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1 Facile preparation of self-healing superhydrophobic CeO<sub>2</sub> surface  
2 by electrochemical processes

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## 1 Highlights

- 2 • The CeO<sub>2</sub>-coating is formed on Type 304 stainless steel by anodic deposition.
- 3 • The hydrophilic CeO<sub>2</sub> surface is transformed to hydrophobic during air exposure.
- 4 • Superhydrophobic CeO<sub>2</sub> surface is obtained on hierarchically rough substrate.
- 5 • Superhydrophobic CeO<sub>2</sub> surface shows self-healing property.

## 7 Abstract

8       Herein we report simple electrochemical processes to fabricate a self-healing  
9 superhydrophobic CeO<sub>2</sub> coating on Type 304 stainless steel. The CeO<sub>2</sub> surface  
10 anodically deposited on flat stainless steel surface is hydrophilic, although high  
11 temperature-sintered and sputter-deposited CeO<sub>2</sub> surface was reported to be  
12 hydrophobic. The anodically deposited hydrophilic CeO<sub>2</sub> surface is transformed to  
13 hydrophobic during air exposure. Specific accumulation of contaminant hydrocarbon on  
14 the CeO<sub>2</sub> surface is responsible for the transformation to hydrophobic state. The  
15 deposition of CeO<sub>2</sub> on hierarchically rough stainless steel surface produces  
16 superhydrophobic CeO<sub>2</sub> surface, which also shows self-healing ability; the surface  
17 changes to superhydrophilic after oxygen plasma treatment but superhydrophobic state  
18 is recovered repeatedly by air exposure. This work provides a facile method for  
19 preparing a self-healing superhydrophobic surface using practical electrochemical  
20 processes.

21

22 Keywords: CeO<sub>2</sub> coating; superhydrophobicity; anodic deposition; self-healing ability

1

2

### 3 1. Introduction

4 Superhydrophobic solid materials have attracted much attention because of  
5 several superior functional properties including self-cleaning, anti-corrosion,  
6 anti-freezing and anti-biofouling [1-4]. Many natural surfaces, including lotus leaves,  
7 water strider legs and morpno butterfly wings, are superhydrophobic [5-9].  
8 Superhydrophobicity of these surfaces is originating from peculiar microscopic  
9 geometrical surface morphology. For example, lotus leaves consist of numbers of  
10 micrometer-size asperities covered by nano-fibrous hydrophobic wax, resulting in  
11 superhydrophobicity [5, 6]. Superhydrophobic surface is usually defined to show a  
12 static contact angle for a water droplet greater than  $150^\circ$  and a low contact angle  
13 hysteresis (the difference between the advancing and receding contact angles) of  $<10^\circ$ .  
14 Inspired by nature, many artificial superhydrophobic materials have been developed  
15 [9-19], since Onda et al. reported a first example of artificial superhydrophobic fractal  
16 surface in 1996 [9].

17 In addition to the high roughness with fractal or hierarchical surface geometry,  
18 the surface must be composed of materials with low surface energy for  
19 superhydrophobicity. Thin organic coatings, including self-assembled fluoroalkyl  
20 monolayers, have been often introduced on rough metallic or inorganic substrates.  
21 However, such superhydrophobic surfaces have low durability because of mechanical

1 instability of thin organic coatings and highly rough hierarchical surfaces. Improved  
2 durability of superhydrophobic surfaces is awaited for practical application.

3           Recently, Azimi et al. reported that rare-earth oxide (REO) surfaces show  
4 thermally stable hydrophobicity up to 1000°C without any organic coating due to their  
5 unique electronic structure [20]. They demonstrated that water droplets bounce on the  
6 surface of REO films formed by magnetron sputtering on silicon wafer. Moreover, they  
7 also revealed that REOs become superhydrophobic with textured morphology. These  
8 inorganic REOs are thermally and mechanically more stable compared to organic  
9 materials, promising as a novel durable hydrophobic coating. Therefore, hydrophobic  
10 REOs are of recent interest [21-24]. Most reports preparing hydrophobic REO coatings  
11 utilized dry processes such as sputtering [21] or atomic layer deposition [24].  
12 Electrochemical deposition process is a simple, cost-effective and more practical  
13 method for oxide coatings [25]. This process also allows us to form a uniform oxide  
14 layer on rough and even porous substrates, suitable for fabrication of hierarchically  
15 rough superhydrophobic surfaces.

16           In the present study, the CeO<sub>2</sub> coating was prepared by anodic deposition on flat  
17 and hierarchically rough stainless steel surface. The rough stainless steel surface was  
18 prepared by electrochemical etching. The surface wettability for water was evaluated by  
19 measuring static and dynamic contact angles. The CeO<sub>2</sub> surface immediately after  
20 deposition was hydrophilic, but transformed to hydrophobic during air exposure. The  
21 self-healing properties of the hydrophilic surface was also examined in the present  
22 study.

1

## 2 2. Experimental

### 3 2.1 Specimen preparation

4       Type 304 stainless steel plates or meshes (with 300, 500, 640 and 795 mesh)  
5 composed of 17–19 wt.% Cr, 8–11 wt.% Ni, < 2 wt.% Mn, < 1 wt.% Si and Fe balance  
6 were used as substrate in this study. Prior to electrochemical etching and anodic  
7 deposition, the plate substrate was electropolished in solution containing HClO<sub>4</sub> and  
8 ethylene glycol (1:9 v/v) at 20 V for 5 min below 283 K. Electrochemical etching of the  
9 plate was performed in solution containing 1.2 wt% HNO<sub>3</sub> and 3.6 wt% HCl at a  
10 constant current density of 1 A cm<sup>-2</sup> for 200 s at 313 K [26]. For mesh specimens,  
11 etching was conducted at 1 A cm<sup>-2</sup> for 1 min in order to prevent excess etching of  
12 specimens. Anodic deposition was carried out at a constant current density of 1 A cm<sup>-2</sup>  
13 in solution containing 0.01 mol dm<sup>-3</sup> Ce(NO<sub>3</sub>)<sub>3</sub> and 0.05 mol dm<sup>-3</sup>  
14 hexamethylenetetramine (pH 6.7) for 60 min at 333 K. The rather low concentration of  
15 Ce(NO<sub>3</sub>)<sub>3</sub> was selected to form a thin coating to maintain the textured morphology  
16 developed by electrochemical etching. A two-electrode cell with a Type 304 stainless  
17 steel counter electrode was used for anodic deposition. For comparison, we also  
18 prepared a barrier-type anodic alumina film on aluminum plate (99.999% purity). Prior  
19 to anodizing, an aluminum plate was electropolished in solution containing HClO<sub>4</sub> and  
20 ethanol (1:4, v/v) at a constant voltage of 20 V for 5 min below 278 K. Then, the  
21 specimen was anodized in 0.1 mol dm<sup>-3</sup> ammonium pentaborate ((NH<sub>4</sub>)<sub>2</sub>B<sub>10</sub>O<sub>16</sub>) at a  
22 constant current density of 5 mA cm<sup>-2</sup> up to 200 V at 293 K, using a two-electrode cell

1 with a platinum counter electrode. The alumina surface thus prepared was smooth and  
2 flat, as reported previously [27].

## 3 4 2.2 Characterizations

5 The surface and cross-section of the specimens were observed by a JEOL  
6 JSM-6500F field emission scanning electron microscope (SEM) and a JEOL  
7 JEM-2000FX transmission electron microscope (TEM) with EDS facilities, respectively.  
8 The cross-sectional specimen was prepared by focused gallium ion beam processing  
9 with a JEOL JIB-4600F/HKD multibeam system. Surface roughness was also evaluated  
10 using a KEYENCE VK09700 laser microscope. Phases in the anodically deposited  
11 CeO<sub>2</sub> layer formed on the stainless steel surface were identified by X-ray diffraction  
12 using a Rigaku RINT-2000 diffractometer with Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm). An  
13  $\alpha$ -2 $\theta$  scan mode with  $\alpha = 1^\circ$  was used in this study. Elemental depth profile analysis  
14 was carried out by glow discharge optical emission spectroscopy (GDOES) using a  
15 Jobin-Yvon 5000 RF instrument in an argon atmosphere of 700 Pa by applying a power  
16 of 30 W. Light emissions of characteristic wavelength were monitored throughout the  
17 analysis with a sampling time of 0.01 s to obtain depth profile. The wavelength of the  
18 spectral lines used were 413.717 nm for cerium, 130.217 nm for oxygen, 385.991 nm  
19 for iron, 425.433 nm for chromium, 341.477 nm for nickel and 165.701 nm for carbon.  
20 The signals were detected from a circular area of approximately 4 mm diameter. The  
21 X-ray photoelectron spectra of the anodically deposited CeO<sub>2</sub> and anodic alumina  
22 surfaces after air exposure for 1, 7 and 12 h in a laboratory atmosphere were measured

1 using a JEOL JPS-9200 spectroscope with Mg K $\alpha$  excitation ( $h\nu = 1253.6$  eV). Binding  
2 energies of the photoelectrons were calibrated with a contaminant carbon peak energy  
3 (285.0 eV).

4

### 5 2.3 Wettability evaluation.

6 Surface wettability was evaluated by static and dynamic contact angle  
7 measurements for water droplet (4  $\mu$ L) on specimen surfaces by a Kyowa Interface  
8 Science DM-CE1 contact angle measurement system after air exposure for various  
9 periods of time in a laboratory atmosphere. Dynamic contact angle measurements were  
10 performed by an expansion and contraction method. Contact angle values used in this  
11 study were average data of five different points on each specimen.

12 For examination of the self-healing hydrophobicity, oxygen plasma was irradiated  
13 for 4 min using a Harrick Plasma PDC-32G air plasma cleaner to the hydrophobic CeO<sub>2</sub>  
14 surface specimen in order to decompose organic contaminants on the surface. Then,  
15 water contact angle (WCA) was monitored during subsequent air exposure. This  
16 process was repeated several times.

17

## 18 3. Results and discussion

### 19 3.1 CeO<sub>2</sub> coating on stainless steel plate

20 Figures 1a and 1b show SEM micrographs of the surface of the electropolished  
21 stainless steel plate after anodic deposition of CeO<sub>2</sub>. The surface appears rather smooth  
22 at low magnification (Fig. 1a), while high magnification micrograph (Fig. 1b) discloses



1 that the coating consists of densely packed nanoparticles with 10-15 nm in diameter. In  
2 Fig. 1a, microcracks are also found in the coating, probably associated with the  
3 shrinkage of the coating, which is caused by dehydration of the anodically deposited  
4 coating during drying [28]. Kulp et al. deposited anodically CeO<sub>2</sub> at 0.5 and 1.1 V vs  
5 Ag/AgCl in Ce(III) acetate solution [29]. They obtained a smooth and crack-free film at  
6 0.5 V vs Ag/AgCl, while a film formed at 1.1 V vs Ag/AgCl contained nanoparticles.  
7 They suggested that the nanoparticles were formed because of indirect oxidation of  
8 Ce(III) with O<sub>2</sub>, which was generated by electrochemical oxidation of water. The  
9 presence of nanoparticles in the present coating suggests such indirect mechanism of the  
10 formation of CeO<sub>2</sub>. In fact, we found gas generation on anode during anodic deposition.

11 TEM observation of the coating cross-section (Fig. 1c) reveals that the coating is  
12 approximately 60 nm thick and uniform in thickness. EDX analysis of the marked  
13 region in Fig. 1c indicated the atomic ratio of Ce:O close to 1:2, corresponding to the  
14 composition of CeO<sub>2</sub>. Figure 2 shows the X-ray diffraction pattern and GDOES  
15 elemental depth profile of the anodically deposited CeO<sub>2</sub> on the electropolished stainless  
16 steel plate. Only a CeO<sub>2</sub> phase (JCPDS card 34-0394) is identified from the X-ray  
17 diffraction pattern, apart from the reflections from the stainless steel substrate (Fig. 2a).  
18 The species (Fe, Ni and Cr) derived from the stainless steel substrate are not detected  
19 within the coating in the GDOES elemental depth profile analysis (Fig. 2b). Thus, rather  
20 pure CeO<sub>2</sub> is deposited on the stainless steel, although, from the depth profile, hydrogen  
21 and carbon impurity species appear to be slightly incorporated in the coating. The

1 incorporated carbon species may be derived from hexamethylenetetramine added in the  
2 coating solution.

3 Then, the wettability of the CeO<sub>2</sub>-coated specimen was examined by static  
4 contact angle measurements. Figure 3 shows the WCAs and optical photographs of  
5 water droplets on the surfaces of the CeO<sub>2</sub> coating on electropolished stainless steel and  
6 the flat alumina film formed by anodizing of aluminum as a function of air exposure  
7 time. The WCA of the CeO<sub>2</sub> coating on the flat stainless steel is only 20° immediately  
8 after deposition; the anodically deposited CeO<sub>2</sub> is hydrophilic. This is contrast to the  
9 hydrophobicity of the magnetron-sputtered CeO<sub>2</sub> surface [20]. However, the WCA  
10 gradually increases with time of air exposure and reaches ~104° after three days. This  
11 means that the CeO<sub>2</sub> surface changes from hydrophilic to hydrophobic during air  
12 exposure. On the other hand, the WCA on the alumina surface remained hydrophilic  
13 even after three days.

14 In order to examine the change in composition of the CeO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> surface  
15 during air exposure, XPS surface analysis was performed. Figures 4a-c show the Ce 3d,  
16 O 1s and C 1s photoelectron spectra of the CeO<sub>2</sub> surface. The Ce 3d spectra in Fig. 4a  
17 are composed of two multiplets (i.e., v and u), which correspond to the spin orbit split  
18 3d<sub>5/2</sub> and 3d<sub>3/2</sub>, respectively. In accord with previous reports [30-34], the v, v'', v''', u,  
19 u'' and u''' peaks are attributed to Ce<sup>4+</sup> state, while the v' and u' peaks are assigned to  
20 Ce<sup>3+</sup> state. The intensity of all the Ce 3d peaks slightly decreases with time of air  
21 exposure. This is because of covering coating surface by hydrocarbon contaminants, as  
22 described below.

1           The O 1s spectra reveal two peaks at 529.5 eV and 531.4 eV; the former is  
2 assigned to Ce-O-Ce and the latter to -OH/H<sub>2</sub>O oxygen, defective oxide or carbonate  
3 oxygen [30, 35, 36]. The presence of surface -OH/H<sub>2</sub>O species probably make the  
4 surface hydrophilic. During air exposure, the intensity of -OH/H<sub>2</sub>O peak decreases  
5 slightly. The most significant change in the spectra was found in C 1s spectra during air  
6 exposure. The contaminant hydrocarbon peak at 285.0 eV becomes intense largely  
7 during air exposure, indicating the accumulation of hydrocarbon layer on the CeO<sub>2</sub>  
8 surface. A small peak at 289.0 eV is assigned to carboxyl or carbonate species [37, 38],  
9 whose intensity remains almost unchanged during air exposure.

10           The change in the XPS spectra of the Al<sub>2</sub>O<sub>3</sub> surface during air exposure was also  
11 examined (Figs. 4d-f). The Al 2p spectra shows a peak at 74.3 eV, corresponding to  
12 Al<sup>3+</sup> state [39]. A broad O 1s peak is owing to overlapping of Al-O-Al (530.9 eV) and  
13 OH/H<sub>2</sub>O (531.8 eV) peaks. The intensity of the C 1s hydrocarbon peak (285.0 eV)  
14 increases with air exposure, but the increase in the intensity for Al<sub>2</sub>O<sub>3</sub> surface is much  
15 less than that on the CeO<sub>2</sub> surface. As a consequence, only CeO<sub>2</sub> surface changes from  
16 hydrophilic to hydrophobic during air exposure.

17           Preston et al. reported the hydrophobicity of a CeO<sub>2</sub> pellet after air exposure for  
18 long time, similar to this study [23]. According to their report, a hydrophilic CeO<sub>2</sub> pellet  
19 surface conversed to hydrophobic due to adsorption of hydrocarbon contaminants  
20 compared to silica or gold surfaces; the WCA reaches 90° after air exposure for 96 h. In  
21 addition, this trend has been shown for a variety of non-noble metal oxide materials  
22 including zirconia and titania, and occurs due to physisorption of hydrocarbons to -OH

1 groups and other energetically favorable sites present on the surface, where physical or  
2 chemical interactions are possible. In other words, hydrocarbon in the atmosphere can  
3 be adsorbed on the surface with high density of –OH groups [23, 40]. Thus, it is likely  
4 that the difference of wettability behavior between CeO<sub>2</sub>-coated stainless steel and flat  
5 anodized alumina is owing to the difference of the amount of –OH groups on the  
6 surfaces. The anodically deposited CeO<sub>2</sub> surface may contain a high density of surface –  
7 OH group, promoting the accumulation of hydrocarbon contaminants from air. As a  
8 consequence, the surface becomes hydrophilic in air exposure. In fact, the  
9 deconvolution of O 1s spectra showed that approximately 40% of oxygen was –  
10 OH/H<sub>2</sub>O-type on the as-deposited CeO<sub>2</sub> and that on the as-formed Al<sub>2</sub>O<sub>3</sub> was only  
11 ~10%.

### 13 3.2 Introduction of surface roughness of CeO<sub>2</sub> for superhydrophobicity

14 Since the WCA as high as ~104° is obtained by anodic deposition of CeO<sub>2</sub> on the  
15 flat stainless steel surface, we tried to introduce surface roughness to make the surface  
16 superhydrophobic. The rough surface was developed in this study by electrochemical  
17 etching of stainless steel prior to CeO<sub>2</sub> deposition. Figure 5 shows SEM micrographs of  
18 the electrochemically etched stainless steel surface before and after CeO<sub>2</sub> deposition.  
19 Numbers of semi-spherical large etch pits with several sizes of 50-100 μm (Fig. 5a), ~5  
20 μm and 0.1-0.5 μm (Fig. 5b) are formed by the etching. Such surface morphology was  
21 remained even after deposition of CeO<sub>2</sub>, and from the comparison of the high  
22 magnification images obtained before and after deposition (Figs 5c and 5f), 10 nm scale

1 roughness is further introduced after the deposition because of the formation of  
2 nano-particular CeO<sub>2</sub>.

3 Figure 6 shows the change in WCA on CeO<sub>2</sub>-coated flat and etched stainless steel  
4 surface with air exposure time. Immediately after deposition, the CeO<sub>2</sub> surface on the  
5 etched stainless steel is again hydrophilic, and the WCA is as low as 13°, which is lower  
6 than that on flat stainless steel (20°). The lower WCA on the etched specimen is  
7 explained from the Wenzel equation [41]:

$$8 \quad \cos\theta_R = R\cos\theta_F \quad (1)$$

9 in which  $\theta_R$  and  $\theta_F$  are the WCAs on rough and flat surfaces and  $R$  is the roughness  
10 factor ( $R > 1$ ). This equation indicates that  $\theta_R$  decreases with surface roughening when  
11 the  $\theta_F$  is less than 90°. Thus, the reduced WCA of the CeO<sub>2</sub> coating on the etched  
12 stainless steel in comparison with that on the flat stainless steel is qualitatively  
13 explained by surface roughening. After air exposure for 3 days, the WCA reaches 130°  
14 on the etched specimen, being higher than that on the flat specimen (104°). The  $R$  value  
15 estimated from the equation 1 is 2.66. The roughness was also estimated using a laser  
16 microscope, which indicated the roughness factor of 2.57. These two values are close to  
17 each other, suggesting that the water droplet on the CeO<sub>2</sub> coating on the etched stainless  
18 steel is in the Wenzel state. The roughness is not high enough for superhydrophobicity.

19 On the superhydrophobic surface, on which a water droplet is readily rolling  
20 off, a Cassie-Baxter state must be achieved. In this case, air pockets are present between  
21 the water droplet and the rough solid surface. Because of the reduced liquid/solid  
22 contact area, the water is rolling off more readily in comparison with the Wenzel state,

1 in which all the rough solid surface is contacted with liquid. To obtain a  
2 superhydrophobic CeO<sub>2</sub> surface by further enhancing the surface roughness, we utilized  
3 stainless steel mesh (mesh opening of 15 μm and wire diameter also of 15 μm) as  
4 substrate. Figure 7 shows scanning electron micrographs of the etched and non-etched  
5 stainless steel mesh with and without CeO<sub>2</sub> coating. The electrochemically etched mesh  
6 (Figs. 7a-c) discloses surface roughness and the grooves developed by the etching  
7 extends along with the wire direction (Fig. 7b). The roughness is remained even after  
8 CeO<sub>2</sub> deposition (Figs. 7d-f) and further nanoscale roughness is introduced by  
9 nanoparticle nature of CeO<sub>2</sub>. High roughness of the etched mesh with CeO<sub>2</sub> is obvious  
10 from the comparison with the non-etched counterpart (Figs. 7g-i).

11 Fig. 8a shows the WCAs on the CeO<sub>2</sub>-coatings on various stainless steel  
12 morphologies after air exposure for 3 days. The WCA on the CeO<sub>2</sub>-coated stainless  
13 steel mesh without etching is only 121.3°, which is lower than that on the etched  
14 stainless steel plate. The electrochemical etching of the stainless steel mesh increases  
15 the WCA remarkably and the WCA reaches 155.7°. The dynamic WCA was also  
16 measured for the CeO<sub>2</sub> coated on the etched stainless steel mesh. The advancing and  
17 receding contact angles were 159.4° and 157.4°, respectively and the contact angle  
18 hysteresis is as low as 2.0° (Fig. 8b); the surface is superhydrophobic.

19 Figure 9 shows the schematic illustration showing the wetting behavior of the  
20 CeO<sub>2</sub> surface coated on etched stainless steel plate and mesh. The coating on the etched  
21 stainless steel plate was hydrophobic but not superhydrophobic. As discussed above, the  
22 surface is in the Wenzel state (Fig. 9a) [41]. Similarly, the CeO<sub>2</sub> coating on the stainless

1 steel mesh without electrochemical etching is hydrophobic from the WCA shown in Fig.  
2 8a, but not superhydrophobic. Rather smooth wire surface of the mesh allows water to  
3 penetrate through the mesh.

4 On the other hand, it is most likely that the CeO<sub>2</sub> coating on the etched stainless  
5 steel mesh surface was in the Cassie-Baxter state due to superhydrophobicity, as shown  
6 in Fig. 9c. Assuming the Cassie-Baxter state, the  $f$  value in the equation (2) is estimated  
7 to be as low as 0.12 from the  $\theta_R$  and  $\theta_F$  values of 155.7 and 104.1, respectively [42].

$$8 \quad \cos \theta_R = f(1 + \cos \theta_F) - 1 \quad (2)$$

9 This  $f$  value suggests that only a limited part of the mesh wires, roughly 4  $\mu\text{m}$  width of  
10 the top part of the mesh wire, may be in contact with water droplet. Pinning of the water  
11 droplet by surface roughness of the mesh introduced by electrochemical etching is  
12 effective in achieving the superhydrophobic state.

13

#### 14 3.4 Self-healing property of superhydrophobic CeO<sub>2</sub> surface

15 Since the superhydrophobic CeO<sub>2</sub> surface was obtained by accumulation of a  
16 carbon contaminant layer from the atmosphere, superhydrophobicity will be self-healed  
17 even after removing the hydrocarbon surface layer. In this study, we examined the  
18 self-healing behavior after oxygen plasma treatment of the superhydrophobic CeO<sub>2</sub>  
19 surface. As shown in Fig. 10, the high WCA of  $>150^\circ$  changes to  $\sim 0^\circ$  after oxygen  
20 plasma treatment, probably because of the decomposition of the contaminant  
21 hydrocarbon layer and the introduction of surface  $-\text{OH}$  group by oxygen plasma [43,  
22 44]. However, the WCA recovers again to  $>150^\circ$  during air exposure for 72 h, and the

1 superhydrophilic to superhydrophobic transition due to re-accumulation of contaminant  
2 hydrocarbons occurs repeatedly as shown in this Figure. Findings demonstrate that the  
3 present CeO<sub>2</sub> coating possess the self-healing nature of superhydrophobicity.

4 Low durability is one of the critical issues for the practical use of  
5 superhydrophobic materials. Self-healing property is, therefore, of crucial importance to  
6 enhance the durability [45-49]. The present superhydrophobic CeO<sub>2</sub> surface on the  
7 stainless steel mesh showed the self-healing property because hydrophobic surface layer  
8 is derived from hydrocarbon in the atmosphere. In addition, rough CeO<sub>2</sub> surface is  
9 readily be prepared by a combination of simple electrochemical processes. The  
10 hierarchical CeO<sub>2</sub> surface formed by the electrochemical approach is, therefore,  
11 promising as a practical self-healing superhydrophobic material.

12

### 13 3.5 Application to oil/water separation

14 Since the etched stainless steel mesh with CeO<sub>2</sub> coating is superhydrophobic and  
15 superoleophilic as shown in Figs. 12a and b, we attempt to apply the CeO<sub>2</sub>-coated  
16 stainless steel mesh for oil/water separation. When a mixture of oil (cyclohexane:  
17 surface tension,  $\gamma = 25.3 \text{ mN m}^{-1}$ ) and water ( $\gamma = 72.8 \text{ mN m}^{-1}$ ) was poured onto the  
18 etched stainless steel mesh coated with CeO<sub>2</sub>, only cyclohexane penetrated through the  
19 mesh, but no penetration of water occurred, resulting in almost complete oil/water  
20 separation (Fig. 11c and Movie S1). Thus, we succeeded in separating an oil/water  
21 mixture by electrochemical etching and CeO<sub>2</sub> coating without low-surface-tension  
22 treatment by another coating such as organic self-assembled monolayers.



1

## 2 4. Conclusions

3 In summary, CeO<sub>2</sub> coating anodically deposited on a flat stainless steel surface is  
4 hydrophilic immediately after deposition, while converts to hydrophobic after exposure  
5 to the atmosphere. This wettability transition is due to accumulation of hydrocarbon  
6 contaminant in air. Superhydrophobic CeO<sub>2</sub> surface is obtained by the deposition of  
7 CeO<sub>2</sub> on the electrochemically etched stainless steel mesh with sufficiently high  
8 roughness after air exposure. The superhydrophobic CeO<sub>2</sub> surface also exhibits  
9 self-healing property. Self-healing property is of crucial importance for the  
10 improvement of low durability of superhydrophobic surfaces.

11

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18

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1 Figure captions

2 Fig. 1 Surface SEM images with (a) low and (b) high magnification and (c) a  
3 cross-sectional TEM image of Type 304 stainless steel plate after anodic deposition in  
4 solution containing  $0.01 \text{ mol dm}^{-3} \text{ Ce(NO}_3)_3$  and  $0.05 \text{ mol dm}^{-3}$  hexamethylenetetramine  
5 at a constant current density of  $10 \text{ A m}^{-2}$  for 60 min at 333 K.

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7 Fig. 2 (a) XRD pattern and (b) GDOES elemental depth profile of the anodically  
8 deposited coating on Type 304 stainless steel plate in solution containing  $0.01 \text{ mol dm}^{-3}$   
9  $\text{Ce(NO}_3)_3$  and  $0.05 \text{ mol dm}^{-3}$  hexamethylenetetramine at a constant current density of  $10$   
10  $\text{A m}^{-2}$  for 60 min at 333 K.

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12 Fig. 3 (a) The WCAs as a function of exposure time in atmosphere and (b) optical  
13 images of water droplets on Type 304 stainless steel plate surface with  $\text{CeO}_2$  coating  
14 and aluminum plate surface anodized in  $0.1 \text{ mol dm}^{-3}$  ammonium pentaborate aqueous  
15 solution up to 200 V at 293 K.

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17 Fig. 4 XPS spectra of (a) Ce 3d, (b, e) O 1s, (c, f) C 1s and (d) Al 2p photoelectrons for  
18 (a-c) the  $\text{CeO}_2$  coating surface anodically deposited on Type 304 stainless steel plate  
19 and (b-f) anodized aluminum surface after exposure for 0, 7 and 12 h in air.

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21 Fig. 5 SEM surface images Type 304 stainless steel plate surface electrochemically  
22 etched in solution containing 1.2 wt.%  $\text{HNO}_3$  and 3.6 wt.%  $\text{HCl}$  at a constant current  
23 density of  $10 \text{ kA m}^{-2}$  up to  $4 \times 10^6 \text{ C m}^{-2}$  at 313 K (a-c) before and (d-f) after anodic  
24 deposition of  $\text{CeO}_2$  in solution containing  $0.01 \text{ mol dm}^{-3} \text{ Ce(NO}_3)_3$  and  $0.05 \text{ mol dm}^{-3}$   
25 hexamethylenetetramine at a constant current density of  $10 \text{ A m}^{-2}$  for 60 min at 333 K.

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27 Fig. 6 The WCAs on stainless steel plate with or without electrochemical etching after  
28 anodic deposition of  $\text{CeO}_2$  as a function of exposure time in air.

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30 Fig. 7 SEM images of Type 304 stainless steel mesh surfaces electrochemically etched  
31 in solution containing 1.2 wt.%  $\text{HNO}_3$  and 3.6 wt.%  $\text{HCl}$  at a constant current density of  
32  $100 \text{ A m}^{-2}$  for 60 s at 313 K (a-c) before and (d-f) after anodic deposition of  $\text{CeO}_2$  in



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2 at a constant current density of  $10 \text{ A m}^{-2}$  for 60 min at 333 K. The  $\text{CeO}_2$  deposited on  
3 the non-etched stainless steel mesh are shown in (g-i).

4  
5 Fig. 8 (a) The static WCAs on  $\text{CeO}_2$  surface anodically deposited on Type 304 stainless  
6 steel plate and mesh surfaces with or without electrochemical etching after air exposure  
7 for 3 days and (b) optical images of the water droplets during dynamic contact angle  
8 measurements for the etched stainless steel mesh with  $\text{CeO}_2$  coating.

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10 Fig. 9 Schematic illustrations showing wetting of the  $\text{CeO}_2$  anodically deposited on  
11 stainless steel: (a) the electrochemically etched stainless steel plate and (b) non-etched  
12 and (c) etched stainless steel mesh.

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14 Fig. 10 The advancing and receding contact angles for water on the  $\text{CeO}_2$  coating  
15 anodically deposited on the electrochemically etched Type 304 stainless steel mesh after  
16 several consecutive oxygen plasma treatment for 2 min and exposure in air for 72 h.

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18 Fig. 11 Optical images of (a) water and cyclohexane droplets on the superhydrophobic  
19  $\text{CeO}_2$  coating on the electrochemically etched Type 304 stainless steel mesh and (b) the  
20 oil/water separation test.

1 Supplementary materials

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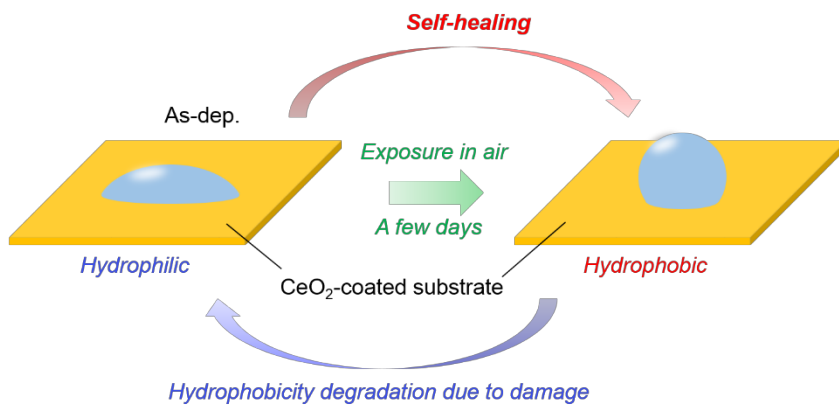
4 Movie S1 Separation of a mixture of water and cyclohexane (1:1, v/v) using a  
5 superhydrophobic CeO<sub>2</sub> coating on the electrochemically etched Type 304 stainless  
6 steel mesh.

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1 Graphical abstract

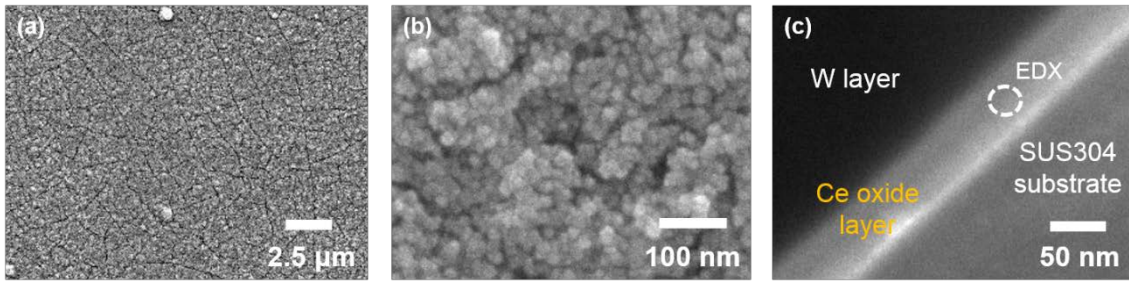
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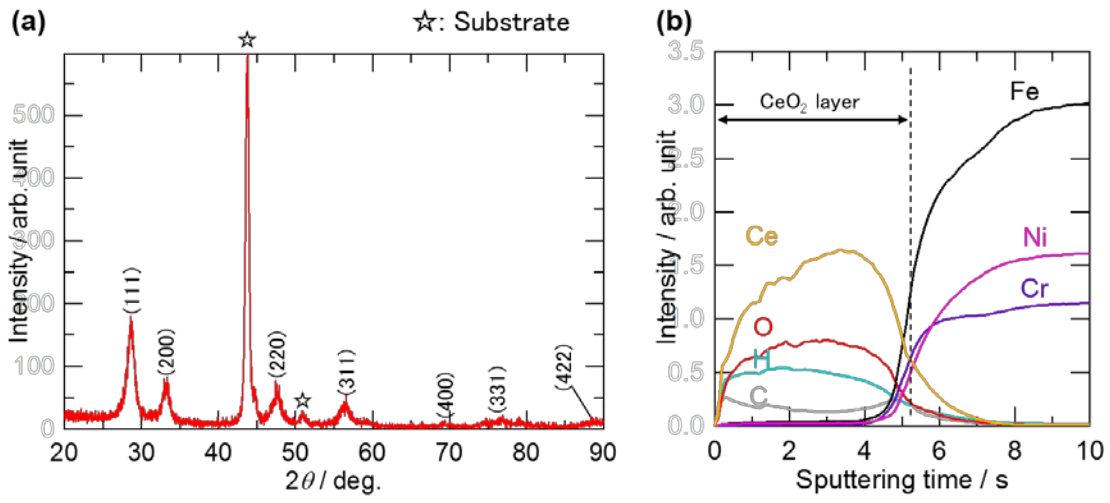


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2 Fig. 1 Surface SEM images with (a) low and (b) high magnification and (c) a  
3 cross-sectional TEM image of Type 304 stainless steel plate after anodic deposition in  
4 solution containing  $0.01 \text{ mol dm}^{-3} \text{ Ce(NO}_3)_3$  and  $0.05 \text{ mol dm}^{-3}$  hexamethylenetetramine  
5 at a constant current density of  $10 \text{ A m}^{-2}$  for 60 min at 333 K.

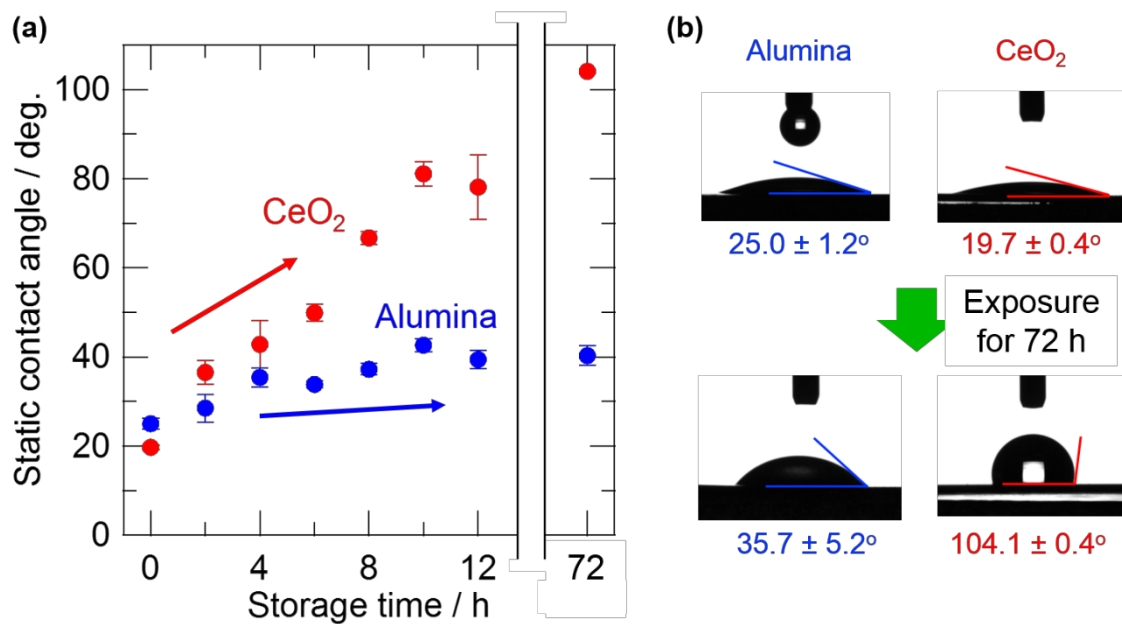
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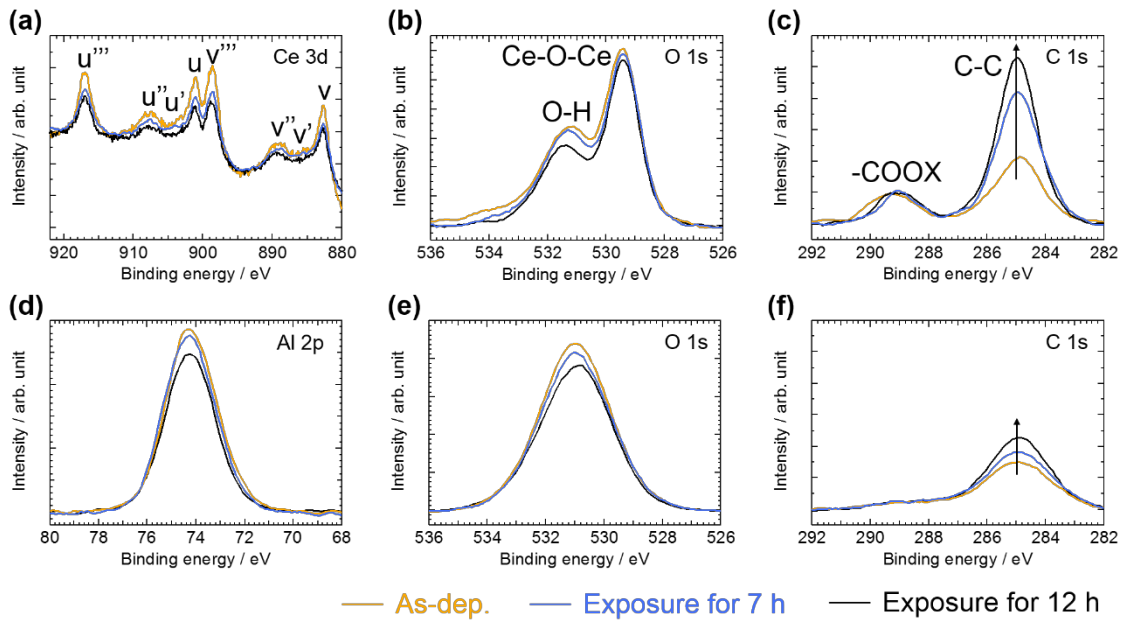
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 2 Fig. 2 (a) XRD pattern and (b) GDOES elemental depth profile of the anodically  
 3 deposited coating on Type 304 stainless steel plate in solution containing  $0.01 \text{ mol dm}^{-3}$   
 4  $\text{Ce}(\text{NO}_3)_3$  and  $0.05 \text{ mol dm}^{-3}$  hexamethylenetetramine at a constant current density of  $10$   
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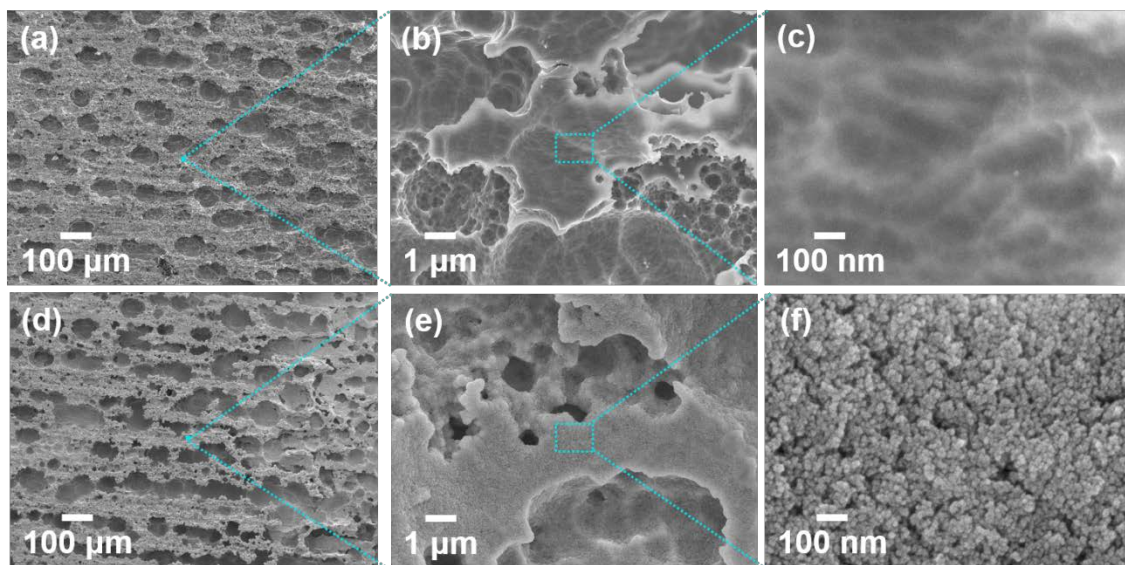
Fig. 3 (a) The WCAs as a function of exposure time in atmosphere and (b) optical images of water droplets on Type 304 stainless steel plate surface with CeO<sub>2</sub> coating and aluminum plate surface anodized in 0.1 mol dm<sup>-3</sup> ammonium pentaborate aqueous solution up to 200 V at 293 K.



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Fig. 4 XPS spectra of (a) Ce 3d, (b, e) O 1s, (c, f) C 1s and (d) Al 2p photoelectrons for (a-c) the  $CeO_2$  coating surface anodically deposited on Type 304 stainless steel plate and (b-f) anodized aluminum surface after exposure for 0, 7 and 12 h in air.

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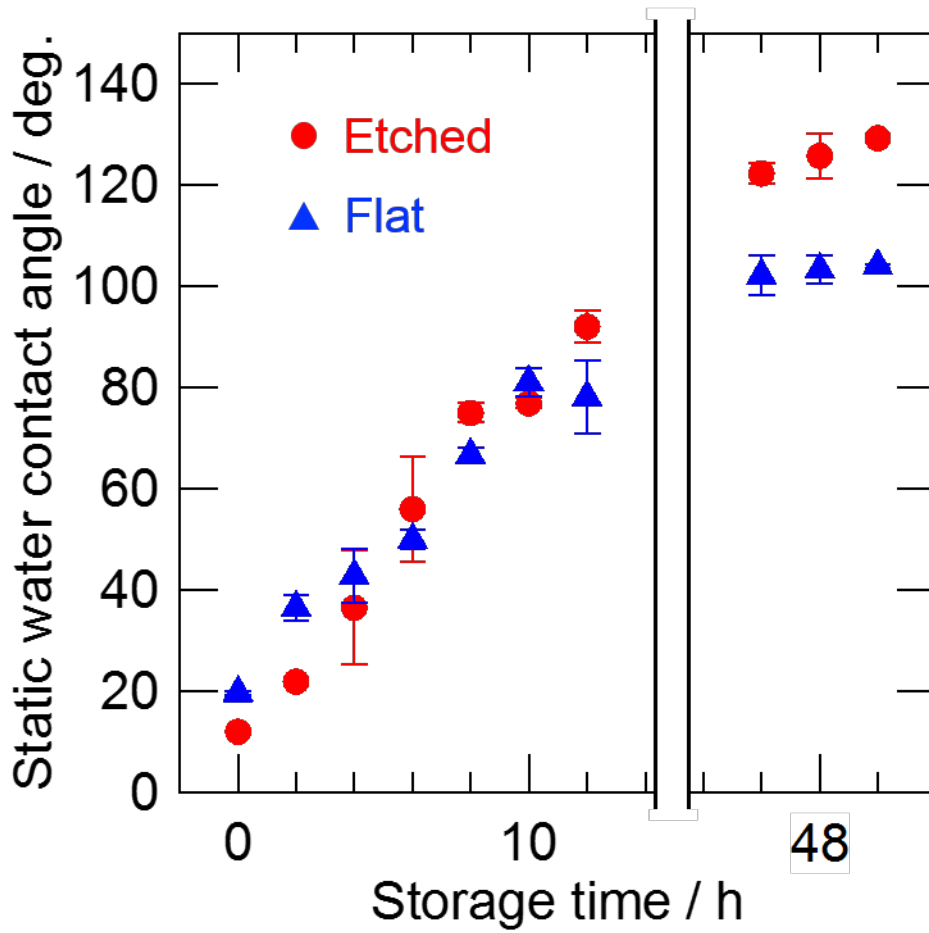
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5 Fig. 5 SEM surface images Type 304 stainless steel plate surface electrochemically  
6 etched in solution containing 1.2 wt.% HNO<sub>3</sub> and 3.6 wt.% HCl at a constant current  
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8 deposition of CeO<sub>2</sub> in solution containing 0.01 mol dm<sup>-3</sup> Ce(NO<sub>3</sub>)<sub>3</sub> and 0.05 mol dm<sup>-3</sup>  
9 hexamethylenetetramine at a constant current density of 10 A m<sup>-2</sup> for 60 min at 333 K.

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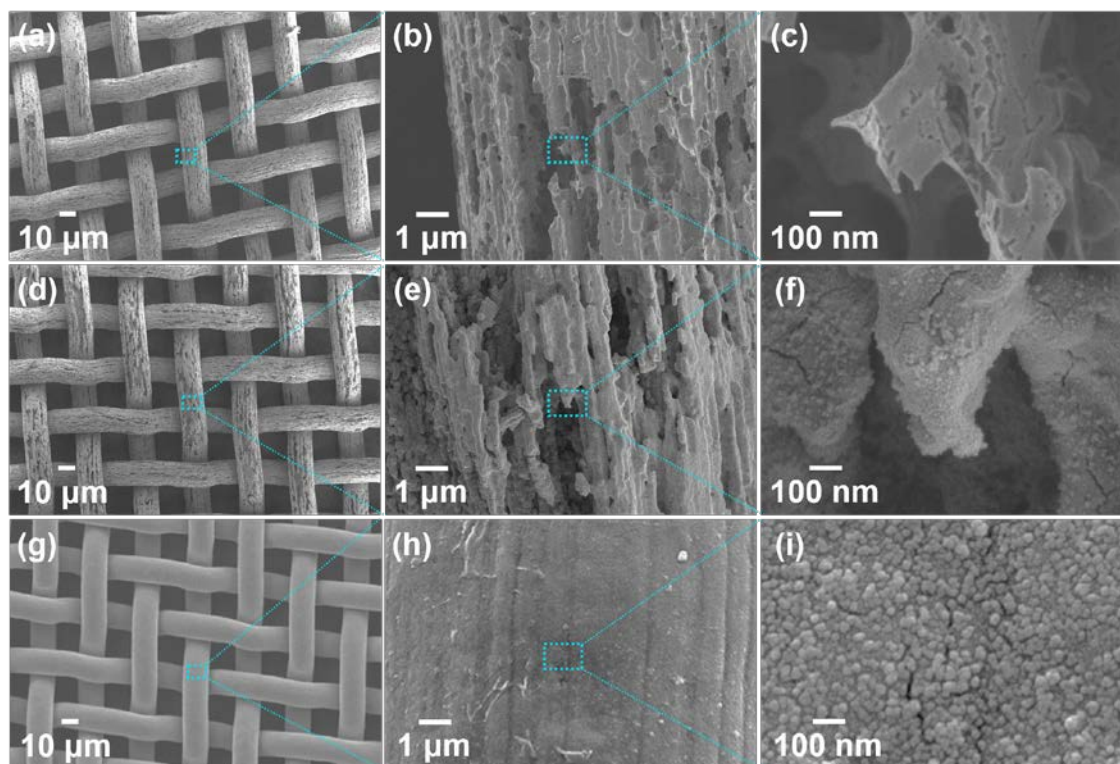
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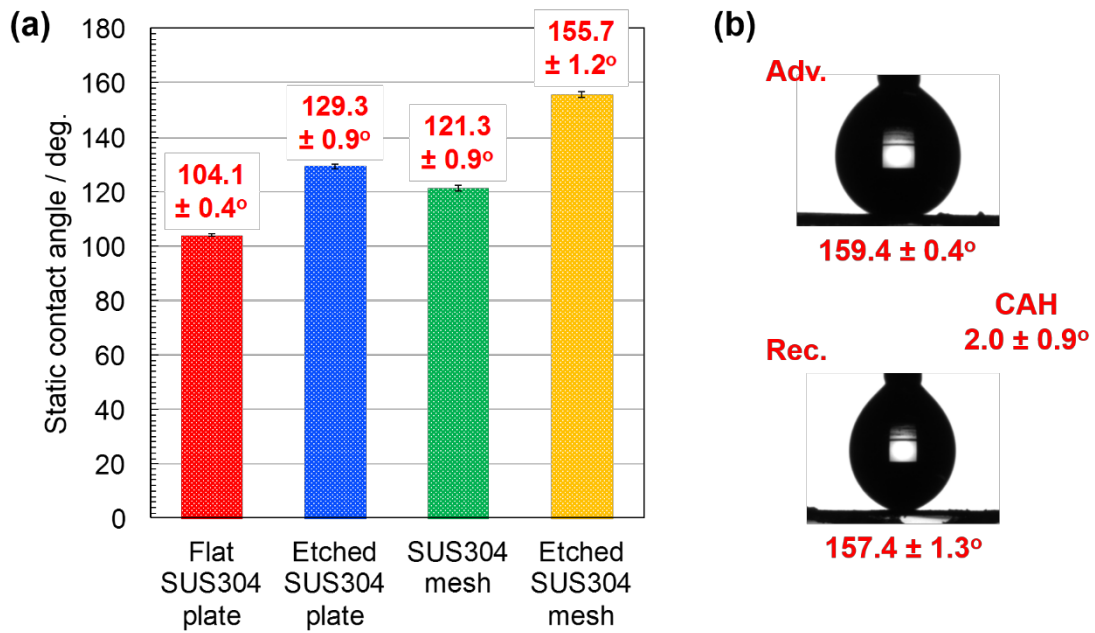
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Fig. 6 The WCAs on stainless steel plate with or without electrochemical etching after anodic deposition of CeO<sub>2</sub> as a function of exposure time in air.



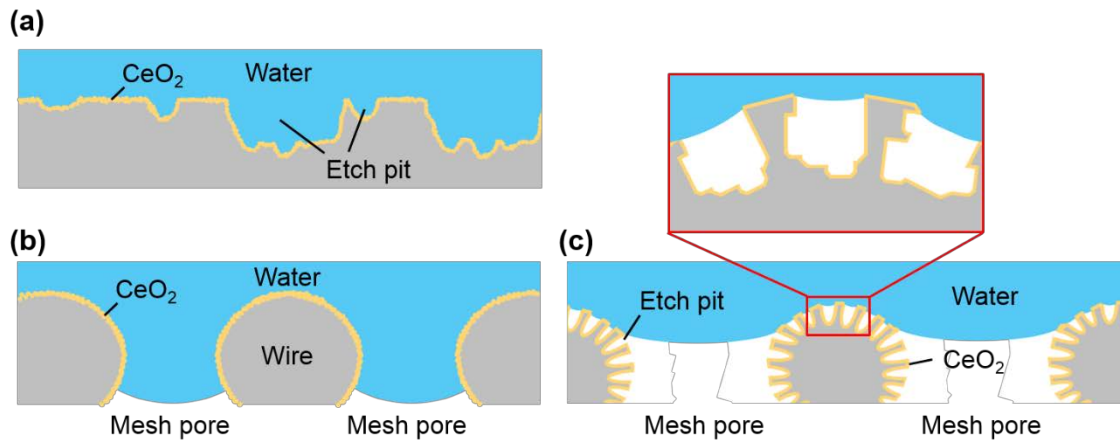
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Fig. 7 SEM images of Type 304 stainless steel mesh surfaces electrochemically etched in solution containing 1.2 wt.% HNO<sub>3</sub> and 3.6 wt.% HCl at a constant current density of 100 A m<sup>-2</sup> for 60 s at 313 K (a-c) before and (d-f) after anodic deposition of CeO<sub>2</sub> in solution containing 0.01 mol dm<sup>-3</sup> Ce(NO<sub>3</sub>)<sub>3</sub> and 0.05 mol dm<sup>-3</sup> hexamethylenetetramine at a constant current density of 10 A m<sup>-2</sup> for 60 min at 333 K. The CeO<sub>2</sub> deposited on the non-etched stainless steel mesh are shown in (g-i).



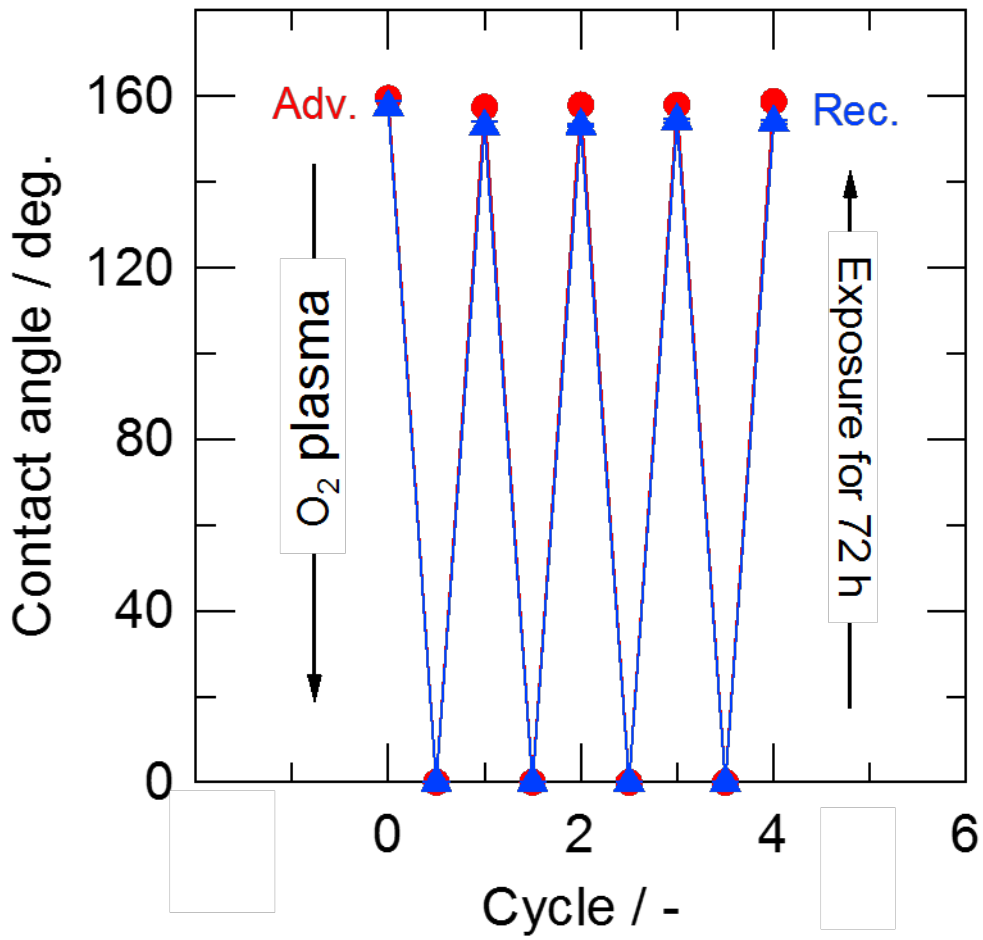
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Fig. 8 (a) The static WCAs on CeO<sub>2</sub> surface anodically deposited on Type 304 stainless steel plate and mesh surfaces with or without electrochemical etching after air exposure for 3 days and (b) optical images of the water droplets during dynamic contact angle measurements for the etched stainless steel mesh with CeO<sub>2</sub> coating.



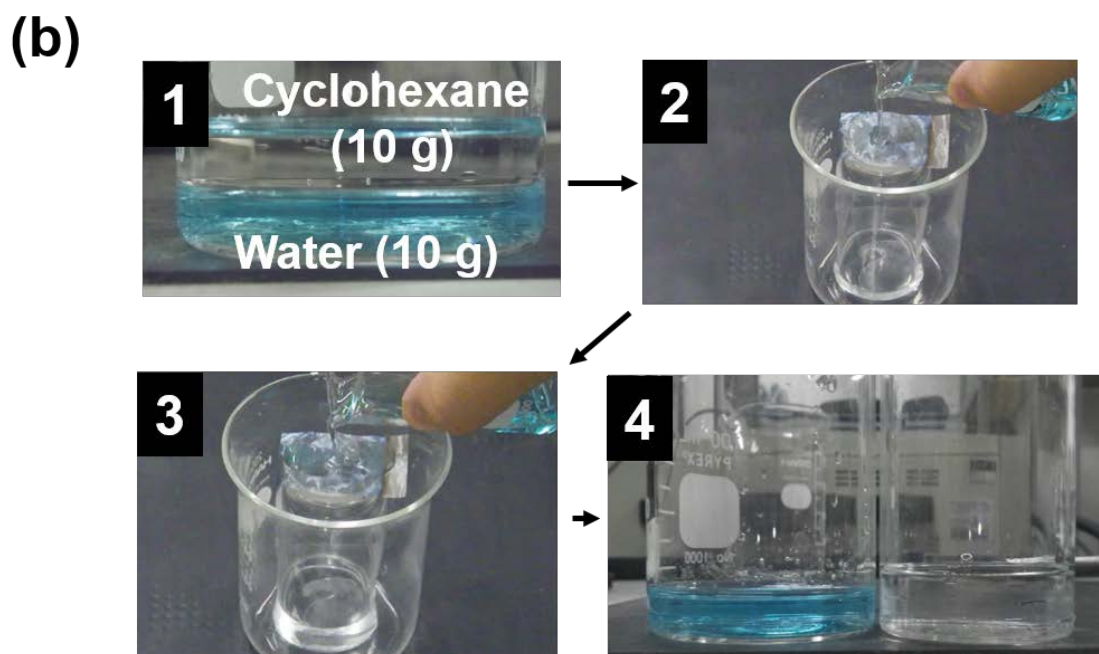
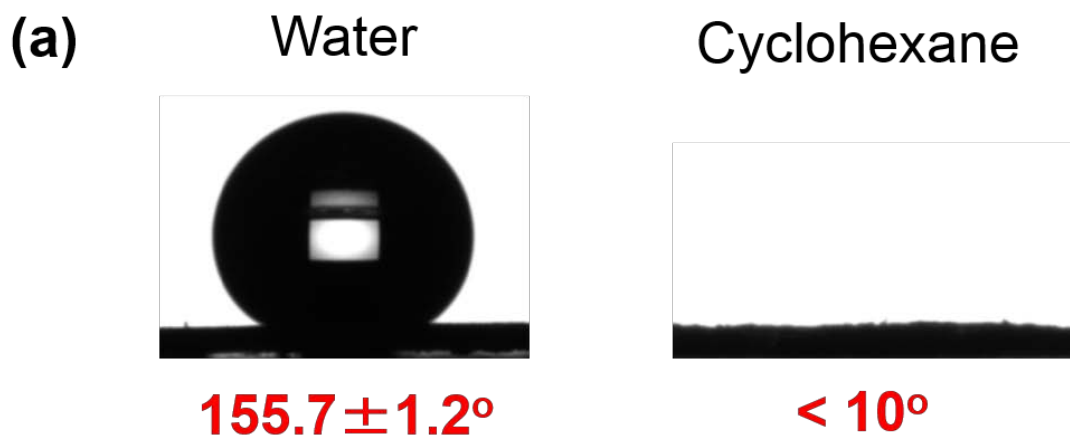
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Fig. 9 Schematic illustrations showing wetting of the  $\text{CeO}_2$  anodically deposited on stainless steel: (a) the electrochemically etched stainless steel plate and (b) non-etched and (c) etched stainless steel mesh.



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Fig. 10 The advancing and receding contact angles for water on the CeO<sub>2</sub> coating anodically deposited on the electrochemically etched Type 304 stainless steel mesh after several consecutive oxygen plasma treatment for 2 min and exposure in air for 72 h.



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Fig. 11 Optical images of (a) water and cyclohexane droplets on the superhydrophobic  $\text{CeO}_2$  coating on the electrochemically etched Type 304 stainless steel mesh and (b) the oil/water separation test.