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Facile preparation of self-healing superhydrophobic CeO₂ surface by electrochemical processes

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Highlights

1. The CeO$_2$-coating is formed on Type 304 stainless steel by anodic deposition.
2. The hydrophilic CeO$_2$ surface is transformed to hydrophobic during air exposure.
3. Superhydrophobic CeO$_2$ surface is obtained on hierarchically rough substrate.
4. Superhydrophobic CeO$_2$ surface shows self-healing property.

Abstract

Herein we report simple electrochemical processes to fabricate a self-healing superhydrophobic CeO$_2$ coating on Type 304 stainless steel. The CeO$_2$ surface anodically deposited on flat stainless steel surface is hydrophilic, although high temperature-sintered and sputter-deposited CeO$_2$ surface was reported to be hydrophobic. The anodically deposited hydrophilic CeO$_2$ surface is transformed to hydrophobic during air exposure. Specific accumulation of contaminant hydrocarbon on the CeO$_2$ surface is responsible for the transformation to hydrophobic state. The deposition of CeO$_2$ on hierarchically rough stainless steel surface produces superhydrophobic CeO$_2$ surface, which also shows self-healing ability; the surface changes to superhydrophilic after oxygen plasma treatment but superhydrophobic state is recovered repeatedly by air exposure. This work provides a facile method for preparing a self-healing superhydrophobic surface using practical electrochemical processes.

Keywords: CeO$_2$ coating; superhydrophobicity; anodic deposition; self-healing ability
1. Introduction

Superhydrophobic solid materials have attracted much attention because of several superior functional properties including self-cleaning, anti-corrosion, anti-freezing and anti-biofouling [1-4]. Many natural surfaces, including lotus leaves, water strider legs and morpho butterfly wings, are superhydrophobic [5-9]. Superhydrophobicity of these surfaces is originating from peculiar microscopic geometrical surface morphology. For example, lotus leaves consist of numbers of micrometer-size asperities covered by nano-fibrous hydrophobic wax, resulting in superhydrophobicity [5, 6]. Superhydrophobic surface is usually defined to show a static contact angle for a water droplet greater than $150^\circ$ and a low contact angle hysteresis (the difference between the advancing and receding contact angles) of $<10^\circ$.

Inspired by nature, many artificial superhydrophobic materials have been developed [9-19], since Onda et al. reported a first example of artificial superhydrophobic fractal surface in 1996 [9].

In addition to the high roughness with fractal or hierarchical surface geometry, the surface must be composed of materials with low surface energy for superhydrophobicity. Thin organic coatings, including self-assembled fluoroalkyl monolayers, have been often introduced on rough metallic or inorganic substrates. However, such superhydrophobic surfaces have low durability because of mechanical
instability of thin organic coatings and highly rough hierarchical surfaces. Improved
durability of superhydrophobic surfaces is awaited for practical application.

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

In the present study, the CeO₂ coating was prepared by anodic deposition on flat
and hierarchically rough stainless steel surface. The rough stainless steel surface was
prepared by electrochemical etching. The surface wettability for water was evaluated by
measuring static and dynamic contact angles. The CeO₂ surface immediately after
deposition was hydrophilic, but transformed to hydrophobic during air exposure. The
self-healing properties of the hydrophilic surface was also examined in the present
study.
2. Experimental

2.1 Specimen preparation

Type 304 stainless steel plates or meshes (with 300, 500, 640 and 795 mesh) composed of 17–19 wt.% Cr, 8–11 wt.% Ni, < 2 wt.% Mn, < 1 wt.% Si and Fe balance were used as substrate in this study. Prior to electrochemical etching and anodic deposition, the plate substrate was electropolished in solution containing HClO₄ and ethylene glycol (1:9 v/v) at 20 V for 5 min below 283 K. Electrochemical etching of the plate was performed in solution containing 1.2 wt% HNO₃ and 3.6 wt% HCl at a constant current density of 1 A cm⁻² for 200 s at 313 K [26]. For mesh specimens, etching was conducted at 1 A cm⁻² for 1 min in order to prevent excess etching of specimens. Anodic deposition was carried out at a constant current density of 1 A cm⁻² in solution containing 0.01 mol dm⁻³ Ce(NO₃)₃ and 0.05 mol dm⁻³ hexamethylenetetramine (pH 6.7) for 60 min at 333 K. The rather low concentration of Ce(NO₃)₃ was selected to form a thin coating to maintain the textured morphology developed by electrochemical etching. A two-electrode cell with a Type 304 stainless steel counter electrode was used for anodic deposition. For comparison, we also prepared a barrier-type anodic alumina film on aluminum plate (99.999% purity). Prior to anodizing, an aluminum plate was electropolished in solution containing HClO₄ and ethanol (1:4, v/v) at a constant voltage of 20 V for 5 min below 278 K. Then, the specimen was anodized in 0.1 mol dm⁻³ ammonium pentaborate ((NH₄)₂B₁₀O₁₆) at a constant current density of 5 mA cm⁻² up to 200 V at 293 K, using a two-electrode cell.
with a platinum counter electrode. The alumina surface thus prepared was smooth and flat, as reported previously [27].

2.2 Characterizations

The surface and cross-section of the specimens were observed by a JEOL JSM-6500F field emission scanning electron microscope (SEM) and a JEOL JEM-2000FX transmission electron microscope (TEM) with EDS facilities, respectively. The cross-sectional specimen was prepared by focused gallium ion beam processing with a JEOL JIB-4600F/HKD multibeam system. Surface roughness was also evaluated using a KEYENCE VK09700 laser microscope. Phases in the anodically deposited CeO$_2$ layer formed on the stainless steel surface were identified by X-ray diffraction using a Rigaku RINT-2000 diffractometer with Cu Kα radiation ($\lambda = 0.15418$ nm). An $\alpha$-2$\theta$ scan mode with $\alpha = 1^\circ$ was used in this study. Elemental depth profile analysis was carried out by glow discharge optical emission spectroscopy (GDOES) using a Jobin-Yvon 5000 RF instrument in an argon atmosphere of 700 Pa by applying a power of 30 W. Light emissions of characteristic wavelength were monitored throughout the analysis with a sampling time of 0.01 s to obtain depth profile. The wavelength of the spectral lines used were 413.717 nm for cerium, 130.217 nm for oxygen, 385.991 nm for iron, 425.433 nm for chromium, 341.477 nm for nickel and 165.701 nm for carbon. The signals were detected from a circular area of approximately 4 mm diameter. The X-ray photoelectron spectra of the anodically deposited CeO$_2$ and anodic alumina surfaces after air exposure for 1, 7 and 12 h in a laboratory atmosphere were measured.
using a JEOL JPS-9200 spectroscope with Mg Kα excitation ($h\nu = 1253.6$ eV). Binding energies of the photoelectrons were calibrated with a contaminant carbon peak energy (285.0 eV).

2.3 Wettability evaluation.

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

For examination of the self-healing hydrophobicity, oxygen plasma was irradiated for 4 min using a Harrick Plasma PDC-32G air plasma cleaner to the hydrophobic CeO$_2$ surface specimen in order to decompose organic contaminants on the surface. Then, water contact angle (WCA) was monitored during subsequent air exposure. This process was repeated several times.

3. Results and discussion

3.1 CeO$_2$ coating on stainless steel plate

Figures 1a and 1b show SEM micrographs of the surface of the electropolished stainless steel plate after anodic deposition of CeO$_2$. The surface appears rather smooth at low magnification (Fig. 1a), while high magnification micrograph (Fig. 1b) discloses
that the coating consists of densely packed nanoparticles with 10-15 nm in diameter. In
Fig. 1a, microcracks are also found in the coating, probably associated with the
shrinkage of the coating, which is caused by dehydration of the anodically deposited
coating during drying [28]. Kulp et al. deposited anodically CeO$_2$ at 0.5 and 1.1 V vs
Ag/AgCl in Ce(III) acetate solution [29]. They obtained a smooth and crack-free film at
0.5 V vs Ag/AgCl, while a film formed at 1.1 V vs Ag/AgCl contained nanoparticles.
They suggested that the nanoparticles were formed because of indirect oxidation of
Ce(III) with O$_2$, which was generated by electrochemical oxidation of water. The
presence of nanoparticles in the present coating suggests such indirect mechanism of the
formation of CeO$_2$. In fact, we found gas generation on anode during anodic deposition.

TEM observation of the coating cross-section (Fig. 1c) reveals that the coating is
approximately 60 nm thick and uniform in thickness. EDX analysis of the marked
region in Fig. 1c indicated the atomic ratio of Ce:O close to 1:2, corresponding to the
composition of CeO$_2$. Figure 2 shows the X-ray diffraction pattern and GDOES
elemental depth profile of the anodically deposited CeO$_2$ on the electropolished stainless
steel plate. Only a CeO$_2$ phase (JCPDS card 34-0394) is identified from the X-ray
diffraction pattern, apart from the reflections from the stainless steel substrate (Fig. 2a).
The species (Fe, Ni and Cr) derived from the stainless steel substrate are not detected
within the coating in the GDOES elemental depth profile analysis (Fig. 2b). Thus, rather
pure CeO$_2$ is deposited on the stainless steel, although, from the depth profile, hydrogen
and carbon impurity species appear to be slightly incorporated in the coating. The
incorporated carbon species may be derived from hexamethylenetetramine added in the coating solution.

Then, the wettability of the CeO$_2$-coated specimen was examined by static contact angle measurements. Figure 3 shows the WCAs and optical photographs of water droplets on the surfaces of the CeO$_2$ coating on electropolished stainless steel and the flat alumina film formed by anodizing of aluminum as a function of air exposure time. The WCA of the CeO$_2$ coating on the flat stainless steel is only $20^\circ$ immediately after deposition; the anodically deposited CeO$_2$ is hydrophilic. This is contrast to the hydrophobicity of the magnetron-sputtered CeO$_2$ surface [20]. However, the WCA gradually increases with time of air exposure and reaches $\sim$104$^\circ$ after three days. This means that the CeO$_2$ surface changes from hydrophilic to hydrophobic during air exposure. On the other hand, the WCA on the alumina surface remained hydrophilic even after three days.

In order to examine the change in composition of the CeO$_2$ and Al$_2$O$_3$ surface during air exposure, XPS surface analysis was performed. Figures 4a-c show the Ce 3d, O 1s and C 1s photoelectron spectra of the CeO$_2$ surface. The Ce 3d spectra in Fig. 4a are composed of two multiplets (i.e., v and u), which correspond to the spin orbit split 3d$_{5/2}$ and 3d$_{3/2}$, respectively. In accord with previous reports [30-34], the v, v$''$, v$'''$, u, u$''$ and u$'''$ peaks are attributed to Ce$^{4+}$ state, while the v$'$ and u$'$ peaks are assigned to Ce$^{3+}$ state. The intensity of all the Ce 3d peaks slightly decreases with time of air exposure. This is because of covering coating surface by hydrocarbon contaminants, as described below.
The O 1s spectra reveal two peaks at 529.5 eV and 531.4 eV; the former is assigned to Ce-O-Ce and the latter to −OH/H2O oxygen, defective oxide or carbonate oxygen [30, 35, 36]. The presence of surface −OH/H2O species probably make the surface hydrophilic. During air exposure, the intensity of −OH/H2O peak decreases slightly. The most significant change in the spectra was found in C 1s spectra during air exposure. The contaminant hydrocarbon peak at 285.0 eV becomes intense largely during air exposure, indicating the accumulation of hydrocarbon layer on the CeO2 surface. A small peak at 289.0 eV is assigned to carboxyl or carbonate species [37, 38], whose intensity remains almost unchanged during air exposure.

The change in the XPS spectra of the Al2O3 surface during air exposure was also examined (Figs. 4d-f). The Al 2p spectra shows a peak at 74.3 eV, corresponding to Al3+ state [39]. A broad O 1s peak is owing to overlapping of Al-O-Al (530.9 eV) and OH/H2O (531.8 eV) peaks. The intensity of the C 1s hydrocarbon peak (285.0 eV) increases with air exposure, but the increase in the intensity for Al2O3 surface is much less than that on the CeO2 surface. As a consequence, only CeO2 surface changes from hydrophilic to hydrophobic during air exposure.

Preston et al. reported the hydrophobicity of a CeO2 pellet after air exposure for long time, similar to this study [23]. According to their report, a hydrophilic CeO2 pellet surface conversed to hydrophobic due to adsorption of hydrocarbon contaminants compared to silica or gold surfaces; the WCA reaches 90° after air exposure for 96 h. In addition, this trend has been shown for a variety of non-noble metal oxide materials including zirconia and titania, and occurs due to physisorption of hydrocarbons to −OH.
groups and other energetically favorable sites present on the surface, where physical or chemical interactions are possible. In other words, hydrocarbon in the atmosphere can be adsorbed on the surface with high density of –OH groups [23, 40]. Thus, it is likely that the difference of wettability behavior between CeO₂-coated stainless steel and flat anodized alumina is owing to the difference of the amount of –OH groups on the surfaces. The anodically deposited CeO₂ surface may contain a high density of surface –OH group, promoting the accumulation of hydrocarbon contaminants from air. As a consequence, the surface becomes hydrophilic in air exposure. In fact, the deconvolution of O 1s spectra showed that approximately 40% of oxygen was –OH/H₂O-type on the as-deposited CeO₂ and that on the as-formed Al₂O₃ was only ~10%.

3.2 Introduction of surface roughness of CeO₂ for superhydrophobicity

Since the WCA as high as ~104° is obtained by anodic deposition of CeO₂ on the flat stainless steel surface, we tried to introduce surface roughness to make the surface superhydrophobic. The rough surface was developed in this study by electrochemical etching of stainless steel prior to CeO₂ deposition. Figure 5 shows SEM micrographs of the electrochemically etched stainless steel surface before and after CeO₂ deposition. Numbers of semi-spherical large etch pits with several sizes of 50-100 μm (Fig. 5a), ~5 μm and 0.1-0.5 μm (Fig. 5b) are formed by the etching. Such surface morphology was remained even after deposition of CeO₂, and from the comparison of the high magnification images obtained before and after deposition (Figs 5c and 5f), 10 nm scale
roughness is further introduced after the deposition because of the formation of nano-particular CeO$_2$.

Figure 6 shows the change in WCA on CeO$_2$-coated flat and etched stainless steel surface with air exposure time. Immediately after deposition, the CeO$_2$ surface on the etched stainless steel is again hydrophilic, and the WCA is as low as 13°, which is lower than that on flat stainless steel (20°). The lower WCA on the etched specimen is explained from the Wenzel equation [41]:

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

in which $\theta_R$ and $\theta_F$ are the WCAs on rough and flat surfaces and $R$ is the roughness factor ($R >1$). This equation indicates that $\theta_R$ decreases with surface roughening when the $\theta_F$ is less than 90°. Thus, the reduced WCA of the CeO$_2$ coating on the etched stainless steel in comparison with that on the flat stainless steel is qualitatively explained by surface roughening. After air exposure for 3 days, the WCA reaches 130° on the etched specimen, being higher than that on the flat specimen (104°). The $R$ value estimated from the equation 1 is 2.66. The roughness was also estimated using a laser microscope, which indicated the roughness factor of 2.57. These two values are close to each other, suggesting that the water droplet on the CeO$_2$ coating on the etched stainless steel is in the Wenzel state. The roughness is not high enough for superhydrophobicity.

On the superhydrophobic surface, on which a water droplet is readily rolling off, a Cassie-Baxter state must be achieved. In this case, air pockets are present between the water droplet and the rough solid surface. Because of the reduced liquid/solid contact area, the water is rolling off more readily in comparison with the Wenzel state,
in which all the rough solid surface is contacted with liquid. To obtain a superhydrophobic CeO₂ surface by further enhancing the surface roughness, we utilized stainless steel mesh (mesh opening of 15 μm and wire diameter also of 15 μm) as substrate. Figure 7 shows scanning electron micrographs of the etched and non-etched stainless steel mesh with and without CeO₂ coating. The electrochemically etched mesh (Figs. 7a-c) discloses surface roughness and the grooves developed by the etching extends along with the wire direction (Fig. 7b). The roughness is remained even after CeO₂ deposition (Figs. 7d-f) and further nanoscale roughness is introduced by nanoparticle nature of CeO₂. High roughness of the etched mesh with CeO₂ is obvious from the comparison with the non-etched counterpart (Figs. 7g-i).

Fig. 8a shows the WCAs on the CeO₂-coatings on various stainless steel morphologies after air exposure for 3 days. The WCA on the CeO₂-coated stainless steel mesh without etching is only 121.3°, which is lower than that on the etched stainless steel plate. The electrochemical etching of the stainless steel mesh increases the WCA remarkably and the WCA reaches 155.7°. The dynamic WCA was also measured for the CeO₂ coated on the etched stainless steel mesh. The advancing and receding contact angles were 159.4° and 157.4°, respectively and the contact angle hysteresis is as low as 2.0° (Fig. 8b); the surface is superhydrophobic.

Figure 9 shows the schematic illustration showing the wetting behavior of the CeO₂ surface coated on etched stainless steel plate and mesh. The coating on the etched stainless steel plate was hydrophobic but not superhydrophobic. As discussed above, the surface is in the Wenzel state (Fig. 9a) [41]. Similarly, the CeO₂ coating on the stainless
steel mesh without electrochemical etching is hydrophobic from the WCA shown in Fig. 8a, but not superhydrophobic. Rather smooth wire surface of the mesh allows water to penetrate through the mesh.

On the other hand, it is most likely that the CeO$_2$ coating on the etched stainless steel mesh surface was in the Cassie-Baxter state due to superhydrophobicity, as shown in Fig. 9c. Assuming the Cassie-Baxter state, the $f$ value in the equation (2) is estimated to be as low as 0.12 from the $\theta_R$ and $\theta_F$ values of 155.7 and 104.1, respectively [42].

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

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

3.4 Self-healing property of superhydrophobic CeO$_2$ surface

Since the superhydrophobic CeO$_2$ surface was obtained by accumulation of a carbon contaminant layer from the atmosphere, superhydrophobicity will be self-healed even after removing the hydrocarbon surface layer. In this study, we examined the self-healing behavior after oxygen plasma treatment of the superhydrophobic CeO$_2$ surface. As shown in Fig. 10, the high WCA of $>150^\circ$ changes to $\sim0^\circ$ after oxygen plasma treatment, probably because of the decomposition of the contaminant hydrocarbon layer and the introduction of surface $-\text{OH}$ group by oxygen plasma [43, 44]. However, the WCA recovers again to $>150^\circ$ during air exposure for 72 h, and the
superhydrophilic to superhydrophobic transition due to re-accumulation of contaminant hydrocarbons occurs repeatedly as shown in this Figure. Findings demonstrate that the present CeO₂ coating possess the self-healing nature of superhydrophobicity.

Low durability is one of the critical issues for the practical use of superhydrophobic materials. Self-healing property is, therefore, of crucial importance to enhance the durability [45-49]. The present superhydrophobic CeO₂ surface on the stainless steel mesh showed the self-healing property because hydrophobic surface layer is derived from hydrocarbon in the atmosphere. In addition, rough CeO₂ surface is readily be prepared by a combination of simple electrochemical processes. The hierarchical CeO₂ surface formed by the electrochemical approach is, therefore, promising as a practical self-healing superhydrophobic material.

3.5 Application to oil/water separation

Since the etched stainless steel mesh with CeO₂ coating is superhydrophobic and superoleophilic as shown in Figs. 12a and b, we attempt to apply the CeO₂-coated stainless steel mesh for oil/water separation. When a mixture of oil (cyclohexane: surface tension, \( \gamma = 25.3 \text{ mN m}^{-1} \)) and water (\( \gamma = 72.8 \text{ mN m}^{-1} \)) was poured onto the etched stainless steel mesh coated with CeO₂, only cyclohexane penetrated through the mesh, but no penetration of water occurred, resulting in almost complete oil/water separation (Fig. 11c and Movie S1). Thus, we succeeded in separating an oil/water mixture by electrochemical etching and CeO₂ coating without low-surface-tension treatment by another coating such as organic self-assembled monolayers.
4. Conclusions

In summary, CeO$_2$ coating anodically deposited on a flat stainless steel surface is hydrophilic immediately after deposition, while converts to hydrophobic after exposure to the atmosphere. This wettability transition is due to accumulation of hydrocarbon contaminant in air. Superhydrophobic CeO$_2$ surface is obtained by the deposition of CeO$_2$ on the electrochemically etched stainless steel mesh with sufficiently high roughness after air exposure. The superhydrophobic CeO$_2$ surface also exhibits self-healing property. Self-healing property is of crucial importance for the improvement of low durability of superhydrophobic surfaces.

Acknowledgement

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References


Figure captions

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

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

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$_2$ coating and aluminum plate surface anodized in 0.1 mol dm$^{-3}$ ammonium pentaborate aqueous solution up to 200 V at 293 K.

Fig. 4 XPS spectra of (a) Ce 3d, (b, c) 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.

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

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

Fig. 7 SEM images of Type 304 stainless steel mesh surfaces electrochemically etched in solution containing 1.2 wt.% HNO$_3$ and 3.6 wt.% HCl at a constant current density of 100 A m$^{-2}$ for 60 s at 313 K (a-c) before and (d-f) after anodic deposition of CeO$_2$ in
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Fig. 8 (a) The static WCAs on CeO$_2$ 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$_2$ coating.

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

Fig. 10 The advancing and receding contact angles for water on the CeO$_2$ 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.

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

Movie S1 Separation of a mixture of water and cyclohexane (1:1, v/v) using a superhydrophobic CeO$_2$ coating on the electrochemically etched Type 304 stainless steel mesh.
Graphical abstract

Self-healing

As-dep. Exposure in air Hydrophilic CeO2-coated substrate Hydrophobic A few days

Hydrophobicity degradation due to damage
Fig. 1 Surface SEM images with (a) low and (b) high magnification and (c) a cross-sectional TEM image of Type 304 stainless steel plate after anodic deposition in solution containing 0.01 mol dm$^{-3}$ Ce(NO$_3$)$_3$ and 0.05 mol dm$^{-3}$ hexamethylenetetramine at a constant current density of 10 A m$^{-2}$ for 60 min at 333 K.
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Fig. 7 SEM images of Type 304 stainless steel mesh surfaces electrochemically etched in solution containing 1.2 wt.% HNO$_3$ and 3.6 wt.% HCl at a constant current density of 100 A m$^{-2}$ for 60 s at 313 K (a-c) before and (d-f) after anodic deposition of CeO$_2$ in solution containing 0.01 mol dm$^{-3}$ Ce(NO$_3$)$_3$ and 0.05 mol dm$^{-3}$ hexamethylenetetramine at a constant current density of 10 A m$^{-2}$ for 60 min at 333 K. The CeO$_2$ deposited on the non-etched stainless steel mesh are shown in (g-i).
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Fig. 11 Optical images of (a) water and cyclohexane droplets on the superhydrophobic 
CeO$_2$ coating on the electrochemically etched Type 304 stainless steel mesh and (b) the 
oil/water separation test.