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## Enhanced photoluminescence of hexamolybdenum cluster by anodic aluminum oxide photonic crystals

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### Abstract

The enhanced photoluminescence of the Mo<sub>6</sub> cluster was first reported by its incorporation into the anodic aluminum oxide (AAO), a photonic structure to delocalize the emission light. Two AAO structures with different pore sizes, densities, and shapes were controlled by pore widening treatment. The deposition of the negatively charged clusters at the bottom of the ordered AAO resulted in narrowing the PL peak at 680 nm with an enhanced intensity of 230%. In addition, the disordered AAO supported the deposition of clusters on the surface that efficiently adjusted the shift of the PL peak position, obtaining a high intensity by more than 300% in comparison with that of clusters deposited on the ITO-coated glass. The cluster-integrated photonic crystal could be an interesting material for applications that require efficient luminescence.

Keywords: hexamolybdenum, octahedral cluster, anodic aluminum oxide, photoluminescence, electrochemistry.

## 1. Introduction

Following the increase in demand for optoelectronic devices, many studies on 1 nm-sized face-capped  $\{\text{Mo}_6\text{X}\}^{i_8}$  metallic cluster core ( $X^i = \text{I}, \text{Br}, \text{Cl}$ ) coordinated with apical ligands ( $L^a = \text{halogen}, \text{H}_2\text{O}, \text{OH}, \text{etc.}$ ) have been reported with high luminescent quantum yields for light-emitting diodes (LEDs), biological applications or visible light absorption for photodetectors, solar cells, and photocatalysts [1-4]. However, the emitting light extraction efficiency was challenged due to the strong scattering effect. Only one study has revealed an enhancement of the photoluminescence (PL) of these clusters (MC) by using the engineering of the 3D silica colloidal photonic crystals but efficiency was not significant [5]. As is known, 1D anodic aluminum oxide (AAO) has been investigated in delocalizing the emitting light resulting in a remarkable improvement of the external quantum efficiency by 1280% for  $\text{CsPbBr}_3$  perovskite LED [6]. The AAO films were able to redirect scattering light to improve the light-reflecting efficiency from 59 to 84% [7]. The photoluminescence properties of the AAO films and their afterglow luminescence with high yield were revealed [8, 9]. In addition, AAO structures have been studied to tune optical and color properties when they are incorporated with other components for bandpass filters, sensors, and surface-enhanced Raman scattering [10-14]. In this study, two AAO structures were prepared by electrochemistry in different electrolytes with various porosities and periodic structures. The dependence of the PL peak position and intensity of MC on pore-widening treatment in phosphoric acid which controls the refractive index has been investigated. The PL intensities of MC at around 680 nm deposited on both AAO structures were improved, moreover, the ordered AAO structure can narrow the PL peak.

## 2/ Experimental

The AAO films were prepared by using alternating current oxidation, including four steps: polishing, anodizing, etching, and anodizing processes [10-11]. The detailed fabrications of disordered anodic aluminum oxide (DAAO) and ordered anodic aluminum oxide (OAAO) structures, obtaining a thickness of about 1  $\mu\text{m}$  are illustrated in Table 1. The pore-widening treatments for both structures were performed in 5%wt phosphoric acid for 3, 5, 7, and 10 minutes at ambient conditions. The pure aluminum plate (99,99%) and chemicals used without purification were purchased from the Wako Pure Chemistry

Industry.

Table 1. The detailed fabrications of the AAO films.

Structure	Polishing	Anodizing	Etching	Anodizing
<b>DAAO</b>	ethanol: perchloric (4:1/v:v); 2 mA; 4.5 minutes; 10°C	0.02v% phosphoric acid; 150V; 3 hours; 12°C	6wt% phosphoric acid and 1.8wt% chromic acid; 3 hours; 60°C	0.02v% phosphoric acid; 150 V; 25 minutes and 6 mA; 1 hour
<b>OAAO</b>		0.15 M oxalic acid; 3 hours; 40 V; 20°C		0.15 M oxalic acid; 40 V; 8 minutes and 6 mA; 1 hour; 20°C

$\text{Cs}_2[\{\text{Mo}_6\text{Br}_8\}\text{Br}_6]$  (MC) was synthesized following the reported procedure [15]. CMB was disassociated in methyl ethyl ketone (MEK, 99 %) at a concentration of 2.5 g/l. The electrophoretic deposition (EPD) of MC on ITO-coated glass and AAO substrates was optimized at 12 V for 60 seconds using a stainless-steel cathode [16]. MC deposited on AAO films was characterized by FE-SEM, reflectance, and photoluminescence.

### 3. Results and discussion

The DAAO structure was successfully prepared as seen in Figs. 1a-b. DAAO reflects mixed colors due to the strong interference of reflecting light from a periodic structure. The irregularly shaped porosities showed various diameters lower than 300 nm, accompanied by a stem layer length of 600 nm and a branched layer length of 200 nm. The negative charge on the  $[\{\text{Mo}_6\text{Br}_8\}\text{Br}_6]^{2-}$  cluster brought an essential advantage to introduce inside the pore of DAAO by using EPD with reported MC formula as  $[\{\text{Mo}_6\text{Br}_8\}\text{Br}_4(\text{H}_2\text{O})_2]$  [16]. The deposition of MC on the surface and stem porosities of DAAO before and after widening for 3 minutes was slightly different with big MC particles highlighted in yellow circles (Figs. 1c-d). From SEM-EDX mapping and spectra,

the Mo element was confirmed mostly at the surface of DAAO (Figs. 1e-f).

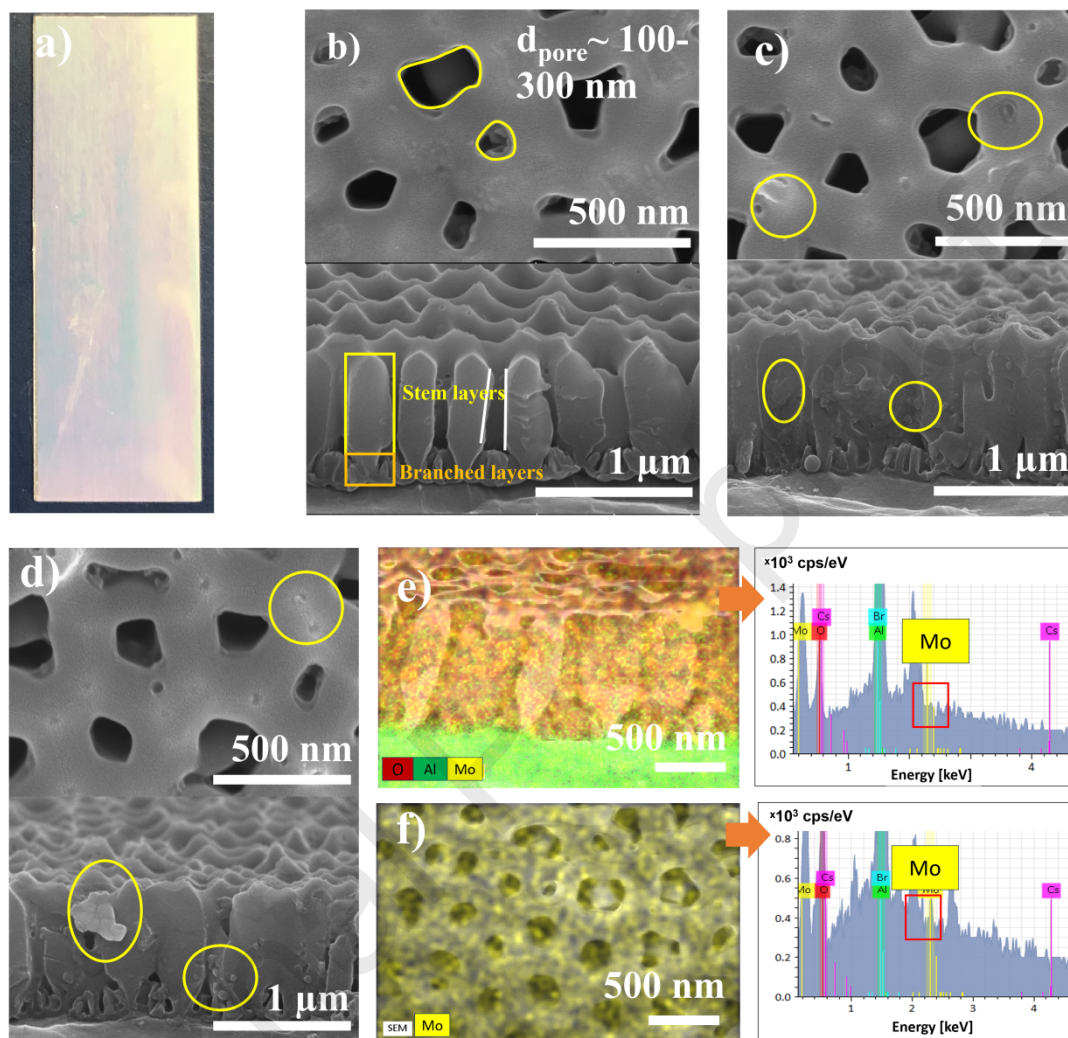


Figure 1. a) Photograph of DAAO. FE-SEM images of the surface and cross-section of b) DAAO, c) MC@DAAO, and d) MC@DAAO widened for 3 minutes. SEM-EDX mapping images of e) cross-section and f) surface of MC@DAAO widened for 3 minutes.

The optical properties of MC deposited on DAAO films with pore-widening treatment for 0, 3, 5, 7, and 10 minutes were demonstrated in Figs. 2a-b. The treatment caused the different periodic structures and porosities, providing the distinctive interference of reflectance (Fig. 2a). The DAAO films showed reflectance peaks in the range from 668

and 727 nm that were close to the PL peak of MC at 680 nm (Fig. 2b). The tunable optical effect between MC and DAAO was discussed. An essential factor that could contribute to enhanced PL intensity was the position of the reflectance peak of DAAO. The approximate stopband position of AAO is calculated by Bragg's law that is expressed in **Eq. 1** while ignoring the effect of branched layers [7]:

$$\lambda_{\max} = 2l_{stem} \sqrt{n_{stem}^2 - \sin^2\theta} \quad (1)$$

Where  $\lambda$  is the stopband for the first-order Bragg diffraction,  $n_{stem}$  is the refractive indices of AAO ( $\sim 1.685$ ), and  $\theta$  is the incidence angle of the light ( $5^\circ$ ). In general, the pore-widening treatment mainly increased the porosities of stem layers that contained air ( $n_{air} \sim 1$ ), resulting in a decrease in the effective refractive index. In connection with Eq. 1, the reflectance peaks will shift to a lower wavelength. As is proven, the PL peaks obtain a similar decreasing trend as seen in Fig. 2c. The linear dependence of the reflectance and PL peaks on the pore-widening time was similar with slightly different rates. Considering the relation of the equation and curve, the stem layer length ( $l_{stem}$ ) value was constant. As a result, the change of  $n_{stem}$  came from the modification of the stem layer width that was distributed by acid treatment. The PL intensity of MC significantly increased in combination with DAAO at all widening times. A treatment time lower than 5 minutes was efficient for controlling the reflectance peak around the PL peak of MC, increasing intensity by more than 300% (Fig. 2d). Summarily, the intensity and position of the PL peaks were modified in the range limited by broad PL spectrum of MC deposited on ITO glass.



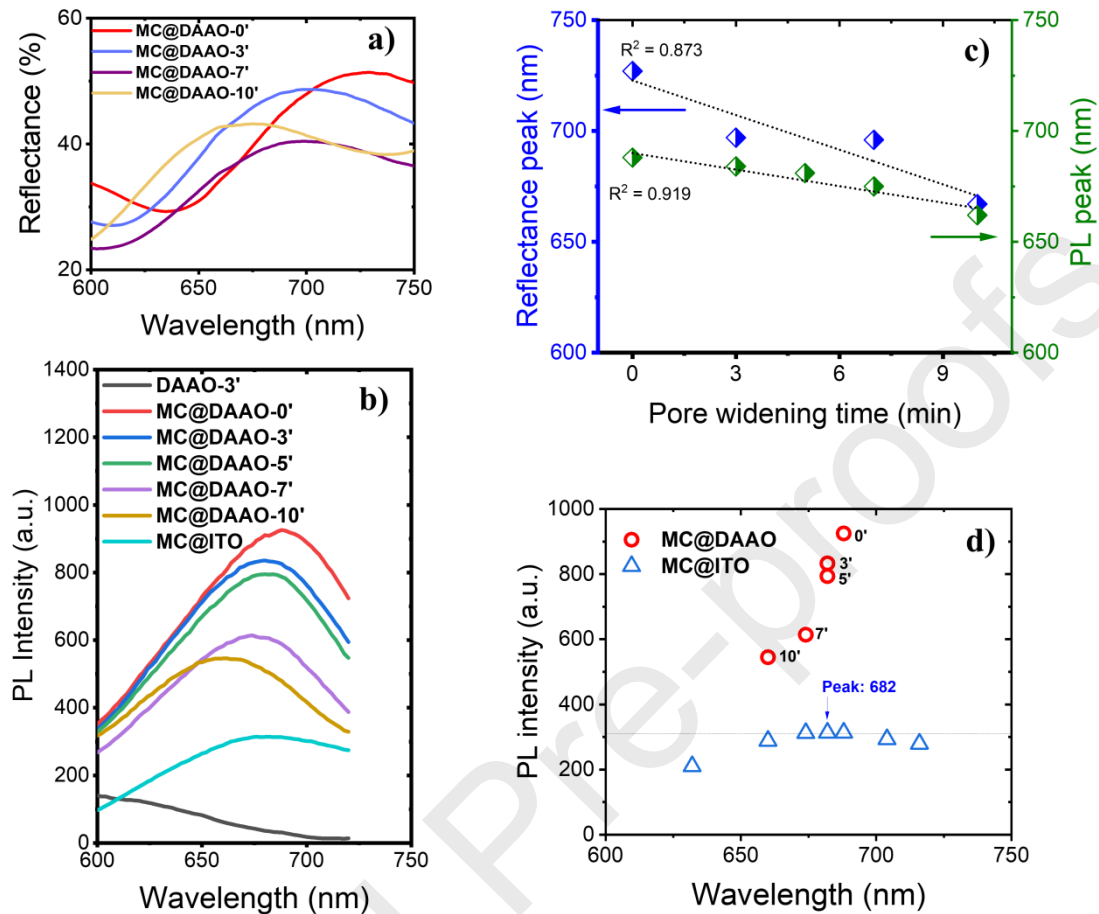


Figure 2. a) Reflectance and b) PL spectra of MC@DAAO widened at different times excited at a wavelength of 365 nm. C) Dependence of reflectance and PL peaks of MC@DAAO on widening time. D) The PL intensity of MC@ITO and MC@DAAO.

The high-ordered porous AAO structure with hexagonal-aligned channels was performed in oxalic acid that was not obtained by using phosphoric acid. The FE-SEM images of OAAO confirmed homogeneous circle pores with a diameter of  $29 \pm 5$  nm, and stem layer length of 1100 nm (Figs. 3a-b). The MC deposition was observed on the surface of the OAAO films without and with treatment (Figs. 3c-d). The SEM-EDX mapping and element spectra indicated that the Mo elements concentrated on branched layers (Figs. 3e-f). Similarly, MC-deposited OAAO provided tunable light emission at around 680 nm which overlapped with the emission band of MC-deposited ITO, increasing intensity by more than 230% (Fig. 3g). In addition, the PL peak shape was narrowed in a shortening



range between 650 and 750 nm while the range was 580 nm and 800nm for MC deposited on flat ITO glass. From Figs. 3h-i, the synchronized shift of reflectance and PL peak position to a lower wavelength occurred when pore-widening treatment was performed. Although the MC amount deposited on AAO films ( $\sim 0.058 \text{ mg/cm}^2$ ) was less than that on ITO glass ( $\sim 0.368 \text{ mg/cm}^2$ ), the PL intensity of MC was remarkably enhanced in comparison with MC-deposited ITO glass. This proved that both AAO structures efficiently contributed to the delocalization of the emitting light. The differently narrowing effects of DAAO and OAAO on PL peaks possibly originated from MC depositing positions, reflectance peak shape, etc.

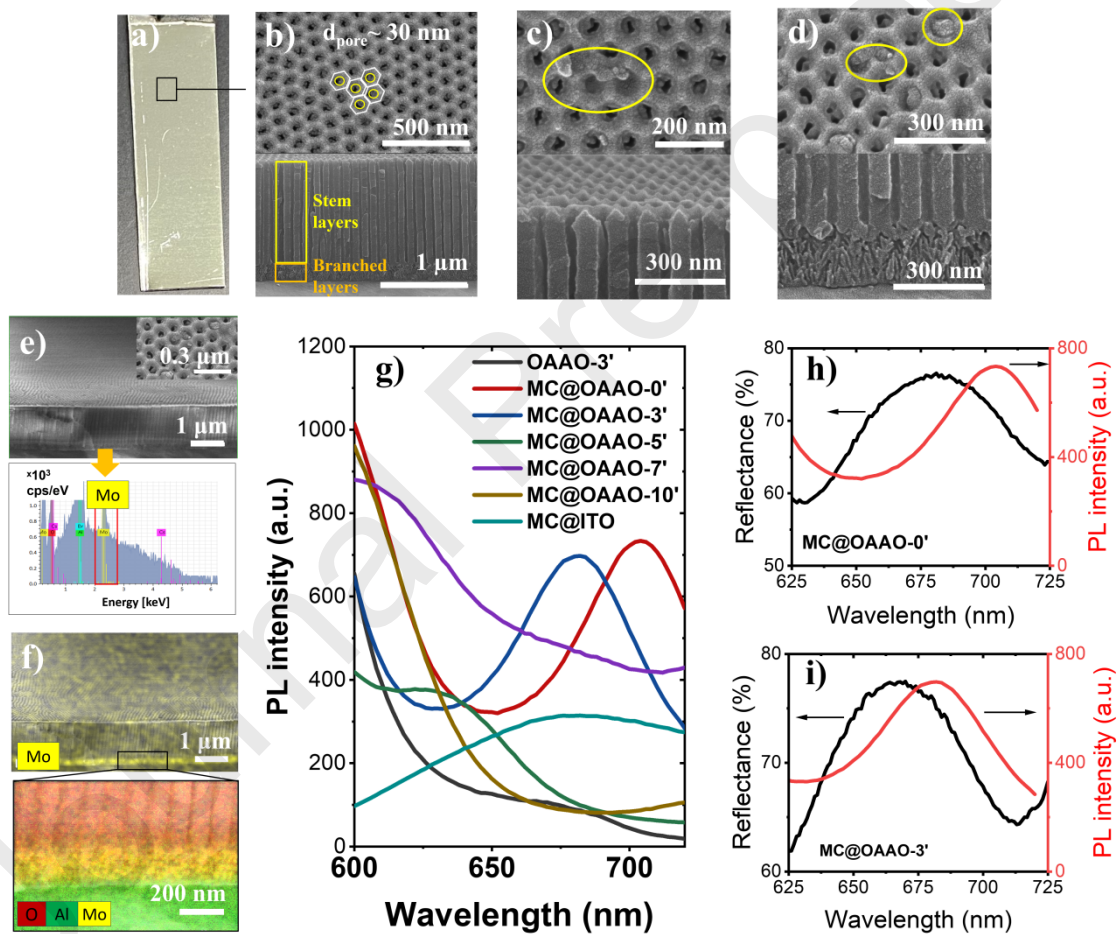


Figure 3. a) Photograph of OAAO. FE-SEM images of surface and cross-section of b) OAAO, c) MC@OAAO, and d) MC@OAAO widened for 3 minutes. e) element spectra and f) SEM-EDX mapping images of MC@OAAO at the bottom widened for 3 minutes. G) PL of MC@OAAO widened at different times. The correlation between reflectance and PL peak positions of MC@OAAO h) without and i) with widening for 3 minutes.

#### 4. Conclusions

The tunable optical properties of the Mo<sub>6</sub> cluster deposited into disordered and highly ordered AAO films were studied. The modified shape and position of the photoluminescence peaks depended on different AAO structures and cluster depositing positions; DAAO was good for controlling the PL peak positions and OAAO was efficient for delocalizing the emitting light in a narrow range. The photoluminescence property of the Mo<sub>6</sub> cluster employed with AAO was enhanced by more than 300% for the best sample.

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## Highlights

The tunable optical property of the Mo<sub>6</sub> cluster deposited into an anodic aluminum oxide (AAO) film was studied.

The modified photoluminescence peak shape and position depended on different AAO structures.

The photoluminescence (PL) property of the Mo<sub>6</sub> cluster was enhanced by more than 300%.