



Reduced reflectivity and golden color of porous anodic aluminum oxide nanostructures filled with maghemite nanoparticles



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ABSTRACT

The reflectivity and consequent color of anodic aluminum oxide (AAO) containing maghemite (γ -Fe₂O₃) nanoparticles (NPs) were investigated. The hexagonally ordered pores of AAO were completely filled with maghemite NPs with \sim 20 nm in diameter by the dip-coating process. The AAOs containing maghemite NPs have a reduced reflectivity of light at the wavelength below \sim 600 nm, resulting in golden color. The reduced reflectivity and golden color of AAOs with NPs was explained by the absorption of light from blue to violet wavelength range by maghemite NPs. These results indicate the potential color-engineering of AAO by means of wavelength-selective absorption by incorporated NPs.

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Introduction

Anodic aluminum oxide (AAO) nanostructures have been actively investigated because they offer the regular array of pore structures with uniform and tunable size [1], which can be used for various applications such as nanopatterning [2], guided growth of nanowires or nanotubes [3], and so on. In addition, they have been used to color the surface of aluminum through pigmentation with organic dyes and metallic elements [4–6]. It has been reported that the metal-pigmented AAO reveals the tunable color depending on the kind of metals and its amount in the pores of AAO [4]. The pigmentation of aluminum surface by incorporating metallic elements into the surface anodic oxide decorates and colors the aluminum; moreover, it can be used for display applications. In addition, reducing reflectance by light scattering or absorption can be applied to improving the solar cell efficiency [5]. The pigmentation of AAO has been generally achieved by electrodeposition of various metals such as Cu, Ag, Au, Mo, and Ni inside AAO pores [4]. The coloring of metal-pigmented AAO has been explained with either altered optical constant of AAO containing metallic elements or absorption of light in the visible range, for example, due to surface plasmon resonance from noble metals (e.g. Cu, Ag, and Au) embedded in dielectric AAO medium. Chen et al. demonstrated the tuning of optical properties of AAO with Ni

nanowires by adjusting the thickness of AAO, where its color was changed due to the interference of light [7]. Xu et al. [8] also reported the tunable color of Co-containing AAO by adjusting anodization time. In addition to coloring of AAO, Vasquez et al. reported the tunable coloration of gold nanoparticles (NPs) embedded porous silica by means changing the concentration of NPs [9].

In this study, we closely scrutinized the reflectivity and consequent color of AAO whose pores are completely filled with colloidal maghemite (γ -Fe₂O₃) NPs with a size of \sim 20 nm by dip-coating process. The incorporated NPs are found to significantly reduce the reflectivity of light at the wavelength below \sim 600 nm, thereby leading to golden color of AAO. The experimentally observed reflectivity and color were discussed by considering the effects of absorption of light by NPs, the interference of light due to the changed of refractive index of AAO as being filled by NPs, and the scattering of light by NPs.

Experimental

The AAO nanostructures were prepared by two-step anodization of Al plate as previously reported [1,10]. They had hexagonally ordered pores with diameter of \sim 80 nm, wall thickness of \sim 60 nm, pore depth of \sim 170 nm, and barrier layer thickness of \sim 40 nm, respectively. These pores were filled with colloidal maghemite NPs with \sim 20 nm in diameter which were stabilized by a surfactant of oleic acid (C₁₈H₃₄O₂) as synthesized by following the method

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developed by Hyeon et al. [11]. The AAO nanostructures were dip-coated with dipping and withdrawing speed of 0.1 mm/s from maghemite colloidal NPs solution with NPs concentration of 1.2×10^{13} /ml dispersed in octane. The dip-coated AAO was annealed at 200 °C for 1 h in air, during which the oleic acid molecules were desorbed from the surface of AAO and NPs layer. Then it was subsequently dipped into the solution for additional adsorption of NPs onto the NPs layer. The dipping and annealing procedures were repeated 5 times in order to completely fill the pores. The size and structure of maghemite NPs were analyzed using transmission electron microscopy (TEM, JEM2010F) and electron diffraction pattern analysis. The colors and morphologies of AAO containing NPs were analyzed using optical and scanning electron microscopy (SEM, LEO SUPRA55). The oblique-angle-view SEM images were obtained by folding and tilting AAO on Al plates. The reflectivity of AAO containing NPs was analyzed using UV-vis spectrometer (Cary 5000, Varian). The measured reflectivity was normalized by the reflectivity of reference Al mirror. The UV-vis absorption properties of maghemite NPs were also obtained from maghemite NPs layers on glass substrate.

Results and discussion

Fig. 1 shows the TEM micrograph and electron diffraction pattern of maghemite NPs dropped on carbon-coated TEM grid. The diameter and phase of NPs were approximately 20 nm and maghemite phase (γ -Fe₂O₃, JCPDS No. 39-1346). The maghemite phase of NPs was also confirmed using x-ray photoelectron spectroscopy [12].

Fig. 2 shows the optical micrographs of AAO before and after dip-coating 5 times, respectively. The AAO on Al plate before dip-coating showed white color and its color was barely changed after dip-coating 1 time (not shown). On the other hand, the AAO after dip-coating 5 times showed a clear golden color. It indicates that the maghemite NPs were attached or incorporated in AAO after dip-coating; thereby changed the color of AAO as proportional to the number of dip-coating, i.e. amount of incorporated NPs in AAO.

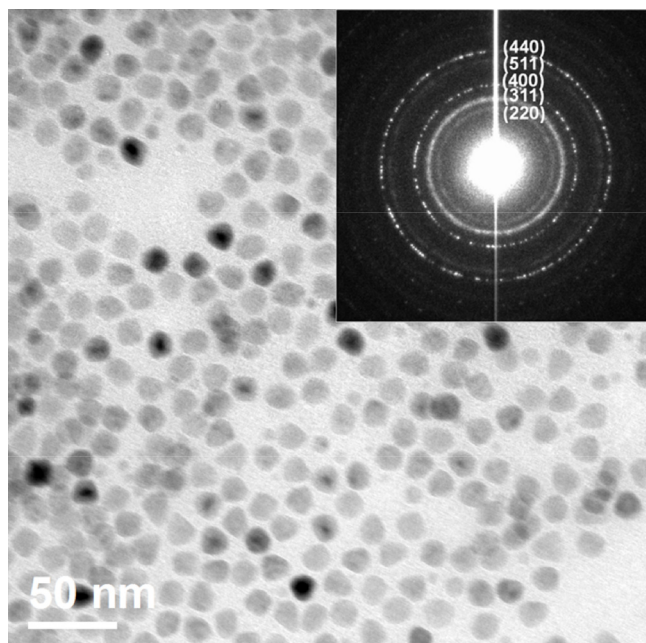


Fig. 1. TEM micrograph and electron diffraction pattern of maghemite NPs dropped on carbon-coated TEM grid.

In order to correlate the incorporation of NPs in AAO with the change of color, the structure of AAO after dip-coating was analyzed using SEM. Fig. 3 shows the SEM micrographs of AAO after dip-coating 5 times. After dip-coating, the NPs were incorporated into the pores of AAO and assembled as filling the pores. During dip-coating, the NPs adsorbed on the surface AAO and were driven into pores by the capillary force upon evaporation of the solvent. The detail mechanism has been previously reported [10]. As previously reported, the NPs were assembled at the bottom of pores as monolayer after dip-coating 1 time. Then, even repeating dip-coating multiple times without annealing steps, the NPs did not attach on the surface of NPs layer because the residual surfactant molecules left on the surfaces of AAO and NPs layer prevented the adsorption of incoming NPs [10,13]. The barely changed color of AAO after dip-coating 1 time was due to insufficient amount of NPs to change the color. On the other hand, the color of AAO was significantly changed to golden color after repeating dip-coating and annealing steps 5 times. The AAO was found to have completely filled pores by NPs as shown in Fig. 3, whose amount of NPs were enough to change the color of AAO.

As for the origin of the change of color, the effect of light interference in AAO on Al structure by adding NPs inside the pores of AAO was examined. The AAO on Al plate was composed of porous aluminum oxide having hexagonally ordered pores at the top region and non-porous aluminum oxide bottom layer, called barrier layer. The volume fraction of pores in porous layer was calculated to be approximately 0.3. Since the reflectivity spectrum by the interference of light is determined by the optical constant, e.g. refractive index of porous layer of AAO, the effective refractive indices were compared between the cases before and after filling the pores with NPs. A Maxwell Garnett effective medium theory (Eq. (1)) [14] was used to calculate the optical constant of top porous layer with or without NPs based on the Rayleigh criterion in which the pores were too small to be discernible in the visible range [15]. In this calculation, we also assumed that the light was neither absorbed nor scattered by AAO and NPs.

$$\epsilon_{\text{eff}} = \frac{(1-f)\epsilon_{\text{Al}_2\text{O}_3} + f\beta\epsilon_{\text{air,np}}}{1-f+f\beta} \quad (1)$$

In Eq. (1), ϵ_{eff} is the effective permittivity of porous layer depending on the fraction of pore f and geometrical factor β . $\epsilon_{\text{Al}_2\text{O}_3}$, ϵ_{air} , and ϵ_{np} are the permittivity of aluminum oxide, air, and maghemite NPs, respectively. For the cylindrical pore shape, β is approximated to be 1. If the pores are filled with spherical NPs, $\beta = 3\epsilon_{\text{Al}_2\text{O}_3}/(\epsilon_{\text{np}} + 2\epsilon_{\text{Al}_2\text{O}_3})$ [14]. From data of refractive indices of $n_{\text{Al}_2\text{O}_3} = 2.65$ for aluminum oxide [16], $n_{\text{np}} = 3.1$ for maghemite NPs [17], and the relation of $n_x = \epsilon_x^{0.5}$, the effective refractive index of porous layer of AAO without NPs was calculated to be ~ 2.3 and that with maghemite NPs was ~ 2.7 . Though these values are not much different each other, the reflected light spectra are quite changed as shown in Fig. 4.

The reflected light spectrum of AAO without NPs (red line) in Fig. 4 shows oscillatory interference peaks but the intensity is almost uniform at whole visible range. Thus, the color of AAO was white. On the other hand, the reflective spectrum of AAO with NPs exhibits the reduced reflectivity to almost zero at the wavelength below ~ 600 nm, which consequently corresponds to golden color [18]. The right axis of Fig. 4 is the absorption spectrum of maghemite NPs on the glass substrate after annealing at 200 °C for 1 h because the maghemite NPs in AAO was also annealed at the same temperature for the multilayer formation. It exhibits the absorption band at ~ 390 nm with tail extending to ~ 600 nm, which is apparently coincident with decreased reflectivity at the wavelength below ~ 600 nm. Therefore, it is thought that the reflectivity spectrum with reduced intensity at blue to violet range

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