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Anodic aluminum oxide with fine pore size control for selective and effective particulate matter filtering

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Abstract
Air pollution is widely considered as one of the most pressing environmental health issues. Particularly, atmospheric particulate matters (PM), a complex mixture of solid or liquid matter suspended in the atmosphere, are a harmful form of air pollution due to its ability to penetrate deep into the lungs and blood streams, causing permanent damages such as DNA mutations and premature death. Therefore, porous materials which can effectively filter out particulate matters are highly desirable. Here, for the first time, we demonstrate that anodic aluminum oxide with fine pore size control fabricated through a scalable process can serve as effective and selective filtering materials for different types of particulate matters (such as PM2.5, PM10). Combining selective and dramatic filtering effect, fine pore size control and a scalable process, this type of anodic aluminum oxide templates can potentially serve as a novel selective filter for different kinds of particulate matters, and a promising and complementary solution to tackle this serious environmental issue.

1. Introduction

Smog, a complex mixture of extremely small particles and liquid droplets suspended in the air, is highly toxic to humans and can cause severe sickness, shortened life or death. These particle matters (PM), made up of a number of components such as organic matter, element carbon, ammonium salt, sulfate, nitrate, mineral and microelement [1], can be grouped into three categories according to the kinetic diameters (KD): inhalable coarse particles (with KD larger than 2.5 micrometers but smaller than 10 micrometer), fine particulate (with KD larger than 0.1 micrometers but smaller than 2.5 micrometers) and ultrafine particulate (with KD smaller than 0.1 micrometers) [2]. Many results from toxicological research have shown that PM have several adverse cellular effects, such as cytotoxicity through oxidative stress mechanisms, oxygen-free radical-generating activity, stimulation of proinflammatory factors, mutagenicity, and even DNA oxidative damage [3, 4]. The size of the particles and their surface area were found to be critical for determining the potential to elicit inflammatory injury, oxidative damage, and other biological effects. The PM2.5 and PM10 are the main monitored index in air quality according to the guidelines by the World Health Organization updated in 2005 [5]. Therefore, to protect the local environment and to improve the health condition, effective strategies that can effectively filter out PM are highly desirable but so far with very limited options. Particularly, selective filters which can filter only specific sizes of PMs can be ideal to reveal all the scaling effect of particulate matters.

With decades of development, Anodic Aluminum Oxide (AAO) templates, fabricated with fine control of the pore diameter (5 nm to 10 μm), cylindrical shape and periodicity [6–8], have been widely utilized in materials science and microbial biotechnology [9]. Many parameters such as electrolyte concentration, the anodic voltage, formation temperature, the oxidation time, the widen process can be used to control the pore size and interpore distance [10]. As they are chemically stable, bio-inert and biocompatible [11–16], AAO templates are also commonly used for direct filtration to obtain pure liquid and gas or to collect the microorganism or particle in mixed fluids [17–21]. Here for the first time, we demonstrate that anodic
Figure 1. (a) Schematics of anodic aluminum oxide (AAO) filtering out particulate matter (PM or aerosol) suspended in the air. (b) Digital picture of the topside of anodic aluminum oxide (AAO) component for filtration test. The central circular area is the filtration area (~12.57 cm²) with supported stainless steel wire on the backside of AAO.

Figure 2. The SEM images of (a) the pristine surface of Al foil, (b) the electropolished Al foil by a mixture of perchloric acid in ethanol (1:4 in volume) under 1 A · cm⁻² and 5 °C for 1–2 min, (c) the Al foil surface after the first oxidation in 0.3 M oxalic acid aqueous solution electrolyte in the voltages of 35–40 V, (d) AAO surface after the second oxidation in the same condition of the first oxidation, the regular and intact shape pores on the surface of AAO. The pore diameter is approximately 65 nm (e) and 250 nm (f).
aluminum oxide with fine pore size control through a novel process can serve as effective and selective filtering materials for all kinds of particulate matters (1 \( \mu \)m, 2.5 \( \mu \)m, 4 \( \mu \)m, 10 \( \mu \)m).

2. Methods

2.1. Fabrication of anodic aluminum oxide

The AAO templates were fabricated by the two-step anodization process. The Al foils (99.997\% pure, Alfa-aesar) were first annealed at 500 °C for 4 h in vacuum tube. Then they were degreased in 5\% NaOH at 60 °C for 1 min, rinsed with deionized water. After that, the samples were electropolished in a mixture of perchloric acid in ethanol (1:4 in volume) under 1 A \( \cdot \) cm\(^{-2}\) and 5 °C for 1–2 min.

In order to acquire different interpore distances and pore diameters, the anodization was performed at 5 °C at different electrolytes and voltages (35–40 V in 0.3 M oxalic acid aqueous solution, 150 V in 0.1 M phosphoric acid aqueous solution). The first anodization, which was intended to create a guided substrate, lasted for 1 h, and then the anodic oxide layer was removed in a mixture of phosphoric acid (0.4 M) and chromic acid (0.2 M). The remained textured Al foils were anodized again as second anodization for 10–30 h under the same condition as the first anodization. The Al barrier layer and Al substrates were then removed in 1 M CuCl\(_2\) solution. The removal of the bottom part of the AAO templates and pore widening were performed in 5\% phosphoric acid at 40 °C for 0.5–1 h.

The morphology of the templates was examined by a Dual-beam electron microscopy (Helios NanoLab 660i, FEI).

2.2. Particulate matter filtration

The mass concentration of PM was measured by an aerosol monitor (Dusttrak Aerosol Monitor 8530, TSI). The monitor exhausts air continuously by an inner pump in a constant quantity of flow: 3 l min\(^{-1}\). Different cutting heads of monitor were used to retain certain diameter PM into inlet of monitor, so we can get the mass concentration of PM whose aerodynamic diameter is below 1 \( \mu \)m, 2.5 \( \mu \)m, 4 \( \mu \)m, 10 \( \mu \)m. Particulate matter filtration test was carried out with a home-built setup (a chamber in connect with the aerosol monitor). The produced AAO templates were cling to a piece of stainless steel wire for mechanical support. Both the AAO and stainless steel wire were stuck to two pieces of stainless steel circular ring with Polydimethylsiloxane (PDMS) as binder and sealant. The whole test component was heated at 100 °C for 1 h to solidify PDMS. The filtration

![Figure 3. SEM images of the AAO templates for filtration (a) 250 nm (b) 105 nm (c) 90 nm (d) 65 nm. The inset indicates the pore diameter distribution of each AAO.](image-url)
Figure 4. (a) The schematics of the entire test setup. (b) Mass concentrations of PM2.5 over time with one AAO template (105 nm pore diameter) put on the inlet opening. The filtration effect of AAO with mean pore size of (c) 65 nm, (d) 90 nm, (e) 105 nm. Each graph is divided into 8 groups by dash lines, representing the mass concentration of PM of chamber before and after filtration with the cutting head of 1 μm, 2.5 μm, 4 μm, 10 μm from left to right. (f) Mass concentrations of PM2.5 over time with and without AAO templates.
property of AAO (Puyuan Nano) templates whose mean pore diameter is approximately 55 nm, 90 nm, 130 nm were tested. The mass concentration of PM was monitored by an aerosol monitor. At first, we measured the mass concentration of PM1, PM2.5, PM4, and PM10 in the room to get the background concentration of room by using four types of cutting heads accordingly. Secondly, we connected the aerosol monitor to chamber to measure the mass concentration of PM of chamber mounted with AAO.

3. Results and discussion

The kinetic diameters of particulate matter are typically around a few microns, while the kinetic diameters of N2 and O2 are sub-nanometers [22]. Therefore, porous structures with pore size around a few hundred nanometers can allow efficient flow of N2 and O2, while blocking out most of particulate matter (figure 1(a)). It is noted that the mechanical strength of AAO is closely linked to its thickness. AAO with thickness between 60 μm and 90 μm are best fit for this type of experiment.

In the manufacture stage of AAO, two-step anodization process was used to obtain fine control of pores. The surface of alumina foil without any treatment is typically very rough (figure 2(a)). After the electropolishing process of alumina foil in a mixture of perchloric acid in ethanol, the roughness of the surface was significantly reduced, and also a large number of small pores were created (figure 2(b)). After the first oxidization, a series of pores were produced with irregular orders (figure 2(c)), and also the pore diameters have large distribution. The first oxidization layer was removed by a mixture of phosphoric acid and chromic acid. Most of the outer layer of the alumina substrate was reserved, which can be used as guided substrate for the second oxidization. Through the process of the second oxidization, both the pore size and the interpore diameter become more uniform (figure 2(d)). To get larger diameter pores, phosphoric acid was used to widen the pore size. Figures 2(e) and (f) are the AAO templates with 65 nm and 250 nm (figure 2(f)) accordingly.

As the pore size is critical for effective PM filtering, the AAO templates with different pore sizes are shown in figure 3. The pore size distributions of each AAO templates are plotted in the inset of each figure. In the filtration test, we chose a normal day with the mass concentration of PM2.5 around 25 μg m⁻³. The mass concentration of PM in chamber is kept to be the same as that in room for each test. As shown in figure 4(a), once AAO templates are put on top of the inlet opening, the mass concentration of PM in chamber gradually reduced to 1 μg m⁻³, which is the minimum detection limit of aerosol monitor. A series of AAO templates with different pore diameters 65 nm (figure 4(b)), 90 nm (figure 4(c)) and 105 nm (figure 4(d)) were tested in this work. Different cutting heads (1 μm, 2.5 μm, 4 μm, 10 μm) was used to monitor the change of mass concentration of PM. As the diameter of cutting head model set an upper limit for the allowing kinetic diameters of PM. The mass concentration number of PM in the chamber will increase as the diameter of cutting head increases. All the data points in different cutting heads and pore diameter of AAO show a consistent phenomenon: as long as the pore size of AAO templates are significantly smaller than the kinetic diameters of PM, AAO templates can effectively filter out most of PM, and the mass concentration can be reduced to 1 μg m⁻³, the detection limit of aerosol monitor. A long-term performance of the filter was taken by AAO templates with pore diameters around 250 nm, as shown in figure 4(f). After 24 h, the mass concentration of PM2.5 after filtering is maintained around 1–5 μg m⁻³, which shows a very good long term stability, feasible for practical applications. It is shown that the particulate matter ranged from 1 μm to 5 μm, sitting on the surface of AAO. (figure S1).

4. Conclusions

In conclusion, we have demonstrated for the first time that AAO templates with finely controlled pore sizes can serve as effective and selective filtering materials for different kinds of PM. This type of AAO templates, with finely controlled pore size, significant filtering effect, a scalable fabrication process and excellent stability, can serve as a promising and complementary filtering material to tackle the pressing air pollution issue.

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References

[2] Li N et al 2002 Ultrafine particulate pollutants induce oxidative stress and mitochondrial damage Environmental Health Perspectives 111 455–60
[22] Li J R, Kuppler R J and Zhou H C 2009 Selective gas adsorption and separation in metal-organic frameworks Chemical Society Reviews 38 1477–504