Highly Sensitive Dissolved Oxygen Sensor with a Sustainable Antifouling, Antiabrasion, and Self-Cleaning Superhydrophobic Surface

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ABSTRACT: Long-term sensing of dissolved oxygen in aqueous solution always suffers from adherence of algae, barnacles, and clams and formation of biofilms on the sensor surface, which strongly influences the diffusion of oxygen into the sensor film. Metabolism of these adhered species consumes oxygen and causes bias on sensor readout. Therefore, commercial sensors are equipped with mechanical brushes to constantly clean the sensor surface, which significantly complicates the sensor design and causes damage to the sensor surface. In addition, extra energy storage and mechanical structures are required, which make an optical sensor bulky and limit its service life. We have developed a robust and highly sensitive dissolved oxygen sensor with good mechanical stability and self-cleaning capability. The sensor was fabricated by doping oxygen-sensitive probe PtTFPP with superhydrophobic coating. The 3 to 5 nm micro/nanostructures formed from silica sol were solidified with silicone resin, which endowed the sensor film with excellent mechanical stability. The sensor film exhibits antifouling, antiabrasion, and self-cleaning properties. There is no need of mechanical brushes to clean sensor surfaces, which greatly simplifies the sensor design. Owing to the porous structure, the sensor shows high quenchability, with \( I_0/I_{100} \) of 77. All these features guarantee that the sensor could be used in harsh and dirty conditions for long-term monitoring of dissolved oxygen concentration.

INTRODUCTION

Molecular oxygen is probably one of the most important chemicals for life on earth. Continuously measuring dissolved oxygen concentration has been proven vital to many industrial areas, including fermentation, dense fish-farming, long-distance transportation of natural gases, biofuel production, biomedical bioreactors, marine research and exploration, and water quality monitoring and pollution control, to name only the major applications.1–3 In early time, dissolved oxygen is mainly measured using a Clark electrode and a Mackereth-type electrode.4 However, with decades of innovation, sensing of molecular oxygen based on luminescence quenching has become one of the major methods of choice, simply because of its high sensitivity, ease of system setup, no consumption of oxygen during measurement, and remote sensing. More importantly, as a fierce competition to the classic Clark and Mackereth-type electrodes, luminescence quenching-based optical oxygen sensors present a unique feature that they could be easily sterilized without worrying about the connecting cable. Such sensors could be glued inside the container, and signal is readout remotely outside. This becomes extremely important for fermentation and biomedical bioreactor applications, where complete sterilization is the key to prevent contamination. The concentration of dissolved oxygen has also been determined using Winkler titration (mostly in an environmental monitoring sector), which is a quantitative analytical method based on chemical reaction. However, this method is not suitable for long-term and online monitoring of dissolved oxygen because of its irreversibility in nature.

Optical sensors are composed of a luminescent sensor film, an optical fiber, and a signal analysis and readout system.5 The sensor film is the key component in optical oxygen sensors, and it always directly contacts with aqueous samples and senses variation of dissolved oxygen concentration. This method has been successfully applied in lots of fields, but is mostly used in clean aqueous solutions. However, in real applications, there are microorganisms, algae, clams, and other...
marine lives in the testing samples. Long-term use of an optical oxygen sensor film in these samples will always result in growth of algae, formation of biofilm, and adherence of shellfish, which will create a barrier for oxygen diffusion in the sensor film. In addition, metabolism of these adhered marine species also influences the local oxygen concentration nearby the sensor film, due to which the dissolved oxygen concentration in the sample could not be correctly measured. In order to prevent adherence of biofilms, algae, and shellfish on the sensing film, commercially available oxygen sensors (especially sensors used in marine monitoring buoys) are equipped with brushes to clean the sensor surface (typical products used in buoys from YSI Inc., www.ysi.com). However, the oxygen sensor materials are not wear-resistant. Continuous abrasion during the brush-cleaning process damages the sensor film and significantly reduces sensor performance and service life, resulting in increases in maintenance frequency and costs. The addition of mechanical component to drive the brush also complicates sensor design, increases sensor cost, and makes the sensor bulky and heavy.

The innovation in superhydrophobic materials provides extraordinary features that these materials could be used as coatings to create antifouling and self-cleaning surfaces. Superhydrophobic surfaces rely on the formation of a thin air layer that can decrease the attractive interactions between the surface and the liquid and are inspired from natural nonwetting structures, particularly the lotus leaf, one of green, nontoxic, non fouling surfaces. However, the major challenges of artificial superhydrophobic surfaces for practical applications are their poor mechanical robustness and difficulties in massive production. The superhydrophobic surface can be formed via the classic top-down, bottom-up, or the combination of both approaches, which require sophisticated fabrication and nanomaterial synthesis process. The assignment of micro/nanostructures on the surface of interest requires precise control of the location at a microscopic scale, which strongly restricts the massive production of the superhydrophobic surface. In addition, the orderly arranged superhydrophobic surface based on the micro/nanostructures is fragile and is highly susceptible to mechanical wear. These surfaces could be easily damaged during practical use. Notable progress has been made over the past decade, and superhydrophobic surface can now be formed via the robust sol–gel approach, which greatly simplifies the fabrication process. However, majority of fabricating superhydrophobic surfaces still rely on the adhesive layer to enhance its mechanical stability, and such a two-layer system is undesirable during practical coating. Chen and co-workers developed a large-scale fabrication method for robust hydrophobic surface coating with high rigidity and good flexibility. Superhydrophobic sol was first fabricated via a one-pot reaction, which was then mixed with silicone resin and applied directly on the surface of interest via routine coating processes. The fabricated superhydrophobic surface exhibits good flexibility, high rigidity, and good mechanical stability.

Because of the superhydrophobic nature and porous structure, superhydrophobic coating could be an ideal material for oxygen sensing because it exhibits excellent oxygen permeability. However, only few attempts have been made to use superhydrophobic coating for oxygen sensing. Mitsuishi and co-workers covalently immobilized an oxygen-sensitive probe PtTPP on an amphiphilic acrylamide-based copolymer and cast the copolymer with another fluoropolymer to form a nanoparticle-based superhydrophobic surface. The fabricated oxygen sensor film exhibited high quenchability, with an $I_0/I_{100}$ over 120, which could be attributed that the probe is directly exposed to the surface and is in direct contact with molecular oxygen. However, fabrication of the sensor requires tedious copolymer synthesis and dye labeling, and the nanoparticle-based superhydrophobic surface may easily be damaged from mechanical abrasion.

In this work, we have developed a highly sensitive dissolved oxygen sensor with excellent mechanical stability and self-cleaning capability. The sensor is composed of micro/nanohierarchical structured superhydrophobic coating that is doped with an oxygen-sensitive probe. The hierarchical structure was then solidified using silicone resin to endow the sensor film with good mechanical stability. After tape-peeling, intensive scratching, and sandpaper abrasion, the sensor film still maintains good superhydrophobic nature with contact angle (CA) larger than 150°. Owing to the porous structure and high gas permeability of silicone resin, the sensor showed excellent quenchability toward oxygen quenching with $I_0/I_{100}$ over 77. Because of its superhydrophobic property, algae, biofilms, and clams are difficult to adhere on the surface of the sensing film. This feature keeps the sensor surface clean over long-term usage, and there is no need to install cleaning brushes, which will make sensor design much simple, more energy-saving, and with largely extended service life. Moreover, the fabrication of the sensor film is very simple, and there is no sophisticated synthesis and fabrication technique involved, which could be applied for massive production.

### RESULTS AND DISCUSSION

The preparation of the sensor film is very simple and straightforward, and there is no sophisticated preparation and nanofabrication involved. Silica nanoparticles with a size of 3–5 nm were synthesized via a classic Stöber method, and their surface is then modified with γ-aminopropyltriethoxysilane (APTES) to form aggregates. These irregular shapes of aggregates form micro/nanohierarchical structures. Then, hydrophobic 1H,1H,2H,2H-perfluorooctytriethoxysilane (PFOTS) was used to lower the surface energy. Finally, the oxygen-sensitive dye PtTFPP and the hydrophobic silica sol were mixed with silicone resin to form a viscous mixture. The mixture was then coated onto a glass slide to form the sensor film. Figure 1a shows three drops of water on the sensor surface, which are perfect spherical water droplets formed with a CA of 168°, illustrating the superhydrophobic nature of the sensor surface. Low surface energy and micro/nanostructures are two essential physical ingredients to prepare the superhydrophobic surface. Figure 1c,d shows the scanning electron microscopy (SEM) images of the sensor film with small and large magnification, respectively. It is obvious that numerous silica nanoparticles are gathered together to form the micro/nanohierarchical structures. The unique structure helps trapping a thin layer of air that decreases attractive interactions between the solid surface and liquid, leading to superhydrophobicity. Besides, the sensor also exhibits a fractal-like porous structure, which is also important to enhance the hydrophobicity. In addition, the sensor surface shows a CA of 145° for methylene iodide (Figure S1 in the Supporting Information), revealing that the sensor could not only prevent contamination and adherence of marine life, but also provide excellent quenchability.
avoid adherence of organic pollutants. These properties would be very useful when the sensor was applied for oxygen monitoring in the area where accidental oil spilling happens.

Figure 2 shows the surface properties of the sensor film after continuous tape peeling, knife scratching, and sandpaper abrasions. The resistance to these external destructions, even in exceptionally harsh conditions, is important in real applications. The current major challenge for practical application is its poor mechanical robustness. To evaluate the mechanical robustness, we first implemented the tape-peeling test for the sensor film. As shown in Figure 2a, after 10 cycles of tape peeling, ignorable effects in superhydrophobicity occurred. The CA of the sensor film slightly declines from 167.6° to 165.7°, and the sliding angle (SA) slightly increases from 2° to 4°. It seems that the increases of SA are related to the decreases of CA. Continuing to 40 cycles, the sensor still reserves its superhydrophobicity. The SEM images of the sensor surface before and after 40 cycles of repetitive tape peeling indicate no obvious surface morphology change (see Figure S2 in the Supporting Information). We also performed a knife scratching test according to the ASTM standard. Figure S3 in the Supporting Information showed that the sensor was well adhered to the supporting matrix. Even after knife scratching with observable crack, the sensor surface maintains its superhydrophobic property with a CA of 162°. We further challenged the sensor surface with a sandpaper abrasion test. Figure 2c shows the schematic of the sandpaper abrasion test; the samples were placed face-down to the sandpaper (240#) under a loading of 100 g and moved along the ruler at a constant speed. A 10 cm abrasion test was defined as one cycle. As summarized in Figure 2d, the sensor preserves its superhydrophobic nature even after 40 cycles of sandpaper abrasion; the CAs were all above 150°. All this information proves the good mechanical stability of the sensor film.

The superhydrophobic sensor surface also exhibits self-cleaning capability. As shown in Figure 3, the sensor film was placed with a tilting angle of 5°, and manganese dioxide powder was put on the sensor surface as manual dirt. When one drop of water containing CuSO₄ (as colorant) slides over the MnO₂ powder, the powder dirt is removed from the sensor surface. There is no adherence and remains of dirt on the sensor surface, demonstrating that the sensor film possesses good self-cleaning capability. In comparison, the hydrophobic sensor surface without superhydrophobic property does not have self-cleaning capability, as shown in Figure S4.

We further studied the distribution of oxygen-sensitive probe PtTFPP in the sensor film. As shown in Figure S5 in the Supporting Information, elemental analysis and imaging reveal that the probes (Pt distribution) are evenly distributed in the sensor film.
superhydrophobic sensor film and there is no obvious aggregation observed. More importantly, the sensor film is semitransparent, and the rough surface could scatter excitation light, resulting in more efficient excitation of the oxygen-sensitive probe and enhanced brightness of the sensor film. Figure 4a shows the luminescence spectra of the sensor film at three different dissolved oxygen concentrations. It is obvious that molecular oxygen could efficiently quench the luminescence of PtTFPP in the superhydrophobic film. The quenchability (expressed as \( I_0/I_{100} \), which stands for the intensity measured in an oxygen-free solution and in a pure oxygen saturated solution, respectively) of the sensor reaches 77. The time trace curve reveals that the sensor could measure dissolved oxygen concentration in the range of 0–20 mg/L, which is shown in Figure 4b. The response time is less than 6 s. (The response time is defined as the time required for the intensity to decrease to 90% of the equilibrium value. Note that the response time is measured in gas phase, as it is difficult to control the filling time of the flow-through cell, Figure S6 in the Supporting Information.)

The high quenchability and fast response could be attributed to the porous structure of the sensor film and good gas permeability of silicone. Such kind of porous silica structure has been proved to be a good matrix for highly sensitive oxygen sensors. The sensor response is fully reversible, which guarantees monitoring of oxygen concentration variation over long term. The almost linear Stern–Volmer plot shown in Figure 4c further proves that the oxygen-sensitive probes are uniformly distributed in the sensor film. The Stern–Volmer constant is 2.65 L/mg. The linear calibration curve is beneficial for two-point calibration and significantly simple sensor calibration process and data analysis.

More importantly, the sensor shows excellent photostability as shown in Figure 4d. The sensor was exposed to intense illumination at 395 nm with a power density of 13.2 W/m²; there is no more than 10% of intensity loss after 1 h of exposure. In addition, the sensor film is fully compatible with a commercial optical oxygen meter, which uses much weaker illumination from light-emitting diodes and measures phase difference rather than luminescence intensity. The influences of photobleaching on sensor performance could be easily eliminated. All these features confirm that the sensor has good quenchability, fast response, and good stability, which is suitable for long-term monitoring of dissolved oxygen.

The sensor film was finally tested for its antifouling property. We have compared the adherence of Navicula pelliculosa on four different surfaces, including polydimethylsiloxane (PDMS), polystyrene, polyethylene terephthalate (PET), and the superhydrophobic sensor film. All the films were immersed in a suspension of Navicula pelliculosa for 48 h and then their surfaces were washed with water. After drying at room temperature
temperature, the *Navicula pelliculosa* on the surface was imaged via autofluorescence of chlorophyll on the fluorescence microscope. The chlorophyll was excited in the wavelength range of 595–645 nm, and the emission was recorded in the range of 665–715 nm. Figure 5 shows the overlay images of bright-field image and autofluorescence image of adherence of *Navicula pelliculosa* on different surfaces after 48 h of incubation. (a) Superhydrophobic sensor film. (b) PDMS sensor film. (c) Polystyrene sensor film. (d) PET support.

Figure 5. Overlay images of bright-field image and autofluorescence image of adherence of *Navicula pelliculosa* on different surfaces after 48 h of incubation. (a) Superhydrophobic sensor film. (b) PDMS sensor film. (c) Polystyrene sensor film. (d) PET support.

bright-field image and autofluorescence image of *Navicula pelliculosa*. Results show that *Navicula pelliculosa* could adhere to all surfaces tested. Statistic results show that there are 40 ± 16.2, 1760 ± 165.1, 1346 ± 369.9, and 786 ± 136.8 *Navicula pelliculosa* per square millimeter attached on the superhydrophobic sensor film, PDMS, polystyrene, and PET support, respectively. Obviously, the superhydrophobic sensor film exhibits much less attachment of *Navicula pelliculosa*. Close observation could conclude that *Navicula pelliculosa* is mainly trapped in the hole of micro/nanostructure and could easily be washed away with repetitive washing steps. However, the adhered *Navicula pelliculosa* on PDMS, polystyrene, and PET surface attached firmly and could not be easily removed via a simple washing step. These results further demonstrate that the superhydrophobic sensor film shows excellent antifouling property.

**CONCLUSIONS**

We have developed a highly sensitive oxygen sensor film with good mechanical stability and antifouling and self-cleaning properties. The sensor film was simply fabricated by doping the oxygen-sensitive probe PtTFPP in superhydrophobic sol suspension and cast along with silicone resin to form superhydrophobic micro/nanoarchitectural structures. Because of the unique porous structure, the sensor film shows fully reversible response toward oxygen quenching, and quenchability (expressed as I/I0) is as high as 77. The oxygen-sensitive probes are firmly encapsulated and uniformly distributed inside the hydrophobic coating so that they do not leach and aggregate. Extensive wear-resistant tests (including continuous tape peeling, knife scratching, and sandpaper abrasions) prove that the sensor film has excellent mechanical stability. More importantly, the sensor film shows excellent antifouling and self-cleaning properties, on which the formation of biofilms and adherence of clams and other marine lives could be minimized. Because of its simple fabrication procedure, this kind of superhydrophobic sensor film could be massively produced. The antifouling and self-cleaning properties of the sensor film greatly simplifies sensor design. A compact sensor could be fabricated without using mechanical cleaning brushes, which significantly reduces sensor cost, maintenance frequency and cost, and extends sensor service life. All these properties endow that the sensor film could be used in harsh and dirty conditions and for long-term monitoring of oxygen concentration without worrying about the influences of surface contamination.

**EXPERIMENTAL SECTION**

**Materials.** All reagents were commercially available and used as received without further purification. PFOTS, tetraethoxysilane (TEOS), APTES, and absolute ethanol were provided by Aladdin-Reagent Co., Ltd., Shanghai, China. Ammonium hydroxide (≥25 wt %, NH3·H2O) was obtained from Jiangu Tong Sheng Chemical Reagent Co., Ltd. The oxygen-sensitive probe PtTFPP was synthesized by Heowns Inc (www.heowns.cn, Tianjin, China). The methyl silicone resin was purchased from High Chemical (Shanghai) International Trade Co., Ltd., China. The PDMS was purchased from Wacker (http://www.drawin.com). Toluene was obtained from Tansoole (http://www.tansoole.com). Polystyrene (average MW 260 000) was bought from J&K Chemical Ltd. (http://www.jkchemical.com). A transparent PET film was obtained from Goodfellow (http://www.goodfellow.com). *Navicula pelliculosa* (10⁶ cells/mL) was purchased from Freshwater Algae Culture Collection at the Institute of Hydrobiology (FACHB, algae.ihb.ac.cn).

**Coating Preparation.** Preparation of Coating Solution. First, H2O (2.14 g), NH3·H2O (0.152 g), and TEOS (1.56 g) were dissolved in 25 mL of anhydrous alcohol. After the solution was stirred 3 h at 40 °C, its pH was adjusted to 4 by dropping acetic acid. Second, APTES (0.15 g) was added to the above solution and then stirred 40 min at 40 °C. Then, PFOTS (0.33 g) was added. The solution was stirred for 2 h at room temperature to form solution A. Lastly, PtTFPP (5 mg) was dissolved to anhydrous alcohol (0.5 mL) to form solution B.

**Preparation of Superhydrophobic Coatings.** Prior to coating treatment, solutions A (6 g) and B (1 mL) and methyl silicone resin (1 g) were mixed together at room temperature to form a coating solution. The samples were flowed with the as-prepared coating solution and then cured at 80 °C for 2 h.

**Antifouling Test.** The initial density of *Navicula pelliculosa* for antifouling test was 10⁶ cells/mL. The temperature of cultural media was controlled at 25 °C. For comparison, PDMS sensor film, polystyrene film, and bare PET foil were tested for their antifouling properties. The concentration of PtTFPP was 2 mg/mL in ethanol. The PDMS sensor film was prepared by mixing PDMS (0.5 g/mL in toluene) and PtTFPP solution at a volume ration of 4:1. The formed viscous mixture was spread onto the transparent PET support using a homemade knife-coating device with a wet thickness of 125 μm. Polystyrene sensor film was prepared in the same way. The only difference is that the concentration of polystyrene solution is 10% (w/w) in toluene. The thickness of all dried sensor layers was around 4 μm.

**Characterizations.** SEM was performed to determine surface morphology using a HITACHI S4800 Field Emission Scanning Electron Microscope.
SEM at an accelerating voltage of 5 kV. Before being imaged, the samples were sputtered with a thin layer of Au. The element distribution was analyzed by energy-dispersive X-ray analysis. The water CAs and SAs were measured by using an optical CA measuring device (DSA100, Kruss, Germany). The CAs are the mean of three independent measurements with 5 μL of water or 2 μL of methyl iodide on different locations applying a Young–Laplace fitting. The surface-free energy was calculated by the software in DSA100 based on the water (polar) and methylene iodide (nonpolar) CAs. To measure the SAs, the slides were tilted step by step (1°) with respect to the horizontal plane until a water droplet starts to slide along the surface.

Surface robustness includes tape peel tests and sandpaper abrasion tests. Two kinds of tape peel tests were employed according to the previous literature. First, repetitive tape application and peel-off cycles were applied by rolling a 4 kg steel roller. After each 10 cycles, water CA and SA were measured. Second, the surface adhesion was tested using the ASTM standard. In this test, 11 cuts are made in two directions using a knife at right angles to each other to form a grid of small squares. A 3 M adhesive tape is applied over the grid and removed by pulling in a single smooth action. For sandpaper abrasion tests, the treated coating was placed face-down to the sandpaper (grit no. 240) and was moved 10 cm along a ruler at a constant speed under a 100 g load. The 10 cycle sandpaper abrasion tests, the treated coating was placed face-down to the sandpaper (grit no. 240) and was moved 10 cm along a ruler at a constant speed under a 100 g load. The 10 cm abrasion test was defined as one cycle. After each cycle, the water CA was measured.

The response of the sensor film to dissolved oxygen was conducted using a homemade flow-through cell (Figure S6 in the Supporting Information). The concentration of dissolved oxygen was controlled by saturating distilled water with a premixed synthetic gas. The oxygen concentration in the synthetic gas was precisely controlled by two mass flow controllers (Red-Y, http://www.voegtlin.com, Switzerland). The sensor film was fixed in the flow-through cell, and excitation light at 395 nm was guided to the cell via a Y-shape optical quartz fiber. The measured illumination intensity at the fiber tip was 0.26 mW. The red emission of the sensor film was guide back via the same fiber and the luminescence intensity is measured on the fluorospectrometer (Hitachi F-7000, Japan). The excitation and emission slits were both set at 5 nm. The voltage of the photomultiplier tube in the fluorospectrometer was set at 400 V.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02464.

CA of sensor surface with methylene iodide; SEM images of sensor surface after repetitive tape application, peel-off cycles and sandpaper abrasion tests; cross-hatch tape peel test; self-cleaning test on hydrophobic PDMS sensor surface without superhydrophobic property; element distribution of the sensor surface; scheme of homemade flow-through cell for sensor characterization; and bright-field and autofluorescence image of Navicula pelliculosa in chemical shift imaging medium (PDF)

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Notes

The authors declare no competing financial interest.

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