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1. Introduction

Self-ordered anodic aluminium oxide (AAO) membranes with hexagonally packed nanochannel arrays have become promising candidates for versatile applications including nanofluidic

- ^c Key Laboratory of Materials Physics and Anhui Key Laboratory of Nanomaterials and Nanostructures, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, China
- ^d School of Opto-Electronic Engineering, Zaozhuang University, Zaozhuang 277160, Shandong, China
- ^e MIIT Key Laboratory of Advanced Display Materials and Devices,
- Institute of Optoelectronics & Nanomaterials, School of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing 210094, China. E-mail: zeng.haibo@njust.edu.cn
- ^f Department of Electronic & Computer Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong SAR, China

Organic-inorganic hybrid self-pigmenting effect of anodic aluminium oxide membranes[†]

Junxi Zhang, ^(b)*^a Wei Zhang, ^(b)^{ab} Wei Xu,^c Kang Xie,^d Qingsong Shan,^e Guangtao Fei, ^(b)^c Junhui Jia,^c Xiaoguang Zhu,^c Lide Zhang, ^(b)^c Zhiyong Fan ^(b)^f and Haibo Zeng ^(b)*^e

Anodic aluminium oxide (AAO) membranes with hexagonally packed nanochannel arrays have been utilized as a promising template to develop functional nanostructures. The characteristics of the AAO membranes are crucial to their functional applications. Great efforts have been made toward the formation mechanism and fabrication techniques of the AAO membranes, however, the characteristics of the AAO membranes have not yet been sufficiently elucidated. Herein, we present an organic–inorganic hybrid self-pigmenting effect based on the AAO membranes; the color of the AAO membranes demonstrates a conversion from straw yellow to achromaticity by tuning the nanochannel size. Consequently, the nanochannel size can be evaluated macroscopically according to the hybrid self-pigmenting maps. Furthermore, the hybrid self-pigmenting behavior depends on both the composition and structure of the AAO membranes. The organic–inorganic hybrid self-pigmenting process includes a dynamic equilibrium between the formation of the aluminium oxide and the dissolution of the oxide, as well as the migration of the oxalate anions towards the inner layer of the nanochannel under the local electric field. The self-pigmenting based on electrochemical anodization not only presents a new route to realize organic–inorganic hybrid pigmenting but also provides some promising applications in optics, biomedical and industrial fields.

transport,¹ filtration,² separation,³ ionic current rectification,⁴ sensors,^{5,6} and biodetection,⁷ as well as the construction of various nanostructures (such as nanorods,^{8,9} nanowires,^{10,11} nanoparticles¹² and nanopillars¹³), and the design of optical devices, ¹³ biosensor^{14,15} and energy conversion devices¹⁶ through the AAO template-based assembly approach, where the composition and the structural characteristics of the AAO membranes play key roles in their functional applications. Interestingly, the compositions of the AAO membranes are not completely composed of aluminium oxide; partially acid anion-contaminated species have been inevitably incorporated into the membrane during the formation of the nanochannels,^{17,18} and the alumina composition in the barrier layer produces a different pattern of surrounding hexagonal walls.18 Moreover, some special properties of the nanostructures and AAO itself, such as photoluminescence,19 electronic transport²⁰ and thermal conductivity,²¹ have a close relationship with the composition of the AAO membranes. Many efforts have been made toward the formation mechanism²²⁻²⁷ and fabrication techniques²⁸⁻³² of the nanochannels in the AAO membranes, however, the characteristics of the AAO itself have received less attention, and the composition, especially the acid anion-contaminated species of the AAO membranes, has not yet been understood clearly.

On the other hand, organic pigments have been widely used in the paint, ink, and plastic industries, and some high-technology

^a School of Instrument Science and Opto-electronics Engineering, Anhui Province Key Laboratory of Measuring Theory and Precision Instrument, Anhui Key Laboratory of Advanced Functional Materials and Devices, National Engineering Laboratory of Special Display Technology, Hefei University of Technology, Hefei 230009, China. E-mail: junxi.zhang@hfut.edu.cn

^b School of Physics, Hefei University of Technology, Hefei 230009, China

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industries.^{33–35} However, the low dispersion ability, poor weather durability and thermal instability exhibit negative effects on their functional applications.³⁶ In this case, organic-inorganic hybrid pigmenting provides an effective approach to solving the above problems,³⁷⁻⁴¹ which results from the advantages of being lightweight and versatile due to the organic materials, and high thermal and mechanical resistance due to the inorganic materials.42 The composites of organic chromophores and inorganic materials exhibit a synergistic effect. The stability and properties of the organic-inorganic hybrid pigments depend on both the structures and the interaction between the inorganic materials and the organic chromophores.43 Currently, the organic-inorganic hybrid pigments have been fabricated through the following three routes: first, encapsulating or trapping organic pigments in inorganic materials by chelation,⁴⁴ coupling^{38,41} and sol-gel45,46 processes; second, the adsorption of organic pigments onto the surfaces of inorganic materials by co-precipitation⁴⁷ and modification⁴⁸ strategies; third, the preparation of core-shell hybrid structures by a mechanical dry milling method⁴⁹ and a dip-coating method.⁵⁰

In this paper, we present a simple and effective method to realize organic-inorganic hybrid pigmenting based on the AAO membranes by an electrochemical anodization approach. The as-prepared AAO membrane is straw yellow, and there is a slight conversion from straw yellow to achromaticity with increasing the nanochannel size. In this case, we propose a facile and nondestructive macroscopic observation method for the nanochannel sizes of the AAO membranes based on their hybrid self-pigmenting maps. The hybrid self-pigmenting behavior is dependent on both the composition and the structure of the AAO membranes. It is interesting to note that this hybrid pigmenting is a self-pigmenting phenomenon during the growth process of the AAO membranes in the oxalic acid solution. The hybrid self-pigmenting process covers a dynamic equilibrium between the formation of the aluminium oxide and the dissolution of the oxide, as well as the migration of the oxalate anions towards the inner layer of the nanochannel under the local electric field.

2. Experimental

2.1. Preparation of the AAO membranes

The self-ordered AAO membranes with hexagonally packed nanochannel arrays were prepared *via* three processes. Firstly, high-purity aluminium sheets (99.999%, 0.3 mm thick) were degreased in acetone, and then an annealing treatment under vacuum (10^{-4} Pa) was carried out at 500 °C for 5 h to remove the mechanical stress and make the grains grow up. The aluminium sheets were electropolished at 23 V in a 1:9 mixture solution of perchloric acid and ethanol at 2 °C. Secondly, the aluminium sheets with very smooth surfaces were then anodized in a 0.3 M oxalic acid solution under a constant voltage of 40 V at 13 °C for 10 h. After that, the anodic oxide layers on the aluminium sheets were removed in a mixture solution of H₃PO₄ (6 wt%) and H₂CrO₄ (1.8 wt%) at 60 °C for 22 h. Then, 4 and 20

aluminium sheets through the first anodization were anodized again for 120 and 640 min, respectively, where the anodization conditions such as voltage, temperature and concentration of the oxalic acid solution, were the same as those used in the first anodization; in particular, the voltage and the temperature were controlled accurately in the whole anodization process. After the two-step anodization, the aluminium substrates were removed in a SnCl₄ solution. Thirdly, the through-channel AAO membranes were achieved by an entire channel-opening of the nanochannels in a 5 wt% H₃PO₄ solution at 30 °C for about 40 min. Whereafter, 20 through-channel membranes prepared via the second anodization at 13 °C for 640 min were divided into four groups. For each group, five through-channel membranes were chemically etched in the 5 wt% H₃PO₄ solution at 30 °C for 0, 10, 35, 60, and 95 min, respectively. Similarly, the 4 through-channel membranes prepared through the second anodization for 120 min were etched in the H₃PO₄ solution at 30 °C for 0, 10, 20, and 30 min, respectively. It is worth noting that the selection of the etching duration is according to the etching velocity of the pore walls; herein the etching velocity for a thin membrane is faster than that for a thick membrane.

2.2. Sample preparation for TEM observations

For TEM observations of the top and bottom surfaces of the nanochannels in the thick AAO membranes, the fragile AAO membranes with 70 µm thickness were directly prepared by an ion milling technique in a precision ion polishing system (PIPS) (Gatan, Model 691), where the sliced membranes were supported by Gilder aperture molybdenum grids (type: GA1000M, 1.0 mm hole, 3.05 mm O.D.). The ion milling was carried out using a double-sector milling mode while fixing the two guns towards the top surfaces of the membranes. To achieve large electron-transparent areas for TEM observations without radiation damage and amorphous sample, control of the milling parameters including beam energy, milling angle, and temperature is important. For example, the TEM sample of the top surface of the AAO membrane without the etching was prepared at a beam energy of 4.6 keV for 315 min and then 4.0 keV for 340 min with a milling angle of 7°, followed by 3.5 keV for 60 min with a milling angle of 4° and finally, 3.5 keV for 60 min with a milling angle of 3°. The TEM sample of the top surface of the AAO membrane through the 95 min etching was prepared at 4.0 keV for 170 min with a milling angle of 7° , then 3.6 keV for 280 min with a milling angle of 4° and finally, 3.3 keV for 60 min with a milling angle of 3°. The milling parameters of the top surfaces of the membranes through the etching for 10, 35, and 60 min were selected between those of the membranes after etching for 0 and 95 min. Also, the milling parameters of the bottom surfaces of the AAO membranes through the etching for 0, 10, 35, 60 and 95 min, respectively, were close to those of the top surfaces of the membranes. Finally, these TEM samples were cleaned in a Gatan advanced plasma system (SolanusTM, Model 950) for 40 min with an Ar/O2 gas recipe for the removal of contamination.

2.3. Characterization of the AAO membranes

TEM images of the top and the bottom surfaces of the AAO membranes were taken on a high-resolution transmission electron microscope with an accelerating voltage of 200 kV (TEM, JEOL 2010). The sizes of the nanochannels both on the top and the bottom surfaces of the membrane were measured using the Gatan DigitalMicrograph (DM) software. The membrane thickness was measured by an optical microscope (Leica, DM2500 M, $50 \times$ objective (N.A. = 0.75), MS 20 encoded stage) controlled by the Renishaw WiRE 3.2 software.

2.4. Spectroscopy measurements

UV-Vis absorption spectra of the AAO membranes were acquired using a UV-Vis-NIR spectrophotometer (Cary 5E), and the UV-Vis reflection spectrum of the aluminium oxalate dihydrate was taken on a diffuse reflectance accessory. Infrared (IR) spectra were collected at room temperature using a Fourier transform infrared spectrometer (Nexus 670).

3. Results and discussion

3.1. The organic-inorganic hybrid self-pigmenting effect of the AAO membranes

Fig. 1 shows organic–inorganic hybrid self-pigmenting maps of the AAO membranes with sub-100 nm nanochannels formed in oxalic acid solution. The as-prepared AAO membrane without etching treatment was straw yellow (see the upper-left photo); increasing the etching duration from 0, 10, 35, 60 to 95 min (see the maps from top to bottom) resulted in the conversion from straw yellow to achromaticity, which corresponds to the



Fig. 1 Organic–inorganic hybrid self-pigmenting maps of the AAO membranes after etching for different durations: (a), (b), (c), (d) and (e) correspond to the etching durations, 0, 10, 35, 60 and 95 min, respectively; 1, 2, 3, 4 denote the maps from left to right for one, two, three, and four stacked membranes with identical nanochannel sizes, respectively.

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increase in the nanochannel sizes from 52.2 nm to 85.4 nm on the top surface of the AAO membrane, as well as from 37.2 nm to 78.6 nm on the bottom surface (Fig. 2 and 3), where the nanochannel sizes were measured using a Gatan DigitalMicrograph (DM) software (Fig. S1, ESI†). It is interesting to note that the size (or diameter) of the nanochannels on the top sections is prominently larger than that on the bottom sections for each AAO membrane (Fig. 3), and the nanochannels formed



Fig. 2 TEM images of the top surfaces of the nanochannels in the thick AAO membranes. Scale bar, 200 nm. (a1), (b1), (c1), (d1) and (e1) display the AAO membranes formed after the chemical etching of the through-channel membranes immersed in a 5% H₃PO₄ solution at 30 °C for 0, 10, 35, 60, and 95 min, respectively. (a2), (b2), (c2), (d2) and (e2) correspond to the size distribution histograms of the top nanochannels in the same membranes, respectively.



Fig. 3 TEM images of the bottom surfaces of the nanochannels in the thick AAO membranes. Scale bar, 200 nm. (a1), (b1), (c1), (d1) and (e1) display the AAO membranes formed after chemical etching of the through-channel membranes immersed in a 5% H_3PO_4 solution at 30 °C for 0, 10, 35, 60, and 95 min, respectively. (a2), (b2), (c2), (d2) and (e2) correspond to the size distribution histograms of the bottom nanochannels in the same membranes, respectively.

in the usual steady-state growth have a truncated conical shape.⁵¹ Furthermore, when two, three and four membranes with identical nanochannel sizes are stacked, respectively, the color conversion with the nanochannel size is visible (Fig. 1, see the maps from left to right). It was observed that the color of the membranes became deep on increasing the membrane thickness by a stacking method with two, three, and four pieces with the same nanochannel sizes.

The UV-vis absorption spectra showed a strong absorption band at 254 nm and a weak absorption band around 300 nm (Fig. 4a), which resulted from the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of a carbonyl group containing double bonds (*e.g.*, C==O), respectively, where the carbonyl group is a chromophore. Moreover, the $n \rightarrow \pi^*$ transition of the carbonyl group is always less intense because the electrons in the non-bonding atomic orbital (*i.e.*, n-orbital) are situated perpendicular to the plane of the antibonding π orbital (*i.e.*, π^* orbital) and consequently, the probability of the jumping of an electron from the



Fig. 4 (a) UV-vis absorption spectra of the AAO membranes after etching for 0, 10, 35, 60, and 95 min, respectively. (b) UV-vis absorption spectrum of aluminium oxalate hydrate ($C_6O_{12}Al_2 \cdot xH_2O$, 99%, lot. No. K16R006, x = 9.14, from Alfa Aesar company) powder by a reflection measurement method. (c) UV-vis reflection spectra of the AAO membranes after etching for 0, 10, 35, 60, and 95 min, respectively.

n to π^* orbital is very low.⁵² In contrast, the $\pi \to \pi^*$ transition of the carbonyl group is more intense because the bonding π orbital and the antibonding π orbital (*i.e.*, π^* orbital) are in the same plane and consequently, the probability of the jumping of an electron from the π to π^* orbital is high. Since the nonbonding n-orbital locates at higher energy than the bonding π orbital, the absorption wavelength of the $n \rightarrow \pi^*$ transition is longer than that of the n $\rightarrow \pi^*$ transition. Since AAO membranes were prepared in oxalic acid solution through the electrochemical anodization, the acid anion-contaminated species (e.g., oxalic acid anions) were likely incorporated into the membranes; as a result, aluminium oxalate may be produced during the combination of oxalic acid anions with aluminium ions during the anodization process. Moreover, the UV-vis reflection spectrum of aluminium oxalate dihydrate (C₆O₁₂Al₂· 2H₂O) exhibited the same absorption band at 254 nm (Fig. 4b), which demonstrated that the absorption band resulted from aluminium oxalate. It has been noted that the absorption intensity decreased with increasing the size of the nanochannels (corresponding to the different etching time) (Fig. 4a), also the intensity increased with increasing the thickness of the AAO membranes (Fig. S2, ESI[†]).

The composition of the oxalic acid anion-incorporated species can be confirmed further by IR spectra. Since the IR absorption bands in the regions from 1660 to 1400 cm⁻¹ are very strong and are even saturated due to the 70 µm thick membranes (Fig. 5a), the IR spectra of 16 µm thick AAO membranes were measured to observe the features of the bands. The IR absorption bands at about 3400 cm⁻¹ are attributed to the -OH group resulting from the H₂O molecules in the AAO membranes. A strong and wide absorption band at 1572 cm^{-1} and a weaker absorption band at 1473 cm^{-1} appeared (Fig. 5b). This is because the C=O stretching vibration will shift to a lower frequency when oxalic acid is converted into oxalate; furthermore, the carboxylate anion has two strongly coupled C=O bonds between C=O and C-O. The coupling interaction between the two equivalent coupled bonds will result in a strong asymmetric stretching band near 1650–1550 cm⁻¹ and a weaker symmetric stretching band near 1400 cm^{-1} ;⁵² in this case, the double vibrations at 1572 and 1473 cm⁻¹ originated from the asymmetric and symmetric stretching vibrations of the aluminium oxalate. The absorption bands of the AAO membranes after 0 and 10 min etching treatments were still very strong, and a large quantity of aluminium oxalate was removed for the 20 min etching due to a remarkable reduction of the double absorption bands. After the walls were further dissolved (e.g., 30 min), the bands became very weak, which showed that the oxalate species were mainly removed. Moreover, the wide absorption band centered around 690 cm⁻¹ mainly resulted from the Al–O bond vibration of aluminium oxide.⁵³ For the 0 and 10 min etching, the absorptions were saturated due to the abundant aluminium oxide located in the outer and inner layers. After the 30 min etching, the outer layers were mostly dissolved but the absorption was still strong, which is primarily due to the contribution of a small amount of aluminium oxide in the inner layer.



Fig. 5 (a) IR spectra of the membranes prepared through the second anodization at 13 °C for 640 min after the etching treatments for 0, 10, 35, 60, and 95 min, respectively. (b) IR spectra of the membranes prepared through the second anodization at 13 °C for 120 min after the chemical etching for 0, 10, 20 and 30 min (with a thickness of about 16 μ m), respectively.

Note that the UV absorption from the aluminium oxalate has a wide absorption band tail at the purple and blue light wavelengths (Fig. 4a), corresponding to a wide and weak absorption band at the dominant wavelengths of 350 to 480 nm (Fig. 4c). In this case, the AAO membrane without the etching mainly radiates the complementary color of the purple and blue light, consequently exhibiting yellow. In contrast to the band edge of pure yellow in the range of 500 to 570 nm,^{54,55} there was a blue shift in the band edge of the AAO membrane (Fig. 4c) and thus, the membrane was straw yellow due to the hypochromic effect. Moreover, the straw yellow became weak with increasing the nanochannel size (e.g. corresponding to the etching from 0 to 60 min) because the absorption became weak and exhibited a blue shift. The membrane with very large nanochannels (e.g., corresponding to the etching for 95 min) became achromatic due to the very weak absorption. Therefore, based on the nanochannel size dependence of the color evolution characteristics due to the self-pigmenting behavior, the nanochannel size of the AAO membrane can be evaluated macroscopically. The deep straw yellow color demonstrated a small nanochannel size (e.g., 37.2 nm for the bottom surface as well as 52.2 nm for the top surface), and an undertint color indicated a large channel size (e.g., 63.2 nm for the bottom

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3.2. Composition and structure dependence of the organicinorganic hybrid self-pigmenting behaviour in the AAO membranes

Since the self-pigmenting originates from the absorption band tail of aluminium oxalate, the color evolution with the nanochannel size is closely associated with the distribution of aluminium oxalate in the nanochannnel walls of the AAO membranes. To calculate the distribution of aluminium oxalate in the nanochannel walls, the characterization of the structure of the nanochannel walls is indispensable. It was found that the nanochannnel walls are sandwich-like structures and consist of dark hexagonal inner layers and bright outer layers *via* the TEM observations of the thick AAO membranes (Fig. 6a and b), and the average thicknesses of the inner layers on the top and the bottom sections of the nanochannels are 7.3 nm and 7.6 nm, respectively (Fig. 6c and d). In this case, the nanochannel walls were partitioned into five regions in each of the hexagonal cells



(*e.g.*, j = 1, 2, 3, 4 and 5) based on the sequential etching treatments with the durations of 0, 10, 35, 60, and 95 min (Fig. 6e). For instance, the region j = 1 corresponds to the removed portion after the etching for the duration interval of 0 to 10 min, while the region j = 5 represents the portion of the nanochannel walls after the etching for 95 min. In this case, the distribution of aluminium oxalate in the partitioned regions of the nanochannnel walls can be calculated further. Firstly, the intensity of the light in an absorbing medium is according to Lambert's law:⁵⁶

$$\frac{I}{I_0} = e^{-\alpha d} \tag{1}$$

where $\frac{I}{I_0}$ is transmittance, α and d represent the absorption coefficient per centimeter and the thickness of the medium, respectively. For the AAO membranes, note that I_0 represents the intensity of the light incident on the top surface and I_i represents the intensity of the light emerging from the bottom surface. Here the subscript *i* means the AAO membrane through the *i* etching treatment (*e.g.*, *i* = 1, 2, 3, 4 and 5), corresponding to the etching durations of 0, 10, 35, 60, and 95 min, respectively. In particular, the reflection losses should be considered, and eqn (1) now becomes^{56,57}

$$\frac{I_i}{I_0} = (1 - R_i)^2 e^{-\alpha_i d_i}$$
(2)

where, R_i denotes the reflectivity, and d_i is the thickness of the AAO membranes (Fig. S3, ESI†). For the normal incidence, we have⁵⁸

$$R_i = \left(\frac{n_i - 1}{n_i + 1}\right)^2 \tag{3}$$

where

$$n_i = \left(\varepsilon_i\right)^{1/2} \tag{4}$$

 n_i and ε_i are the effective refractive index and the dielectric function of the AAO membranes, respectively. The contribution of the dielectric function from the small quantity of aluminium oxalate is slight; in particular, the AAO membranes are composed of nanochannels and nanochannel walls, and the period of the nanochannel arrays in the AAO membranes is at the sub-wavelength scale and far less than the wavelength of the light wave, thus, the AAO membranes can be equivalent to a dielectric metamaterial. ε_i is related to the effective refractive index, and can be calculated approximately according to the effective medium theory:⁵⁹

$$\varepsilon_{i} = \frac{\varepsilon_{a}\varepsilon_{b} + \overline{\varepsilon}(f_{a,i}\varepsilon_{a} + f_{b,i}\varepsilon_{b})}{\overline{\varepsilon} + (f_{a,i}\varepsilon_{b} + f_{b,i}\varepsilon_{a})}$$
(5)

Fig. 6 High-magnification TEM image of the top (a) and the bottom (b) surfaces of the nanochannels of the as-prepared AAO membrane without the etching, scale bar, 100 nm. Histograms of the thickness of the inner layers of the nanochannel walls on the top (c) and the bottom (d) surfaces. (e) Schematic illustration of the partitioned regions of the outer layer of the channel walls in one hexagonal cell, corresponding to the different channel sizes through the sequential etching.

where

$$\bar{\varepsilon} = \frac{1-q}{q} \varepsilon_{\rm h} \tag{6}$$

 ε_{a} , ε_{b} represent the dielectric functions of alumina and air, respectively, $f_{a,i}$ and $f_{b,i}$ correspond to the volume fractions of

alumina and air. q is a screening parameter in the range 0–1, and q = 1/2 for a two-dimensional system.⁵⁹ $\varepsilon_{\rm h}$ is the host dielectric function; the nanochannels (air) are embedded in alumina, $\varepsilon_{\rm h} = \varepsilon_{\rm a}$ based on the Maxwell Garnett effective medium expression.⁵⁹ Eqn (5) is now written as

$$\varepsilon_{i} = \frac{\varepsilon_{a} + \varepsilon_{b} - f_{b,i}(\varepsilon_{a} - \varepsilon_{b})}{\varepsilon_{a} + \varepsilon_{b} + f_{b,i}(\varepsilon_{a} - \varepsilon_{b})} \varepsilon_{a}$$
(7)

Since the nanochannel arrays are ordered nanostructures with a hexagonal arrangement on large areas, the volume fraction of the nanochannels $f_{b,i}$ is written as

$$f_{b,i} = \frac{\frac{\pi}{4} (D_{t,i}^2 + D_{t,i} D_{b,i} + D_{b,i}^2) d_i}{\frac{3\sqrt{3}}{2} S^2 d_i}$$
$$= \frac{\pi (D_{t,i}^2 + D_{t,i} D_{b,i} + D_{b,i}^2)}{6\sqrt{3}S^2}$$
(8)

 $D_{t,i}$ and $D_{b,i}$ correspond to the average sizes of the top and the bottom nanochannels (Fig. 3). *S* denotes the average spacing between adjacent nanochannels; it has been noted that the average spacings on the top nanochannels are the same as those on the bottom nanochannels for each of the AAO membranes (*e.g.*, 103.1 nm). The volume fraction of the alumina $f_{a,i}$ is given by

$$f_{a,i} = 1 - f_{b,i}$$
 (9)

In eqn (7), $\varepsilon_{\rm b}$ = 1, and $\varepsilon_{\rm a}$ = 1.834² at 254 nm.⁶⁰

If we replace the absorption coefficient α_i with an extinction coefficient $k_i(k_i = \log^e \alpha_i)$,⁶¹ eqn (2) can also be expressed as

$$\frac{I_i}{I_0} = (1 - R_i)^2 10^{-K_i d_i}$$
(10)

Considering that the extinction coefficient k_i is proportional to the concentration of aluminium oxalate, based on Beer's law,⁶² we have

$$k_i = \varepsilon c_i \tag{11}$$

where c_i represents the concentration of aluminium oxalate in the whole membrane through the *i* etching treatment. ε is the molar extinction coefficient or molar absorptivity of aluminium oxalate (Appendix, Fig. S4, ESI[†]).

On the other hand, the absorbance A_i at 254 nm obtained from the UV-vis spectra of the AAO membranes is defined by

$$A_i = \log\left(\frac{I_0}{I_i}\right) \tag{12}$$

In terms of eqn (10)-(12), we have

$$A_i = 2\log(1 - R_i) - \varepsilon c_i d_i \tag{13}$$

Eqn (13) indicates, in addition to the aluminium oxalate in the AAO membranes, the reflectivity of the structure with the nanochannel arrays contributes to the absorbance, which has also influenced the organic–inorganic hybrid self-pigmenting, the concentration of aluminium oxalate can be given by

$$c_i = \frac{A_i + 2\log(1 - R_i)}{\varepsilon d_i} \tag{14}$$

Considering eqn (14), the mass m_i of aluminium oxalate in the AAO membranes through the *i* etching treatments can be given by

$$m_i = c_i V_i M \tag{15}$$

$$V_i = N_{\mathrm{nc},i} V_{\mathrm{cell},i} \tag{16}$$

where V_i denotes the volume of the nanochannel walls, respectively. *M* is the molar mass of aluminium oxalate. $N_{\text{nc},i}$ and $V_{\text{cell},i}$ represents the nanochannel number and the wall volume of a hexagonal cell, respectively. From eqn (15), the density of aluminium oxalate is given by

$$\rho_i = c_i M \tag{17}$$

The calculations indicate that the density of aluminium oxalate is reduced with increasing the nanochannel size (Fig. 7). It is clear that the deep color of the membrane without the etching arises from the maximum density of aluminium oxalate. The color becomes weak when the density decreases with increasing the nanochannel size (Fig. 7). In particular, the membrane after the 95 min etching displays achromaticity because of the very low density of aluminium oxalate (Fig. 7). Thus, the reduction of the absorption at 254 nm with increasing the nanochannel size originated from the gradual decrease of the density of aluminium oxalate. Furthermore, when the nanochannel size increased from 37.2 nm to 63.2 nm (e.g. for the bottom surface), the UV absorption tail at 380-480 nm was reduced due to the decrease in the density of the oxalate species, thus, the straw yellow color became weak. In particular, a large quantity of aluminium oxalate was removed for the nanochannel size of 72.8 nm; as a result, the AAO membrane approaches achromaticity and finally, the AAO membrane becomes achromatic due to the nearly complete removal of the oxalate species for the nanochannel size of 78.6 nm.



Fig. 7 Density of aluminium oxalate in the membranes with the nanochannel size on the bottom surfaces.



Fig. 8 The organic–inorganic hybrid self-pigmenting process during the electrochemical anodization of aluminium in oxalic acid solution.

3.3. The organic-inorganic hybrid self-pigmenting process and mechanism in the AAO membranes

The mechanism of the organic-inorganic hybrid selfpigmenting in the AAO membranes was analyzed further. The organic-inorganic hybrid self-pigmenting process in the AAO membranes covers three procedures.

Firstly, during the electrochemical anodization process of aluminium, aluminium oxide forms at the aluminium/oxide interface with the migration of Al^{3+} and O^{2-} , wherein the chemical reactions are as follows:

$$AI \to AI^{3+} + 3e \tag{18}$$

$$2\mathrm{Al}^{3^+} + 3\mathrm{O}^{2^-} \to \mathrm{Al}_2\mathrm{O}_3 \tag{19}$$

Simultaneously, the aluminium oxide is dissolved at the oxide/ electrolyte interface in the oxalic acid solution, the corresponding chemical reaction is given by

$$Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O$$
 (20)

The formation and dissolution processes of aluminium oxide were explored in detail by Prof. Martín-González's group.⁶³ With increasing the anodization duration, a dynamic equilibrium between the formation of the aluminium oxide and the dissolution of the oxide was established (Fig. 8).

Secondly, the nanochannel grows from top to bottom along its long axis under the constant anodization potential. Moreover, the nanochannel wall is gradually etched in the lateral direction perpendicular to the long axis of the nanochannel in the oxalic acid solution, which results in enlarging the nanochannel size.

Thirdly, during the anodization process of aluminium under the local electric field, the oxalate anions with a slower mobility will migrate across the oxide/electrolyte interface and towards the inner layer of the nanochannel walls, and the oxalate anions combine with aluminium ions to produce aluminium oxalate; this has been confirmed by the UV-vis (Fig. 4) and IR (Fig. 5) spectra illustrated above, the reaction takes the form

$$2Al^{3+} + 3C_2O_4^{2-} \rightarrow Al_2(C_2O_4)_3$$
(21)

As a result, both the aluminium oxalate and the aluminium oxide are produced, which gives rise to the organic–inorganic hybrid self-pigmenting in the nanochannel wall (Fig. 8).

The organic–inorganic hybrid self-pigmenting behavior depends on both the composition and the structure of the AAO membranes. Specifically, in addition to the inhomogeneous distribution of aluminium oxalate in the AAO membranes, as described above, the reflectivity of the structure with the nanochannel arrays contributes to the absorbance, and the nanochannel arrays as a dielectric metamaterial also influence the organic–inorganic hybrid self-pigmenting.

4. Conclusions

The organic-inorganic hybrid self-pigmenting based on the AAO membranes formed in oxalic acid solution was investigated systematically. The as-prepared AAO membrane was straw yellow, and the color underwent a slight conversion from straw yellow to achromaticity with increasing the nanochannel size. In this case, the nanochannel sizes of the AAO membranes can be macroscopically observed by a facile and nondestructive method based on the hybrid self-pigmenting maps. It was found that the hybrid self-pigmenting effect is closely associated with the oxalic acid anion-incorporated species in the AAO membranes. Moreover, the UV-vis and IR spectra demonstrated that the oxalic acid anion-incorporated species consists of aluminium oxalate, and the straw yellow of the AAO membranes resulted from the absorption band tail of the carbonyl chromophore group of aluminium oxalate in the nanochannel walls. Hybrid pigmenting is a self-pigmenting phenomenon during the growth process of the AAO membranes in the oxalic acid solution. The hybrid self-pigmenting process involves both a dynamic equilibrium between the formation of the aluminium oxide and the dissolution of the oxide, and the oxalate anions incorporated into the nanochannel walls with a slower migration towards the inner layer of the nanochannel under the local electric field. The organic-inorganic hybrid selfpigmenting behavior depends on both the composition and the structure of the AAO membranes. Specifically, in addition to the inhomogeneous distribution of aluminium oxalate in the AAO membrane, the reflectivity of the structure with the nanochannel arrays contributes to the absorbance, and thus the nanochannel arrays as a dielectric metamaterial also influence the organic-inorganic hybrid self-pigmenting. This investigation will be useful for understanding the characteristics of the AAO membranes. The self-pigmenting based on electrochemical anodization not only presents a new route to realizing organic-inorganic hybrid pigmenting but also provides some promising applications in the optics, biomedical and industrial fields.

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Author contributions

Junxi Zhang: conceptualization, data curation, funding acquisition, investigation, methodology, and writing – the original draft. Wei Zhang: formal analysis, methodology, validation, and writing – review and editing. Wei Xu: data curation and methodology. Kang Xie: resources. Qingsong Shan: formal analysis. Guangtao Fei: resources. Junhui Jia: data curation and methodology. Xiaoguang Zhu: methodology. Lide Zhang: formal analysis and supervision. Zhiyong Fan: formal analysis, writing – review and editing. Haibo Zeng: formal analysis, supervision and writing – review and editing.

Conflicts of interest

There are no conflicts to declare.

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