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Fabrication and characterization of chemically sensitive needle tips with aluminum oxide nanopores for pH indication

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Abstract

This paper presents aluminum rods and needle surfaces coated with anodic aluminum oxide (AAO) in order to absorb indicators. The submicron tips of the aluminum needles, produced by the electro-polishing method, were coated with AAO film by anodization. Due to the large surface area of the AAO, the film can absorb indicators to make it chemically sensitive to testing materials. When attaching with pH indicators of bromophenol blue and universal indicator, the AAO film allows sensitive pH detection of solutions and vapor changes. The AAO rods and needles can be used for precise measurement in biotechnology, convenient measurement in industrial engineering, and vapor detection in gas sensors. When AAO carrying bromophenol blue was tested in a dilute HCl solution of pH 2.0 and in DIwater, the color alternated between yellow and violet. When the AAO absorbed with universal indicator was tested in ammonia, water, and hydrochloric acid solutions, the color reversibly changed to green, gold, and red.

Keywords: Color; Needle tip; Anodic aluminum oxide; pH indicators

1. Introduction

Anodic aluminum oxide, also known as Al_2O_3 or AAO, is ceramic with a high melting point and high hardness. Anodic alumina is known by various names: anodic aluminum oxide (AAO) [1–5], anodic alumina nanoholds (AAN) [6], anodic alumina membrane (AAM) [7,8], or porous anodic alumina (PAA) [9]. The surface area of AAO can be computed based on structural parameters such as thickness (D), pore size (2R), pore density (ρ), and sample size (unit area). According to Chen's report [10], AAO has an ordered nano-structure arrangement. When aluminum is anodized in an acid electrolyte under suitable conditions, it forms a porous oxide called AAO with very uniform and parallel cell pores. Each cell contains an elongated cylindrical sub-micron, or nanopore, that is normal to the aluminum surface and extends from the surface of the oxide to the oxide/metal interface. Aluminum and AAO are sealed by a thin barrier oxide layer with approximately hemispherical geometry. The structure of AAO can be described as a closely packed array of columnar cells. Schematic diagrams of AAO are shown in Fig. 1. Fig. 1(a) shows a schematic diagram of AAO template on Al substrate and the barrier layer was between AAO and Al. The film width (H), length (L), thickness (D), and pore diameter (d) define the AAO structure. The pore diameter and pore density can be controlled by applied voltage, and the film thickness can be controlled by anodization time. Fig. 1(b), a side view of the AAO structure, shows an open pore on the top, a closed pore or barrier layer on the bottom, and the Al substrate under the AAO film. Each cell that is extending from the surface of the oxide to the oxide/metal interface contains an elongated cylindrical sub-micron or nanopore that is normal to the aluminum surface where it is sealed by a thin barrier oxide layer with approximate hemispherical geometry. The AAO surface area ($\pi h^2 \rho h$) increases with film thickness. A large AAO surface can serve as a host for chemical absorption. AAO is also an environmentalfriendly and biologically compatible material used in medical and biotechnology applications [11–14].

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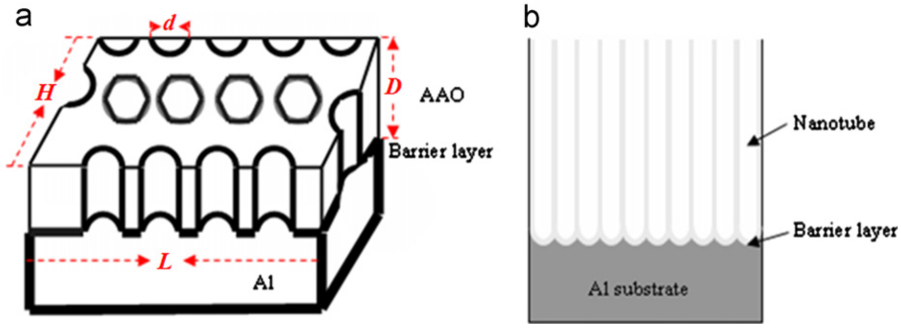

Fig. 1. schematic diagrams of AAO, including (a) barrier layer on AAO–Al interface, and *L, D, H, d* to define the AAO structure, (b) side view showing structure of Al_2O_3 film with nanotubes.

Bromophenol blue and universal indicators are two organic dyes commonly used for pH indication or the chemical stoplight demonstration. Bromophenol blue and universal indicator can dissolve in ethanol and slightly dissolve in water. The bromophenol blue indicator changes from yellow (pH 2) to violet (pH 7), but it decomposes in a strong basic solution and becomes transparent. Universal indicator is an ethanol solution containing 0.05 wt% of each of the following: methyl red, methyl yellow, thymol blue, and bromothymol blue. The working indicated that a range of universal indicator is from pH 4 to 10, but it decomposes in strong acidic and basic solutions. Universal indicator changes from red (pH 2), to green (pH 7), and to purple (pH 11) when the pH value goes from acidic to basic [15].

In this research, we grew AAO film on Al rods and needles and used the large surface area of AAO film to absorb pH indicators. Once the pH indicator was absorbed, the Al needle tip was sensitive to variations in pH. Al needles with indicator-absorbed AAO film can be used as precise measurement tips in biotechnology, physical, or chemical applications.

2. Material and methods

The 6061-T6 aluminum wire is 8 mm in diameter with a chemical composition of (wt%) 0.7 Si, 0.7 Fe, 0.1 Mn, 1.0 Mg, 0.4 Cu, 0.1 Cr, 0.25 Zn, 0.15 Ti, and balance Al. In Al wire/AAO process, 6061-T6 Al wire was anodized in 3wt% oxalic acid ($C_2H_2O_4$) electrolyte at 20 °C for 1hat 40 V using a platinum plate as the counter electrode. The random AAO pores were further improved to ordered pores by immersing the AAO sample in 6 vol% H_3PO_4 for 20 –45min at 20 °C.

Al needle tips with 1μm diameter were fabricated by electrolyte polishing. In order to obtain the Al tip, the Al wire was upside-down to the electrolyte for 3sec each period during electro-polishing. The tip diameter reduced as the electro-polishing time increased. The electro-polished condition was applied 15 V in a bath of 15 vol% perchloric acid ($HClO_4$), 70 vol% ethanol (C_2H_5OH), and 15 vol% butyl cellosolve ($CH_3(CH_2)_3OCH_2CH_2OH$) solution for 5min at 20 °C. Then the cleaned Al needle surface was anodized at 80 V using a platinum plate as the counter electrode in 1 vol% phosphoric acid (H_3PO_4) electrolyte at 2 °C for 30min, and AAO was formed by anodizing at 40 V in 3 wt% oxalic acid ($C_2H_2O_4$) electrolyte at 20 °C for 30min.

The topography of the AAO-coated rods and needle tips was observed using an FEI QUANTA 600 field emission scanning electron microscope. To coat the rods and needles with pH indicators, they were immersed in 0.05 wt% bromophenol blue or 0.05 wt% universal indicator for 5 minutes at room temperature. The sensitivity of the attached AAO was tested in HCl solutions of various concentrations, DIwater, and dilute NH_4OH solutions of various concentrations.

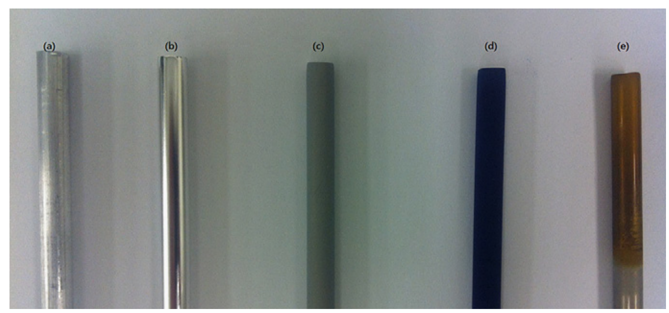

Fig. 2. Optical images of 6061-T6 Al wire surface characteristics.

3. Results and discussion

The macrosize of 6061-T6 Al with a surface coating of AAO and absorbed pH indicator is convenient for detection rods for acidic–basic testing. Fig. 2(a) shows the optical image of the raw surface of 6061-T6 Al wire, and Fig. 2(b) presents the bright and smooth Al surface after electro–polishing. In order to obtain a high quality AAO film on the Al surface, the Al rod must be electro-polished. Fig. 2(c) shows AAO film deposited on the surface via anodization, which offers a larger host surface area for the absorption of the chemical agent. Fig. 2(d) is an image of the rod carrying bromophenol blue and tested in pH 7.0 of DIwater. The rod turned violet. When the rod was further tested in dilute HCl solution with pH 2.0, it turned yellow

(Fig. 2e). In repeated testing of the rod in the pH 7.0 and 2.0 solutions, the color alternated between violet and yellow. At neutral pH, the bromophenol blue absorbed red light most strongly and transmitted blue light. Bromophenol blue solution therefore showed blue. At low pH, the bromophenol blue most strongly absorbed ultraviolet and blue light and appeared yellow in solution. The result showed the aluminum novel micron or sub-micron needle with nanotube film covered on the surface. This result expects to provide not only the tiny needle tip but also large needle surface area to significantly boost the achievable sensitivity of chemical tests.

Fig. 3(a) shows an optical microscope image of the Al needle tip formed by electro-polishing. Universal indicator has a wider pH detection range than that of bromophenol blue. Fig. 3(b) shows an optical image of AAO needles absorbed with universal indicator and tested in various solutions and vapors. Needle 1, covered by AAO film absorbed with universal indicator, was tested in a HCl solution (pH 2) and turned red. Needle 2 was tested in a pH 4.0 diluteHCl solution, and the color changed to orange. Needle 3 was immersed in pH 9.0 NH_4OH solution, and it turned green. Needle 4 turned gold after immersion in DI water, and Needle 5 turned blue when

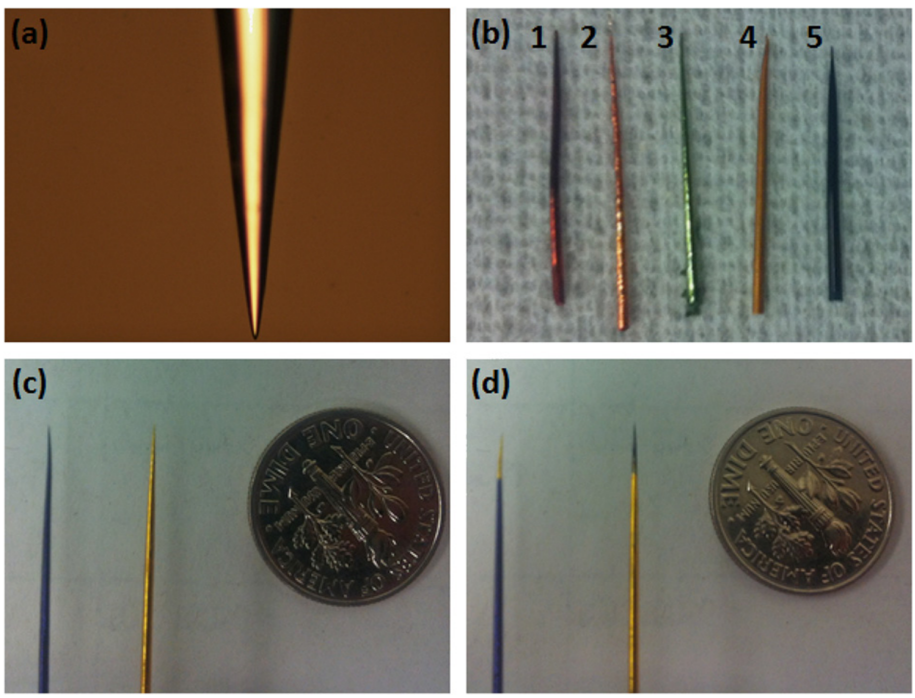

Fig. 3. Optical images of pure Al (99.99%) surface characteristics.

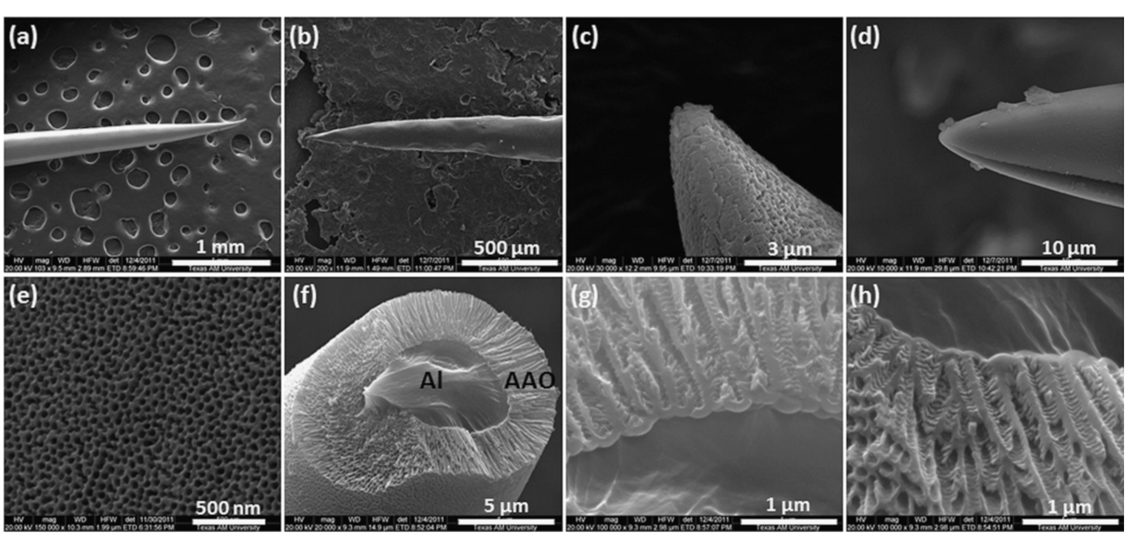

Fig. 4. SEM images of Al needle with AAO on the surface.

tested in 0.1 M NH_4OH solution. Fig. 3(c) shows needles with AAO film absorbed with bromophenol blue after immersion in DI water (violet) and 0.1 M HCl solution (gold). Fig. 3(d) shows that the tips changed color immediately upon contact with different solutions. The AAO needle tip is very sensitive to testing materials because the nanoporous structure of the tip provides an extremely large surface area for indicator absorption.

Fig. 4(a) is an SEM image of Al needles formed by electro-polishing. Because the current density was focused on the tip, the diameter of the tip was reduced to a sub-micron size during electro-polishing. Fig. 4(b) shows AAO formed on the needle tip via anodization in 1 vol% H_3PO_4 solution at 80 V for 30 min, and Fig. 4(c) is an enlarged image showing the nanopore structure of that AAO. Fig. 4(d) is an SEM image of AAO grown on the needle tip by anodization in oxalic acid solution at 40 V for 30 min, and Fig. 4(e) is an enlarged image showing the nano-pore structure of that AAO on the needle tip. The pore diameter of AAO is controlled from 10 to 500 nm by anodization in sulfuric acid, oxalic acid, and phosphoric acid electrolytes. The small pores and resultant large surface area of AAO act as a host for the second materials. Fig. 4(f) shows the structure of a broken needle, revealing the inner Al substrate and outer film of AAO template, which give the needle both toughness and hardness. Fig. 4(g) and (h) shows side view images of AAO, revealing the barrier layer on the bottom and isotropy of the cross-growth barrier layer, which provides the saw-tooth shape of the AAO pore wall. The ceramic property of the AAO tip also makes the Al needle harder and stronger for contact with test samples.

For future applications, a denser sub-micron needle array can be achieved. For example, a 1 cm^2 transdermal patch, that includes 10,000 needles with sub-micron tip and 500 μm length, is able to be fabricated. An ultra-sharp sub-micron needle array can easily overcome the barrier of the skin's outer layer and achieve painless injection. A large surface area and dense needle array of nanotube film can also store more capacity of drug.

4. Conclusions

In this paper, we present a convenient and cheap method to fabricate pH sensitive rod and needle detectors by electropolishing and anodization processes. The rod and needle surfaces are covered with AAO, which have a large surface area, so they can quickly absorb pH indicators. The rods and needles, when absorbed with pH indicators, can be used for chemical or biological detection. The AAO film can also be grown on specific needles by Al deposition and anodization processes. Furthermore, such needles can also be used with thermal and hydrophilic–hydrophobic sensitive film, e.g., poly (N-isopropylacrylamide, PNIPAM), to develop an accurate tip for drug detection and release. Our research clearly suggests that needle tips covered with nanopore films of TiO_2, WO_3, Ta_2O_5, or MoO_3 can also be formed by electropolishing and anodization processes.

Acknowledgements

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