

Photoluminescent blue-shift of organic molecules in nanometre pores

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Abstract

Poros alumina was fabricated by anodization in sulfuric acid and oxalic acid, where a laser dye, rhodamine 6G (RG6), and another luminescent organic molecule 8-hydroxyquinoline aluminum (Alq₃) were impregnated. The morphology determined by atomic force microscopy shows that the size of the pores is about 10–15 nm for alumina prepared in sulfuric acid (H₂SO₄) and about 40–50 nm in oxalic acid (H₂C₂O₄). An obvious blue-shifted photoluminescence (PL) of Alq₃ and RG6 in nanometre-sized holes was observed. The measured spectral characteristics demonstrate the influence of the pore size on the emission of the organic molecules. The PL blue-shift of the molecules in smaller nanometre-sized holes is larger than that in larger holes.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In recent years there has been considerable interest in the remarkable structural properties of porous alumina (P-Al) [1–4]. By controlling the preparation conditions, nanometre-sized holes in a regular honeycomb array can be obtained. This has been used as a nanometre template to prepare nanosize electronic and optoelectronic particles and devices, such as gold nanoparticles [5–8] and CdS nanometre semiconductor wire [9]. Most research has focused on the growth process and fabrication mechanism. The purpose of this paper is to draw attention to a complementary approach that utilizes P-Al technology to develop the luminescence of organic molecules in a nanometre-sized structure. The compound 8-hydroxy quinoline aluminum (Alq₃) has been intensively investigated as an organic electroluminescent material [10], and rhodamine 6G (RG6) is a typical laser dye which is usually used in the liquid state. This paper presents the first report of photoluminescence (PL) and relevant features of Alq₃ and RG6 in P-Al which may be used to develop a luminescent array based on P-Al with high density. This has promising applications in

novel optoelectronic devices, such as microcavities, solid state lasers, flat panel displays and quantum devices.

2. Experimental

The P-Al was fabricated by anodizing a high purity aluminum (99.999%) plate at a constant voltage in 0.3 M sulfuric acid (H₂SO₄) and oxalic acid (H₂C₂O₄) solution at room temperature for 12 h, respectively. The anodizing voltage was 20 V for H₂SO₄ and 30 V for H₂C₂O₄. Before anodizing, the aluminum plates were washed ultrasonically in ethanol and acetone, then electrochemically polished in a mixture of sulfuric acid and phosphoric acid. After the formation of P-Al, the samples were immersed in a chloroform solution of 10⁻² M Alq₃ and RG6 for 2 h, then taken out from the solution. As a result, the surface of the P-Al was covered by a thin layer of organic molecular powder.

Before and after the surface was rinsed with chloroform, the PL of the P-Al plate containing organic molecules (P-Al:Alq₃) and the corresponding excitation spectra were measured by a Shimadzu F-5000 fluorescence spectrophotometer, and the absorption spectra were measured by

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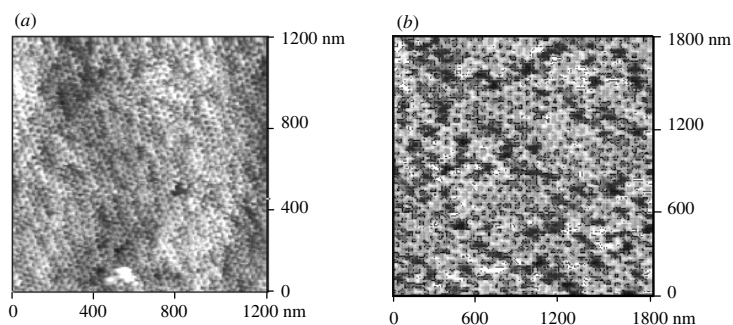


Figure 1. Surface morphology of P-Al and the rinsed P-Al:Alq₃. The alumina was fabricated in H₂SO₄ (a) and in H₂C₂O₄ (b), respectively.

a Shimadzu UV-2010 ultraviolet–visible spectra-photometer. The morphology of the films was measured by a Nanol Scopy III atomic force microscope (AFM). The composition of the samples was analysed by the measurement of the Fourier transfer infrared (FTIR) spectrum on a Nicolet system. For comparison, the PL and excitation spectra of P-Al films and the organic molecular solution were also measured.

3. Results

Figure 1 shows the AFM image of the P-Al:Alq₃ films after rinsing with chloroform. It can be seen that the size of the alumina pores is about 10–15 nm for the P-Al:Alq₃ surface prepared in H₂SO₄ and 40–50 nm for that prepared in H₂C₂O₄, while Alq₃ powder is hardly observable.

The sample fabricated in H₂SO₄ showed different PL peak positions before and after rinsing. As shown in figure 2(a), the peak was at 520 nm before the surface was rinsed, and shifted to 488 nm after rinsing. By contrast, the PL peak of the sample prepared in H₂C₂O₄ was located at 518 nm before washing with chloroform, then shifted to 510 nm after washing, as shown in figure 2(b). For comparison, figure 2(c) shows the PL of Alq₃ solutions of concentration 10⁻² and 10⁻⁶ M with peaks appearing at 512 and 490 nm, respectively. Similar results, as shown in figure 3, were observed for the sample of the P-Al:RG6. The PL peak of RG6 shifted from 622 to 600 nm after the surface was swilled with chloroform. For the sample formed in H₂C₂O₄, the peak shifted very slightly towards the short-wavelength region after rinsing. Besides the peak position, the PL intensity of P-Al:RG6 also changed in different states. It is very weak before rinsing and greatly enhanced after rinsing. The PL of the sample prepared in H₂SO₄ is stronger than that in H₂C₂O₄.

4. Discussion

The morphology of the rinsed samples showed no powder on the surfaces of the alumina films. This indicates that the emission bands at 488 nm for P-Al:Alq₃ and at 600 nm for P-Al:RG6 originate from the organic molecules impregnated in the pores or from the P-Al itself.

Before immersing the P-Al film into organic solution, the absorption and photoluminescent spectra were measured. As shown in figure 3, the PL of P-Al formed in H₂SO₄ is a broad band with a main peak at 440 nm under our experimental conditions. The PL characteristics and possible mechanism of

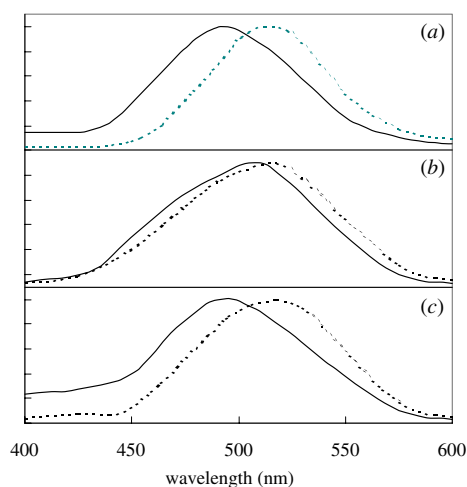


Figure 2. PL spectra of Alq₃ solution (a) and P-Al: Alq₃ (b and c). The P-Al substrates were prepared in H₂SO₄ (b) and in H₂C₂O₄ (c). The dotted curves represent Alq₃ solution with 10⁻² M concentration or unrinsed P-Al:Alq₃. The solid curves represent Alq₃ solution with 10⁻⁶ M concentration or rinsed P-Al:Alq₃.

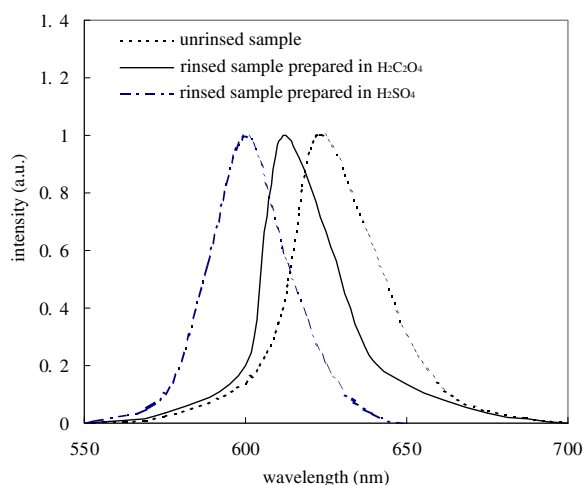


Figure 3. PL spectra of P-Al:RG6 before and after swilling with chloroform. The P-Al substrates were fabricated in H₂SO₄ and in H₂C₂O₄.

P-Al have been reported by some authors [11–13]. However, this broad band disappeared when Alq₃ or RG6 molecules were

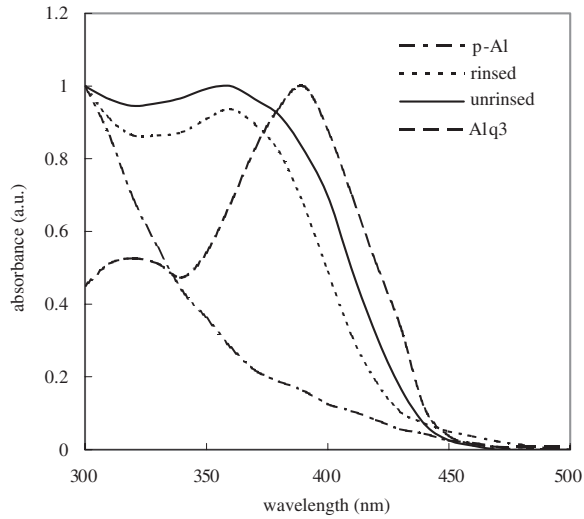


Figure 4. Absorption spectra of Alq₃, the P-Al and the P-Al:Alq₃.

introduced into the holes or onto the surface of P-Al. Figure 4 shows the absorption spectra of P-Al and P-Al:Alq₃ films. It is obvious that the absorption peaks at about 370 nm originate from the π to π^* transition of Alq₃. Deducting the contribution of P-Al, the absorption spectra of P-Al:Alq₃ with rinsing and without rinsing are almost the same as that of Alq₃. This proves that the emission peak at 488 nm does not originate from the P-Al but from Alq₃ immersed in the P-Al pores. The FTIR measurements of P-Al and the rinsed the P-Al:Alq₃ film further proves the existence of Alq₃ in the holes. As shown in figure 5, the dotted curve corresponding to P-Al has two main absorption bands around 1475 and 1571 cm^{-1} , and a weak band at about 3419 cm^{-1} . For the rinsed P-Al:Alq₃ sample,

the former two bands become higher and wider because two other bands at about 1601 and 1468 cm^{-1} from the vibration of the aromatic rings of Alq₃ overlap, and the IR absorption band around 3409 cm^{-1} become much stronger. This enhanced band mainly originates from the stretch vibration of the bound alcohol groups. For the P-Al:RG6 sample, similar UV-visible and FTIR spectra are also observed, in which the blue-shifted PL peak at 600 nm is from the emission of RG6 in the nanometre pores.

Considering the nanometre pore size of the alumina substrate and comparing with the behaviour of the organic molecules in chloroform solution, we believe that the blue shift indicates that the aggregates of Alq₃ or RG6 are repressed in the nanometre-sized pores. Before the sample was rinsed, Alq₃ or RG6 molecules were deposited on the surface and adsorbed in the holes of P-Al. In this case, dimers or multimers can form due to the strong interaction between the molecules. This would result in an increase in the gap between the excited states of the molecules and enhancement of the interaction between the electrons and phonons [14], so a red shift in the PL is observed. After the sample was rinsed, the remaining molecules were buried in the nanometre-sized holes, so the interaction between the molecules is reduced, and the spectra shift to the short-wavelength region.

For the rinsed sample, the PL blue shift for the sample prepared in H_2SO_4 is smaller than for that prepared in $\text{H}_2\text{C}_2\text{O}_4$. The AFM microphotographs showed the pore size of alumina in oxalic acid is about four times larger than that in sulfuric acid. The organic molecules are more easily packed in a 40–50 nm pore so dimers or multimers are more easily formed than in a 10–15 nm pore. In other words, the PL of organic molecules in a small nanometre-sized hole resembles that of monomers, but in a large hole, the spectrum is closer to that of molecules in a high-concentration solution or film. This explanation is

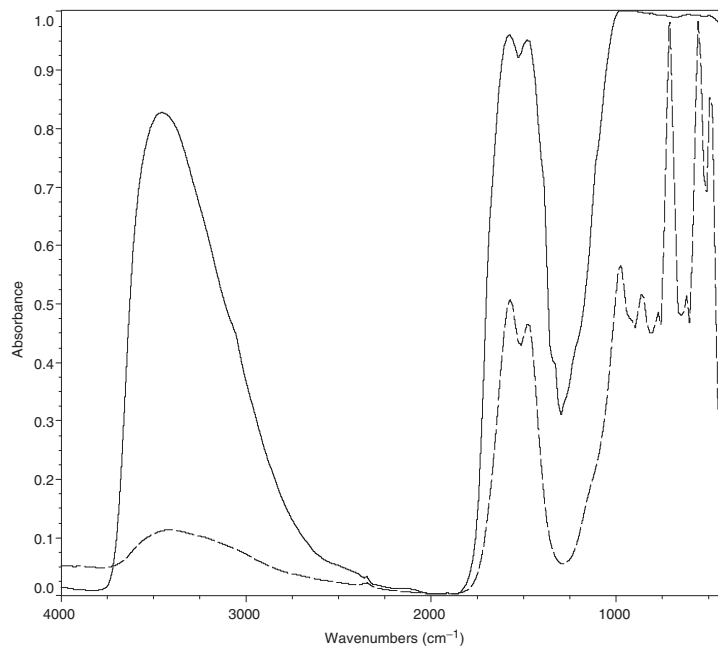


Figure 5. FTIR spectra of the P-Al (dashed curve) and the rinsed P-Al:Alq₃ (solid curve).

also shown by the PL intensity of the P-AI:RG6 prepared under different conditions. As is well known, the PL intensity of RG6 is quenched when the concentration is high enough. The PL intensity is very weak before rinsing because of the strong aggregation. When the molecules are impregnated into the holes, the PL intensity increases more than one order of magnitude. The molecules aggregate more easily in the bigger holes of P-AI prepared in $\text{H}_2\text{C}_2\text{O}_4$, therefore the emission is quenched more strongly than that in H_2SO_4 .

The reason why the PL of the P-AI almost disappeared when the organic molecules were introduced can be explained by comparing the spectra of Alq₃, RG6 and P-AI. The Alq₃ and RG6 have a broad excitation spectrum at 400 and 465 nm, respectively, which greatly overlap with the emission of P-AI. This gives rise to a strong re-absorption of the P-AI emission. As a result, the organic molecules show efficient and intense luminescence in spite of the small number of organic molecules left in the pores. After the P-AI:Alq₃ sample was further rinsed for a sufficiently long time, the emission of these organic molecules and the re-absorption became so weak that the peak at 440 nm became strong again.

5. Conclusion

In summary, P-AI samples with nanometre-sized holes were prepared with electrochemical etching under different conditions. The luminescent organic molecule Alq₃ and the laser dye RG6 were adsorbed into the different sized pores. Intermolecular action was limited by the nanometre hole size, so the emission spectra shifted to the short-wavelength region when the hole was small enough. The blue-shifted PL of organic molecules arise from electronic transfer from the lowest unoccupied molecular orbits to the highest occupied molecular orbits. In large pores, the formation of dimers or multimers induces a red-shift of the PL due to the stronger molecular interaction. In small pores, the organic molecules exhibit efficient and intense PL as monomers. Our results suggest a new

approach for preparation of novel optoelectronic devices such as display matrices of high density, high resolution and high uniformity by suitable control of the electrochemical reaction. It is also predicted that the integration of luminescent organic molecules and the P-AI can also be used to develop effective microcavities, solid state lasers and organic quantum dots.

Acknowledgments

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