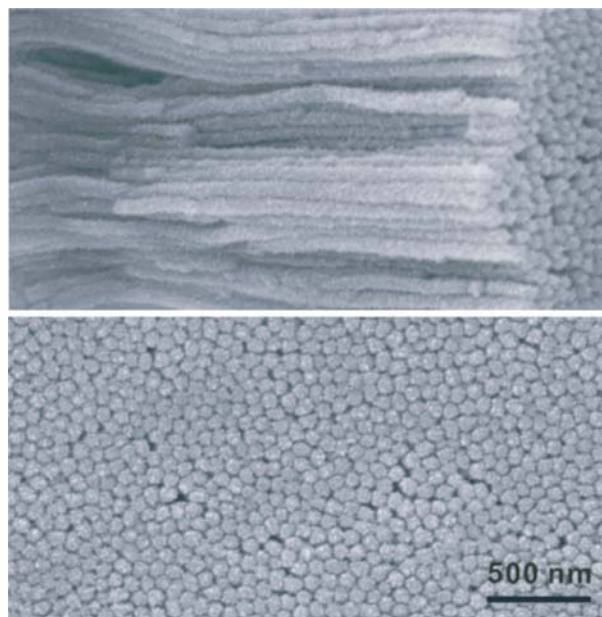


Fig. 1. FESEM images of the side (top) and the top views (bottom) of arrayed alumina nanowires.

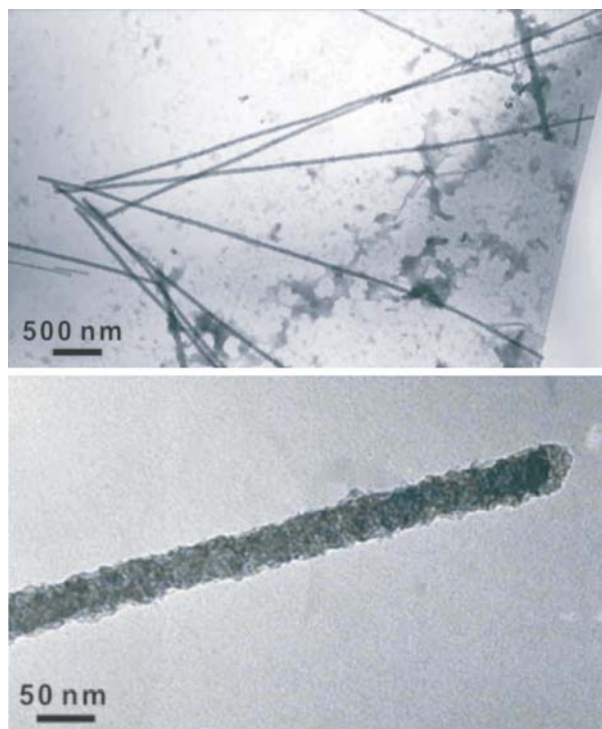


Fig. 2. TEM images of alumina nanowires (top) and a closely viewed alumina nanowire (bottom).

400–600 nm has been suggested to arise from two kinds of different luminescent centers: F^+ and F centers [21–23]. The blue shift of the photoluminescence in certain PAMs has been attributed to the increased contribution of F^+ luminescence. Thus, we have deconvoluted each emission spectrum with two Gaussian functions to understand the nature of luminescence from alumina nanowires (bottom

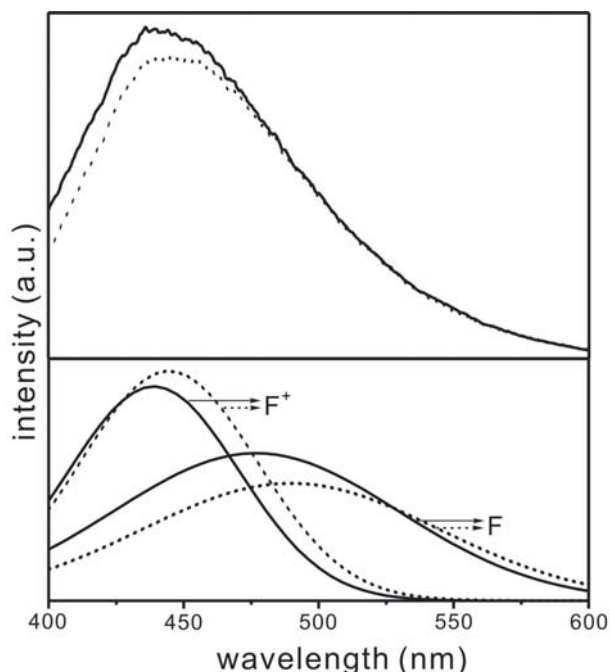


Fig. 3. (Top) Emission spectra of alumina nanowires having 70 nm in diameter and 6 μm in length (solid) and PAM (dotted) with excitation at 355 nm. (Bottom) Gaussian functions deconvoluted from the emission spectra shown in the top, showing that each emission spectrum consists of F^+ and F emission bands and that the blue shift of nanowire emission from membrane emission is due to the blue shifts of both F^+ and F bands rather than the increased contribution of the F^+ band.

of Fig. 3). The photoluminescence of alumina nanowires consists of an F^+ emission band (47%) at 439 nm and an F emission band (53%) at 477 nm, whereas that of PAM consists of F^+ emission (51%) at 444 nm and F emission (49%) at 487 nm. Thus, these suggest that each emission spectrum contains F^+ and F emission bands and that the blue shift of nanowire emission from membrane emission is due to the blue shifts of both F^+ and F bands rather than the increased contribution of the F^+ band. This also implies that the structure of nanowires is quite different from that of PAMs. It is noteworthy that the relative contribution of F^+ emission is even smaller in nanowires than in PAM. This suggests that the smaller fraction of F centers are oxidized to form F^+ centers in the nanowires than in the membranes and that alumina nanowires are chemically more stable than PAM templates as described already.

The reflectance spectrum of alumina nanowires measured using a porous alumina membrane as the reference sample shows a negative absorption band at 216 nm and a positive band at 276 nm (Fig. 4). We attribute the negative and the positive bands to the smaller concentration of F^+ centers and the larger concentration of F centers, respectively, in nanowires than in PAM, as suggested already with Figure 3 [23–26].

We have suggested with Figures 2–4 that alumina nanowires are chemically more stable than PAM templates

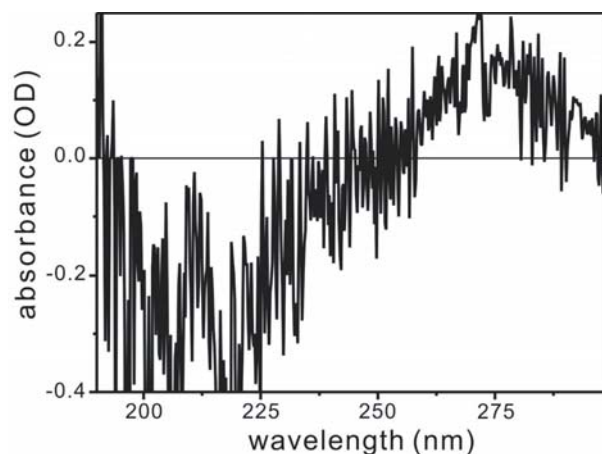


Fig. 4. The reflectance spectrum of alumina nanowires having 70 nm in diameter and 6 μm in length, measured using porous alumina membrane as the reference sample.

and that the structure of nanowires is quite different from that of PAMs. The relative presence of F^+ centers compared with F centers in PAMs has been reported to depend on electrolysis conditions [21,22]. Considering the blue shift of F emission compared with that in PAMs and our experimental conditions, we speculate that our fabricated alumina nanowires have the structure of the δ -form of Al_2O_3 [27,28].

In summary, arrayed alumina nanowires with uniform diameters and lengths have been fabricated electrochemically with a high yield using two-step anodized PAMs as templates. The diameters and the lengths can be controlled in the ranges of 30–90 nm and 2–10 μm , respectively. The observed photoluminescence of the nanowires arising from the emission of F^+ and F centers is strong and blue-shifted compared with that of porous alumina membranes due to the structural difference of alumina. The relative contribution of F^+ emission is even smaller in nanowires than in PAMs. The smaller fraction of F centers are oxidized to form F^+ centers in the nanowires than in the membranes and the alumina nanowires are chemically more stable than the templates.

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