Research Article

A Three-Dimensional Enormous Surface Area Aluminum Microneedle Array with Nanoporous Structure

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We proposed fabricating an aluminum microneedle array with a nanochannel structure on the surface by combining micromachining, electrolyte polishing, and anodization methods. The microneedle array provides a three-dimensional (3D) structure that possesses several hundred times more surface area than a traditional nanochannel template. Therefore, the microneedle array can potentially be used in many technology applications. This 3D microneedle array device can not only be used for painless injection or extraction, but also for storage, highly sensitive detection, drug delivery, and microelectrodes. From the calculation we made, the microneedle array not only increases surface area, but also enlarges the capacity of the device. Therefore, the microneedle array can further be used on many detecting, storing, or drug delivering applications.

1. Introduction

Puncturing the human skin with a needle or a patch is the most common invasive medical procedure to deliver or extract fluids from the human body. During the past few years, developing painless needles or patches to replace the traditional hypodermic needles has been investigated [1–3]. The mosquito's proboscis should be a good model for painless insertion. Up to 1.5 mm penetration depth can be painless [4]. The type of drug release needle offers the advantages of convenience inset in the skin, high surface area for drug absorption, easy to control the period of drug release by temperature, and high resolution and quick of detection when the needle with indicator absorption. Because of a fast switching time and high quantity of the drugs, this needle could be used for emergency therapy, which requires acute and on-demand drug delivery [5–7].

Silicon has been processed to make microneedles and microneedle arrays by conducting micromachining or photolithography technology. This microneedle array, with a needle length of 0.15 mm, diameter of 80 μm at the base and a tip radius of 1 μm, can be a painless device for injection or extraction [8]. However, crystal silicon anisotropy limits the sharpness of the microneedle, and micromachining of silicon is costly and complex. Thus, we propose aluminum as an alternative material for fabricating microneedles or arrays of microneedles. The micromachining technique is able to construct a high-density micropillar array on aluminum. In addition, we fabricated a very sharp AAO needle with 1 μm diameter by electrolyte polishing in previous work [9]. A nanochannel structure of anodic aluminum oxide that has controllable pore sizes from 10 nm to 500 nm, pore density from $10^7$ to $10^{10}$ pore $\cdot$ cm$^{-2}$, and tube length from 0.1 μm to 30 μm [10–13].

Aluminum anodization is probably the most controllable self-assembly processes at lower cost. The anodized aluminum oxide (AAO) possesses unique features, such as high aspect ratio, uniform pore size, high surface area, and high structural ordering degrees. The AAO template has been used for one-dimensional organic nanostructures, nanowires, and solar cell applications [14–16]. Unlike microstructures made of glass, metal, silicon which may fracture, or polymeric which may bend the toughness aluminum/anodic aluminum oxide (Al/AAO) microneedle array do not break or bend.
under extreme force. Therefore, a more dense and sub-micron needle array can be achieved. A large surface area and dense needle array of nanotube film which can also carry more drug capacity. In this research, we have developed a novel electrochemical processes investigation and fabrication a tiny needle array and nanotube film under ambient conditions, thereby enabling low-cost and mass production of the needle array.

2. Experimental Procedures

The aluminum micropillar array was fabricated by micro-machining process using diamond blade on an aluminum piece (99.99% purity) with 10 mm thickness. There were 20 cuts in each direction (x and y), and the distance between two pillars were 500 um and the depth was 5 mm. The sharpening process was conducted by electrochemical polishing. The aluminum pillar array was electropolished at 15 V, in a bath of 15 vol.% perchloric acid (HClO₄), 70 vol.% ethanol (C₂H₅OH), and 15 vol.% butyl cellosolve (CH₃(CH₂)₂OCH₂CH₂OH) solution at 20°C for 5 min. Then the aluminum needle array was anodized at 80 V using a platinum plate as the counter electrode in 1 vol.% phosphoric acid (H₃PO₄) electrolyte at 2°C for 30 minutes, or at 40 V in 3 wt.% oxalic acid (C₂H₂O₄) electrolyte at 20°C for 30 minutes. After anodization, a 3D microneedle array structure with large AAO surface area can be formed. Figure 3 shows the scheme of the aluminum needle array. The topography of the AAO-coated needle array was observed using an FEI QUANTA 600 field emission scanning electron microscope.

3. Results and Discussion

Anodic aluminum oxide, also known as Al₂O₃ or AAO, is a ceramic with a high melting point and great hardness. AAO is also an environmentally friendly and biologically compatible material used in medical and biotechnology applications. Figure 1 shows a schematic diagram of the AAO template on an aluminum substrate; (a) AAO structure with aluminum substrate and barrier layer, (b) AAO side view with straight channels, and (c) ordering nanopores arrangement on the AAO film. The pore diameter and pore density can be controlled by applied voltage, and the film thickness can be controlled by anodization time. Figure 1(b), a side view of the AAO structure, shows an open pore on the top, a closed end or barrier layer on the bottom, and an aluminum substrate under the AAO film.

The AAO surface area can be calculated based on structural parameters such as thickness (D), pore size (2r), pore density (ρ), and sample size (unit area). The AAO surface area (2πρrD) increases with film thickness. If AAO pores are ordering closed packaging arrange the AAO with pore diameters of 15 nm, 60 nm, and 500 nm, the pore density can be computed as 2.6 × 10¹¹, 1.5 × 10¹⁰, and 1.5 × 10⁸ pore/cm². Figure 2 showed the AAO surface area and SEM images, (a) evaluated curves of AAO surface area based on a 1 cm² substrate, (b) AAO with 15 nm pore size, (c) AAO with 60 nm pore size, and (d) AAO with 500 nm pore size. For example, when AAO thickness is 20 μm, the pore surface areas are 2150 cm², 537 cm², and 64 cm² for diameters of 15 nm, 60 nm, and 500 nm, respectively.

When the aluminum column was electropolished, the column end surface has greater electrical field than the side surface of column. Therefore, the column end can be polished to a tip. Figure 3 showed the schematic diagram of aluminum needle formation. Figure 3(a) showed aluminum column formation by mechanical cutting. The number of columns and dimension were controlled by the diamond blade. For example, in this research, there were 400 aluminum columns formed by 20 cuts in each direction (x and y) and the distance between two pillars was 500 um and the depth was 5 mm. Based on electrical field characteristic that the column tip has a larger current density compared to the column side.
Figure 2: The AAO surface area and SEM images; (a) evaluated curves of AAO surface area based on a 1 cm$^2$ substrate, (b) AAO with 15 nm pore size, (c) AAO with 60 nm pore size, and (d) AAO with 500 nm pore size.

Figure 3: The schematic diagram of aluminum needle formation; (a) aluminum column formation by mechanical cutting, (b), (c) trapezoid-shaped formation by a short time of electropolishing, (d) needle-shaped formation by a long time of electropolishing. The tip size decreased with electropolishing time increased. Figures 3(b) and 3(c) showed a trapezoid-shaped formation by a short time of electropolishing, and Figure 3(d) showed a needle-shaped formation by a long time of electropolishing. The schematic diagrams of 3D aluminum array of (a) aluminum array columns formation by mechanical cutting, (b) aluminum array needles formation by electroolishing were showed in Figure 4. And, Figure 5 showed SEM images of (a) aluminum array columns formation by mechanical cutting, (b) aluminum array needles formation by electroolishing on a 10 mm thickness aluminum sheet. Figure 6 showed SEM images of (a) aluminum needle with 3.2 μm tip diameter after
Figure 4: The schematic diagrams of aluminum array, (a) aluminum array columns formation by mechanical cutting, (b) aluminum array needles formation by electroolishing.

Figure 5: The SEM images of aluminum array, (a) aluminum array columns formation by mechanical cutting, (b) aluminum array needles formation by electroolishing.

There were some wider tips because aluminum is soft and easy to break. Figure 7(a) showed the SEM image of the microneedle covered by an AAO film. The surface area of the microneedle array became much larger after anodization. Furthermore, anodizing the aluminum needles not only increases the surface area, but also enhances the mechanical strength. The ceramic property of the AAO tips also makes the microneedle array harder and stronger for contact or attachment with test samples. Figure 7(b) showed the SEM image of the nanoporous structure on the microneedle array. The pore diameter is about 60 nm, and the pore density is $10^{10}$/cm$^2$.

The surface area of a single microneedle is $\pi R L$ ($L$ is the length of the microneedle, and $R$ is the pillar radius). There were 400 microneedles surface area more than a 2D AAO structure. For the microneedle with 5 mm length and 0.3 mm bottom diameter, the surface area of the microneedle array can be calculated as 10 cm$^2$ in a 1 cm $\times$ 1 cm sample. Comparing this AAO microneedle array with 2D AAO plate, the surface area increased 10 times. Therefore, the aluminum microneedle array has 10 times more surface area for forming AAO than an aluminum sheet.

The capacity of the painless microneedle array can be calculated from the surface area of the painless microneedle tip. According to Khumpuang et al. report [4], 1.5 mm depth and 100 um diameter can be painless. Thus, the aluminum pillars can be sharpened by electropolishing to obtain 5 mm length and 300 um bottom diameter microneedles as mentioned above. The upper 1.5 mm part of microneedle has 75 um diameter, so the total surface area for 400 microneedles is 1.41 cm$^2$. Then, the aluminum microneedle tip can be anodized to form AAO nanotubes with 5 um length, 60 nm diameter, and $10^{10}$/cm$^2$ pores density. Hence, the capacity ($C$) of the microneedle array can be calculated as $2 \times 10^{-4}$ cm$^3$ in a 1 cm $\times$ 1 cm sample by $C = A \times \rho \times \pi \times r^2 \times D$, where $A$ is the total surface area for the 400 microneedle tips, $\rho$ is the pore density, $r$ is the pore size, and $D$ is the thickness of AAO nanochannel.

4. Conclusions
In this paper, we present a convenient and cheap method to fabricate a large surface area 3D microneedle array by micromachining, electrolyte polishing, and anodizing processes. The microneedles are covered by an AAO film, which
Figure 6: The SEM images of aluminum needle tips; aluminum needle (a) with 3.2 μm tip diameter after 60 sec electropolishing and (b) with 0.8 μm tip diameter after 90 sec electropolishing.

Figure 7: The SEM images of (a) nanopores formation on the aluminum needle by anodization and (b) pore sizes are less than 100 nm.

has a large surface area, so they can enlarge the surface area and capacity and enhance the mechanical properties as well. The aluminum microneedle array, which is able to absorb with detecting indicators, can be used for chemical or biological detection. It can also be applied to drug delivery or storage applications because it can approach painless injection/extraction and high capacity. Furthermore, such needles can also be used with thermal and hydrophilic-hydrophobic sensitive film, for example, poly (N-isopropylacrylamide, PNIPAM), to develop an accurate device for drug detection and release. Our results clearly provide a concept that the microneedle covered with nanopore films such as TiO$_2$, WO$_3$, Ta$_2$O$_5$, or MoO$_3$ can also be formed by micromachining, electropolishing, and anodization processes.

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