Communications

Reversible Optical Sensor Strip for Oxygen**

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Oxygen sensors have attracted great attention in recent years because of their extensive applications in oceanography, meteorology, biology, environmental science, and life science.[1] Up to now, many oxygen sensors based on pressure, electrochemistry, and photochemistry have been made for accurate quantitative determinations.[1] However, sophisticated scientific instruments with complicated data-collecting and -processing systems are required, and thus the high costs and the requirement for a professional operator severely limit their usage. Following the first report of a novel luminescence-based colorimetric oxygen sensor with a "traffic light" response,[2] a new approach has been available for colorimetric oxygen determination without the need for additional measuring instruments. However, the complicated relationship between apparent color and oxygen concentration makes quantitative determination difficult without the assistance of intricate data processing. Furthermore, several disadvantages, including low resolution, high cost, the lack of simultaneous excitation at a single wavelength, and not fully achieving diverse color change according to different usage, limit the application of this approach.

Herein, we report the development of a novel optical sensor strip for oxygen based on cadmium telluride (CdTe) quantum dots (QDs) and [*meso*-tetrakis(pentafluorophenyl)-porphyrinato]platinum(II) ($PtF_{20}TPP$), which achieves col-orimetric oxygen determination with precise, distinct, and tunable color. An additional advantage of this oxygen sensor is that the strip is reversible in its response and, therefore, can be used many times.

Figure 1 shows a diagram and scanning electron microscopy (SEM) image of the reversible optical sensor strip for oxygen. $PtF_{20}TPP$ ($\lambda_{em,max} = 648$ nm, red),[3] which was chosen as the oxygen-sensing probe, was embedded in an organically
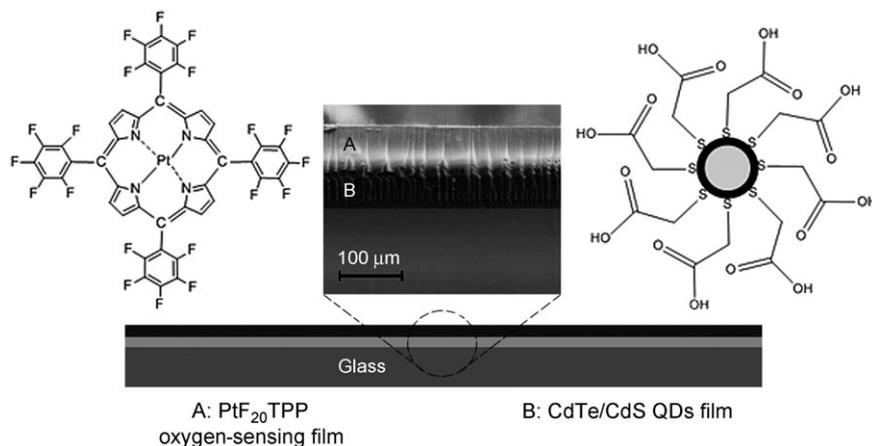
**Figure 1.** Construction of the optical sensor strip for oxygen.

A: $PtF_{20}TPP$ oxygen-sensing film

B: CdTe/CdS QDs film

modified silica (ormosil) matrix[4] and is indicated by "A" in the SEM image. To facilitate colorimetric oxygen determination, a layer of background color "B" was then designed underneath the oxygen-sensing layer. To achieve a diverse change in color, quantitative oxygen determination, and simultaneous excitation at a single wavelength, the materials for the background color were critical.

Many inorganic QDs have a narrow and symmetric photoluminescence, which is color-tunable by simply controlling the size, a wide excitation wavelength, and are cheap, and were therefore one of the best choices. Water-soluble CdTe QDs are ideal fluorophores because of their unique optical properties and ease of scale-up,[5] and have been widely used as a consummate toner for multicolor sensing and encoding.[6] To embed the water-soluble CdTe QDs[7] under the oxygen-sensing layer, but to avoid the aggregation of QDs and their solution into the water during oxygen determination, a modification of Murase's method[8] was developed. Tetraethoxysilane (TEOS; 1.0%, v/v) in a solution of (3-aminopropyl)trimethoxysilane (APTMS) in methanol was introduced during the preparation of the background color layer of CdTe/CdS core-shell type QDs, as TEOS can cross-link with APTMS to form a relatively stable net structure that prevents the prepared films from being damaged in aqueous solution.

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Figure 2 shows the response of the sensor towards various concentrations of oxygen. Under different oxygen concentrations, the sensor displayed distinguishable colors with a resolution up to 0.50%, which could be identified with the naked eye or a charge-coupled device (CCD) camera. The
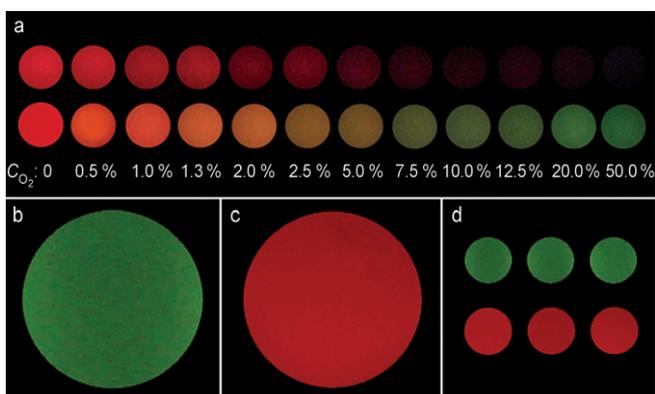
Figure 2. a) Apparent colors of the prepared sensor, with (bottom) and without (top) a layer of QDs, in different concentrations of oxygen. b) Distribution of QDs in the sol–gel layer. c) Distribution of $PtF_{20}TPP$ in the ormosil layer in a nitrogen-only environment. d) Chroma of three sensing films prepared in different batches at 25.3 °C.

change of color originates from the change in fluorescence intensity of the oxygen-sensing layer (Figure 3). Ordinarily, the naked eye has limited resolving power towards intensity change in homochromatism (ca. 64 grades), but has high sensitivity in the identification of color change (ca. 10 million
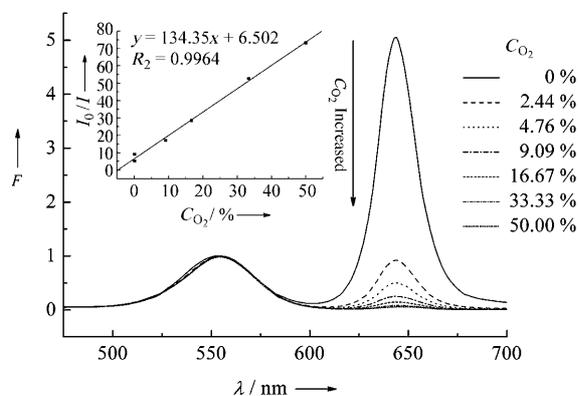

Figure 3. Response of the sensor towards various concentrations of oxygen at 25.3 °C.

color types). Without the green background emitted by the layer of QDs, the naked eye has low resolution towards the fluorescence intensity change of $PtF_{20}TPP$, even when this has no signal in high oxygen concentrations (Figure 2 a).

Figure 3 also shows that the CdTe/CdS core–shell QDs presented excellent stability under different oxygen concentrations (relative standard deviation (RSD) of 1.0%, $n = 10$). This could be attributed to the rigid matrix and the existence of the CdS shell, which prevented the QDs from aggregating

and being oxidized. $PtF_{20}TPP$, on the other hand, presented high sensitivity towards oxygen. Its fluorescence intensity F was reversibly modulated by different concentrations of oxygen, which correlated well with the Stern–Volmer equation (inset in Figure 3). Such a stable background color intensity and linear relationship between the concentration of oxygen and the fluorescence intensity of the $PtF_{20}TPP$ sensing layer assured a precise and quantitative determination of oxygen. Furthermore, the change in color of the oxygen sensor from green to red, which indicates a decrease of the concentration of oxygen in the environment, is well known to the public and easily draws people's attention.

Uniform distribution of QDs and $PtF_{20}TPP$ in the sensing film was an important factor because it directly affected the generation of a homogeneous color. As the SEM image in Figure 1 shows, both the QD and oxygen-sensing layers had a rigid, dense structure with uniform thickness. Figure 2b and c indicate that the fluorophores were incorporated homogeneously in the whole range of the sensing film. Both the chroma of three sensing films prepared in different batches (Figure 2 d) and the fluorescence intensities with an RSD < 15% confirmed that the construction process used for producing uniform sensing films was reproducible.

As oxygen sensors are prone to the influence of temperature, the effects of temperature on the QD layer, oxygen-sensing layer, and apparent color were systematically investigated. As shown in Figure 4 a, the luminescence intensity of
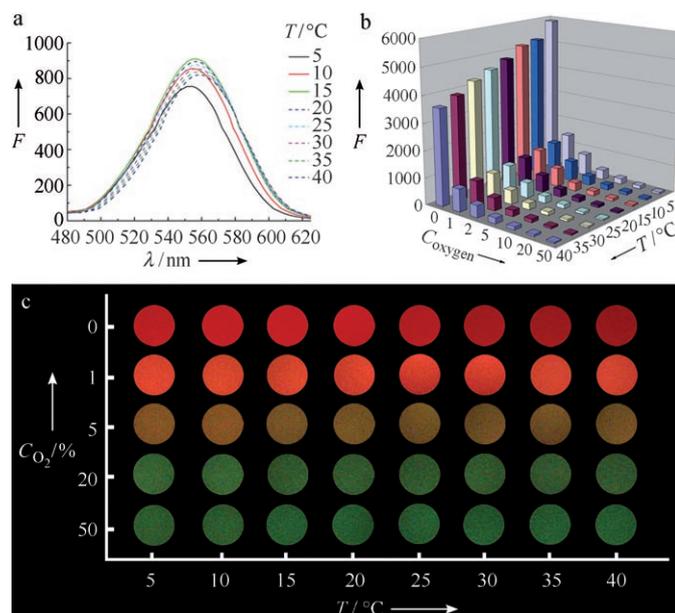
Figure 4. Effects of temperature on the a) QD layer, b) oxygen-sensing layer, and c) apparent color.

the QD layer presented a slight but abnormal dependence on temperature. The temperature quenching of the luminescence of the QDs above 15 °C was reversed to temperature antiquenching[9] below 15 °C. This was accompanied by a slight red shift of the spectrum with increasing temperature, which could be attributed to inter-QD dipole–dipole inter-

actions.[10] Figure 4b shows the variation in fluorescence intensity decay with temperature as a function of oxygen concentration in the oxygen-sensing layer. In a nitrogen-only environment, the oxygen-sensing layer exhibited obvious thermal quenching but, with increasing oxygen concentration, even for a small amount of oxygen (1.0%), this quenching effect became tenuous.

Comparison of a combination of these two effects with the apparent color of the prepared oxygen sensor (Figure 4c) indicated that temperature had an inconspicuous influence at various oxygen concentrations at the resolution employed, but at much higher resolution, temperature effects should be taken into account. In consideration of this temperature influence, dual sensors with automatic compensation for the temperature effect have been developed.[11] In our study, there was a relationship between the temperature behavior of the QD layer and the oxygen-sensing layer, and so the temperature effect could also be calibrated for the precise, quantitative determination of oxygen.

It should be mentioned that the prepared QD layer presented good stability in both ambient and aqueous media. After being kept in darkness for two months, no obvious decrease in luminescence intensity was found. In aqueous media, the stability of the QD layer increased from 30 min to 48 h as a result of the addition of TEOS in comparison with that by Murase's method. By covering the QD layer with ormosil, the fluorescence intensity of the QDs lasted for more than a week. Furthermore, it has been proved that the prepared sensor possesses a good reversibility. After continuous usage in an oxygen atmosphere for ten cycles, 96.8% of the fluorescence intensity in oxygen-free circumstances can be recovered.

In summary, we have fabricated a novel reversible optical sensor strip for oxygen. The sensor could be applied both in rapid colorimetric oxygen determination with high resolution and in quantitative oxygen determination, in which the QDs performed as an internal fluorescence standard. We believe that portable devices with a warning function could be developed and used to monitor oxygen in dangerous places (such as mines, the deep sea, and oxygen-free preservation). Furthermore, based on the above principle, a range of gas, temperature, pH, or ion sensors could be developed.

Experimental Section

Core–shell QDs: Thioglycolic acid (TGA)-capped CdTe/CdS core–shell QDs were synthesized by following the literature method.[12] Typically, $CdCl_2 \cdot 6H_2O$ (0.02 mol) was dissolved in ultrapure water (100 mL, 18.2 MΩ) followed by addition of TGA (0.048 mol). The pH value of the solution was adjusted to 9–10 with NaOH (1.0 mol L^{-1}). The Cd precursor solution was then deaerated for 30 min. Under stirring, NaHTe (0.01 mol) solution, which was obtained from the reaction of Te powder and $NaBH_4$, was pressed into the Cd precursor solution by a nitrogen flow, then the mixture was refluxed and the particle size was controlled by the reflux time. The prepared CdTe QDs were illuminated under sunlight to form the CdS shell and enhance the fluorescence.

CdTe QD layer: TEOS (100 μL) was introduced to a solution of APTMS (10 mL) in methanol at a molar ratio of 1:50, followed by ultrapure water (2 mL), and the mixture was stirred for 1 h to promote hydrolysis. The mixture was kept for 48 h in an incubator at (30 ± 0.2)°C, then a solution (1 mL) of CdTe/CdS core–shell QDs ($\lambda_{em,max} = 552$ nm) and Cd precursor solution (0.3 mL) were added. The mixture was stored again in the dark in an incubator at (30 ± 0.2)°C for 4 h, then a glass slide (48 × 12.4 × 0.9 mm^3) was dipped into the mixture (60 μL) to obtain a layer of QDs. The prepared glass slides were dried in darkness in the same incubator.

Oxygen-sensing layer: This layer was prepared according to the previous description.[4] Typically, tetramethoxysilane (1.0 mL) and dimethoxydimethylsilane (1.8 mL) were placed in an open vial. The mixture was magnetically stirred for approximately 1 min, then hydrochloric acid (1.5 mL, 0.01 mol L^{-1}) was added. The vial was immersed in a water bath at 60°C and the mixture stirred for about 3 h. The emulsion formed during this step (0.4 mL) and $PtF_{20}TPP$ (0.1 mL, 2.0 g L^{-1}) in THF were mixed and vigorously stirred for 20 min to ensure homogenization. The mixture (40 μL) was dip-coated onto the surface of the QD layer to form an oxygen-sensing layer.

Characterization of the prepared sensor: Fluorescence profiles were obtained from a Hitachi F-4500 fluorometer. A light-emitting diode with a maximum wavelength of 395 nm was used to excite the QDs and $PtF_{20}TPP$. A 1-cm cuvette holder with a 450-nm filter was employed as the fluorescence imaging system (Ocean Optics Inc., USA). A Nikon D300 CCD camera was used to record chromophotographs. A scanning electron microscope (LEO1530, Leo, Germany) was used to obtain images of the oxygen sensor. Temperature was controlled by a Julabo F12-ED refrigerated/heating circulator (Julabo Inc., Germany).

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