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Fabrication of superhydrophobic niobium pentoxide thin films by anodization

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ABSTRACT

We report a simple method to fabricate a niobium oxide film with a lotus-like micro–nano surface structure. Self-assembled niobium pentoxide (Nb_2O_5) films with superhydrophobic property were fabricated by an anodization and a hydrophobic treatment. This process has several advantages such as low cost, simplicity and easy coverage of a large area. The surface of fabricated Nb_2O_5 film was changed from hydrophilic to superhydrophobic surface by a treatment using fluoroaldyltrimethoxysilane (FAS) solution. This value is considered to be the lowest surface free energy of any solid, based on the alignment of —CF_3 groups on the surface. In particular, among FAS coated surfaces, the micro–nano complex cone structured Nb_2O_5 film showed the highest water-repellent property with a static contact angle of ca. 162°. This study gives promising routes from biomimetic superhydrophobic surfaces.

1. Introduction

Niobium is one of rare metals and a transition metal with the properties of ductility and high temperature oxidation-resistance. And Nb_2O_5 has been essentially used for catalyst and new materials such as high alloy steel, superconductor, medical equipment because Nb_2O_5 presents superconductivity below particular critical temperature and there is no allergy to human body [1,2].

In addition, Niobium oxide has been used for several applications of dielectric, capacitor, catalyst, biosensor and solar cell because it has a wide energy band gap and stable electrical property [3–8].

Recently, the extensive studies have been reported to mimic a functional surface in nature. Especially, the surface structure of lotus leaf is a suitable example to fabricate a superhydrophobic surface between liquid and a solid surface [9,10].

Basically, the wettability of material surface is determined by surface energy and changed by controlling the microstructure of surface with micro–nano complex structure.

Superhydrophobic surface with water contact angle of over 150° are fabricated by creating a rough structure on a substrate and modifying the rough surface by fluorinated or silicon compounds with a low surface free energy [11–16].

To modify a rough surface, fluoroalkyltrimethoxysilane (FAS, $CF_3(CF_2)_7CH_2CH_2Si(OCH_3)_3$) has been widely used because FAS has a fluoromethyl (—CF_3) group with a very low surface energy (~8 mJ/m^2) to modify a solid surface [17,18]. This phenomenon is also showed on the surface of the wing of butterfly, the leg of water strider, the toe of gecko [10].

An anodization method has been employed to fabricate various nano-structures by controlling an applied voltage, temperature and electrolytes [19–21].

To fabricate a superhydrophobic surface on an aluminum substrate, a micro–nano structure is formed on the surface of aluminum by an anodization and, then the surface are modified by silane coupling agents with fluoroalkyl groups [22,23].

Niobium has been used for fabricating a porous nano-structure as well as a microcone structure by controlling the parameters of an anodization method. However, there is no report to control the reaction of solution on the nano-structure surface of niobium.

In this study, we fabricated a niobium nano-structure formed with the shape of nanorods and microcone and, then superhydrophobic treatment was carried out on the surface of niobium oxide [24–25]. The effects of the size, roughness, and contact angle of microcone structure on the hydrophobic property of surface were studied as a function of anodization parameters.

2. Experimental procedure

Ni foil with a thickness of 0.25 mm and a purity of 99.9% was obtained from Goodfellow. Ni foils were ultrasonically agitated in

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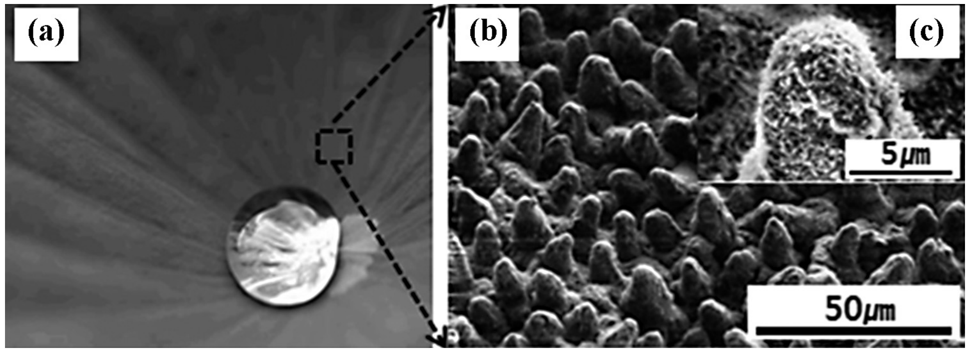

Fig. 1. SEM images of a lotus leaf: (a) extraordinary water repellency on an upper side of leaf, (b) image of the upper leaf with a micro-sized cone structure and (c) nano-structure surface of a micro-sized cone.

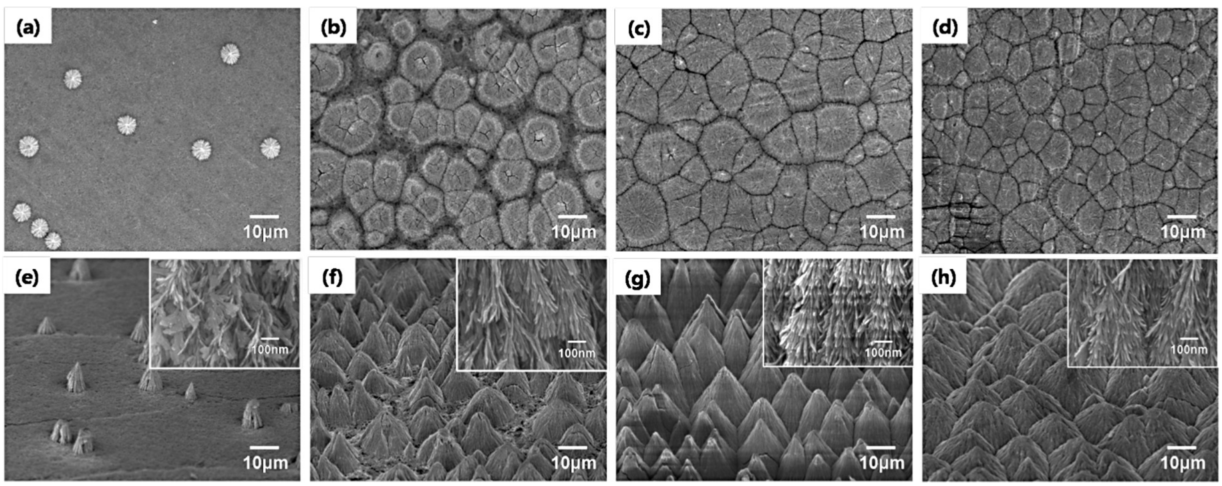

Fig. 2. SEM images of microcone Nb_2O_5 prepared in 0.5 M NaF + 1.5 wt% HF electrolyte for 1 h at various voltage: (a and e) 20 V, (b and f) 30 V, (c and g) 40 V, (d and h) 50 V (a–d: top-view and e–h: cross-sectional view).

acetone solution and dried with a stream of N_2 gas. Anodization was carried out by applying voltage on a Pt mesh as the counter electrode and a Ni foil as the working electrode. During the anodization, 0.5 M NaF mixed with a little of HF solution was used as a electrolyte for 1 h and the range of applied voltage was from 10 V to 50 V. Anodized niobium oxide foil was immersed in a FAS solution (3.0 wt.%) in hexane for 1 h to fabricate a superhydrophobic surface.

The microstructure and the surface roughness of a superhydrophobic Nb_2O_5 thin film was measured by a field emission scanning electron microscopy (FE-SEM, JSM-6700F, JEOL) and a dektak (Veeco).

The crystal structure of N_2O_5 thin film was measured by an X-ray diffraction (XRD, Rigaku D/max-RB apparatus, Tokyo, Japan). X-ray photoelectron spectroscopy (XPS, PHI 5000 Versaprobe, ULVAC-PHI) was used to measure the presence of fluorine (F) components of the Nb_2O_5 thin film after a FAS surface treatment.

The wettability of the Nb_2O_5 thin film was characterized by measuring a water contact angle (Easy Drop, KRUSS). The volume of the distilled water droplet for measuring the contact angle was 1.0 μl.

3. Results and discussion

As shown in Fig. 1, lotus leaves show a superhydrophobic surface with over a water contact angle of 150° because the micro–nano complex structure are formed on the surface of leaves and a hydrophobic wax with low surface free energy is coated on the outmost surface of leaf. Therefore, to obtain a superhydrophobic Nb_2O_5 thin film, we first anodized niobium foil to fabricate micro–nano complex structure on a surface of foil.

Fig. 2 shows the surface structures of anodized niobium oxide foils with micro-corn structure as a function of various applied voltage. Complex electrolyte mixed with 0.5 M NaF and 1.5 wt% HF

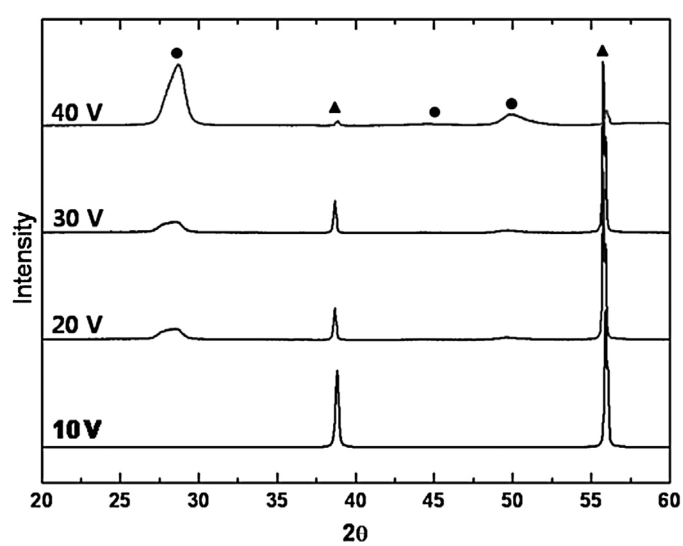

Fig. 3. All diffraction spots could be indexed onto Nb_2O_5 with an orthorhombic structure (JCPDS 30-0873). Note that the symbols represent the following phase: circle, orthorhombic Nb_2O_5 and triangle, Nb peak.