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COMMUNICATION

Chameleon clothes for quantitative oxygen imaging†

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We fabricated a chameleon cloth which changed its vivid colours at different oxygen concentrations under ultraviolet excitation. Combined with a photographing technique, the chameleon cloth possesses the ability for real-time quantitative imaging of oxygen distribution, which could be used for quick location of dangerous oxygen-deficiencies and oxygen-free regions.

Oxygen is the most essential gas for supporting life on earth. Quick and fast real-time monitoring of oxygen-deficient areas and even oxygen-free regions to avoid potential danger has great implications in our daily life, especially in food packaging,[1] mineral mining, polar expeditions, high altitude and deep cave adventures, and even in aviation[2] and space exploration. Quite recently, oxygen has been detected *via* colorimetric assays based on dual-colour systems[3–7] rather than the conventional instrumental analysis,[2,6,8–11] these systems greatly reduce measurement cost, simplify the assay and equipment, and most importantly, make real-time oxygen level monitoring by the naked eyes become possible. However, colorimetric oxygen sensors could only achieve semi-quantitative measurement and are not precise enough for real-time oxygen monitoring in daily life. The precise and real-time quantitative measurement of oxygen still strongly relies on instrumental analysis and complicated data-processing. Previously, although we have combined colorimetric oxygen sensors with photographic technology,[12–15] and have successfully achieved fast and real-time quantitative imaging of oxygen, several factors limit wide spread daily usage, such as 1) the requirements for special excitation lamps and the corresponding optical filters; 2) the inhomogeneous dye distribution causing chromatic aberration and system error; 3) rigid shape and relatively weak luminescence; and 4) the release of harmful chemicals from the sensing films.[16] In order to solve these problems, in this study, we constructed a kind of flexible chameleon cloth for oxygen monitoring. As shown in Fig. 1(A), when excited with a small hand-held UV-LED (λ_{max}, 365 nm), the oxygen-exposed chameleon cloth displayed very bright luminescence and vivid colour. Combined with the photographic technique,[12–15] quantitative oxygen imaging could be simply and rapidly achieved by just taking a picture of the chameleon cloth.

The chameleon cloth was constructed using two different colour dyes: a blue stilbene dye (4,4-bis(2-benzoxazolyl) stilbene, reference signal) and an oxygen-sensitive red emitting dye (platinum octaethylporphyrin, PtOEP). These dyes were encapsulated in polystyrene microparticles with diameters around 2–3 μm, and they were coated onto a piece of cloth which did not contain any fluorescent brightener to obtain the chameleon cloth. Fig. 1(A) shows the apparent colour of the chameleon cloth exposed in air when excited using the UV-LED. The chameleon cloth presents bright luminescence and vivid purple colour. When it was exposed to a stream of nitrogen, its apparent colour around the nitrogen flow became reddish, and showed an obvious gradient in the colour distribution. Since the dual emissions (Figure S1 in supporting information†) from PtOEP and 4,4-bis(2-benzoxazolyl) stilbene could totally match the blue and red channels of a commercially available complementary metal oxide semiconductor (CMOS) camera (Figure S2†), it is possible to apply the previously described photographic technique[12–15] to achieve quantitative oxygen distribution imaging. As depicted in Fig. 1(B), the gradient oxygen distribution around the nitrogen flow is clearly presented, and the precise oxygen concentration at any position could be simply and easily read out after processing using the photographic technique.[12–15] The quantitative oxygen distribution imaging gives more detail compared with the colorimetric readout (Fig. 1(A)), the

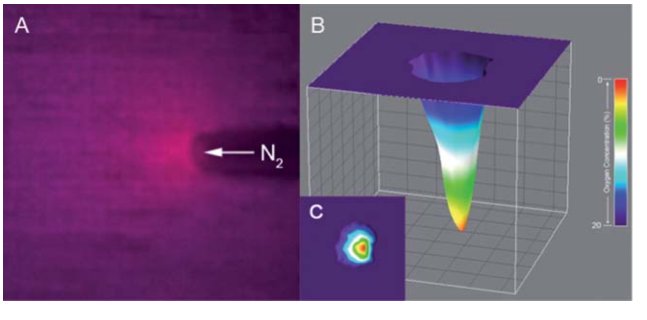

Fig. 1 (A) Apparent colour of the prepared chameleon cloth exposed to a flow of nitrogen in air; (B) Quantitative imaging of oxygen distribution using photographic technique[12–15] (corresponding to Fig. 1(A)); (C) Top-view of Figure 1(B) shows the oxygen deficiency range and oxygen-free area.

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oxygen deficiency range and oxygen-free area (Fig. 1(C)) could be precisely located. This characteristic will be helpful for the quick monitoring of oxygen levels and locating dangerous places.

The apparent colour change of the chameleon cloth around the nitrogen flow originated from the intensity change of the dual-emission (Figure S1†). The blue fluorescence of the stilbene dye presented no response to oxygen, and its intensity remained the same at different oxygen concentrations. However, the platinum porphyrin complex was very sensitive to oxygen, and its red emission gradually decreased with increasing oxygen concentration. Through mixing the stable primary blue colour background with different intensities of primary red colour emission, new colours were produced. When the chameleon cloth was exposed to atmospheres containing different concentrations of oxygen, it displayed different vivid colours (Fig. 2). The colour gradually changed from red to purple to blue with increasing oxygen concentration, and displayed a distinguishable colour change with a resolution up to 1.0%. Using the naked eye, the detection range was from 0 to 60% oxygen partial pressure.

Since both the dyes could be effectively excited using a 365 nm UV-LED (Figure S3†) and the UV excitation was invisible to the naked eye and the CMOS chip (Figure S2†), the bright blue and red emissions from the two dyes were located in the visible region, and so no additional optical filters or focusing lenses were needed. This characteristic could effectively avoid the influence of scattered excitation light, simplify the apparatus setup and reduce the measurement cost. Furthermore, without using any additional optics, precise and quantitative oxygen distribution could be simply imaged using a digital camera equipped with a UV flash lamp as the excitation source. This oxygen sensing approach is nearly ready to be made accessible to anybody, which would advance daily oxygen monitoring to a large extent.

To obtain bright luminescence and a vivid apparent colour, high concentrations of dyes are usually applied. However, most dyes tend to self-quench or even aggregate when their concentrations are too high.[17] In order to prevent concentration quenching, and to enhance the brightness of the chameleon cloth as well as ensuring its safety for daily use, micro-size polystyrene particles were synthesized and used to encapsulate both dyes. The scanning electron microscope images of the oxygen-sensitive polystyrene microparticles clearly revealed that the particle size was around 2–3 μm, with very uniform size, and mono-dispersed without any aggregation (Fig. 3(A) and 3(B)). The hydrophobic polystyrene microparticles were not easily dispersed in water, perspiration or body fluids, and the two hydrophobic dyes were firmly encapsulated inside the polystyrene microparticles, thus blocking their cell penetration and making them very safe even when in direct contact with the skin in daily use. The fluorescence microscope images (Fig. 3(C) and 3(D)) show that both the stilbene dye and the oxygen-sensitive dye were successfully encapsulated inside the particles and displayed bright and uniform colour. This characteristic ensures that each particle gives the same colour under a certain oxygen concentration and further avoids the chromatic aberration caused by inhomogeneous dye distribution. When the oxygen-sensitive polystyrene particles were coated on a flexible supporting material (such as cotton cloth without fluorescent brightener) at a high concentration, these mono-dispersed particles would successfully prevent dye aggregation and concentration quenching, and result in the oxygen-sensitive chameleon cloth presenting bright luminescence and vivid colours under UV excitation. It should be mentioned that both the blue and the red luminescence were emitted from the same oxygen-sensitive polystyrene microparticles, thus, the inaccuracy caused by distance-dependent luminescence intensity decay could be removed by using the blue emission as a reference. This could effectively enhance measurement accuracy and enable oxygen sensing on irregular surfaces.

Since the oxygen-sensitive polystyrene microparticles emit bright luminescence under an excitation source, we could not only fabricate wearable chameleon clothes for oxygen sensing, but also construct oxygen-sensitive markers on wearable clothes. We tried to coat these oxygen-sensitive microparticles onto a spool of cotton thread, and further embroidered the thread onto a piece of cloth to obtain an oxygen-sensitive cloth marker, the "O_2" character shown in Fig. 2(A) and 2(B). When excited with the 365 nm UV-LED, the oxygen-sensitive marker presented bright red luminescence in oxygen-free conditions and a vivid blue colour in a pure oxygen atmosphere

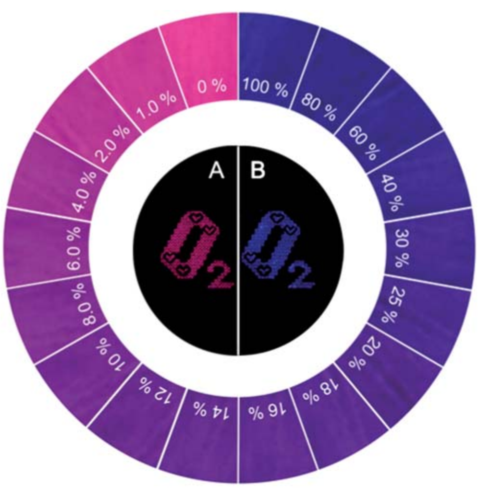

Fig. 2 Apparent colours of the chameleon cloth at different oxygen concentrations. (A) real picture of the chameleon cloth marker exposed in an oxygen-free environment; (B) real picture of the chameleon cloth marker under UV excitation in pure oxygen.

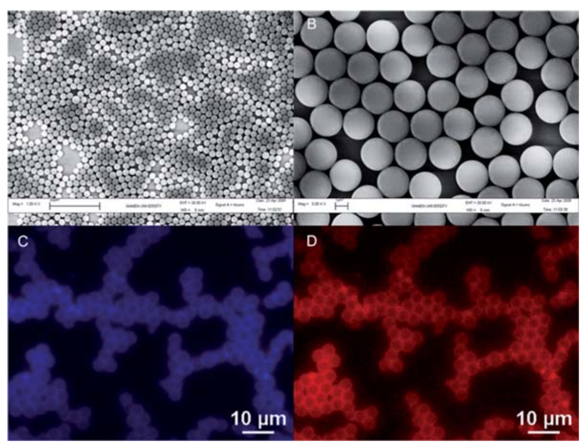

Fig. 3 Scanning electron microscope images of the oxygen-sensitive polystyrene microparticles at low (A) and high (B) magnification; and fluorescence microscope images of the oxygen-sensitive polystyrene particles: (C) the blue emission of the stilbene dye, (D) the red emission of the PtOEP oxygen probe in air.

(Fig. 2(B)). Using these markers, the oxygen level could be rapidly and simply read out *via* both semi-quantitative colorimetric and quantitative photographic methods.[12–15]

For daily use, the photostability, response time and physical stability of the chameleon cloth are also important parameters and should be taken into consideration. Our results showed that both the stilbene and PtOEP dye had very good photostability (Figure S5†). When the chameleon cloth was continuous exposed to sunshine for seven days (Figure S6†), both the dyes show photobleaching but at similar rates, which could ensure the fluorescence intensity ratio (I_{642}/I_{435}) remains nearly identical and guarantee the measurement accuracy. The dye-loaded polystyrene microparticles presented outstanding oxygen permeability, short response time (around 2 s from N_2 to O_2, the video is shown in supporting information) and excellent reversibility (Figure S7†). After immersion of the chameleon cloth in water for 24 h or washing using detergent, as shown in Figure S8,† neither obvious particle leakage nor change of the apparent colour could be found under UV excitation. This result further proves that the oxygen-sensitive chameleon cloth has very good physical stability. All these features ensure that the chameleon cloth could be an ideal sensing material for fast and real-time monitoring of oxygen deficiency and oxygen-free regions in daily use.

This oxygen-sensitive chameleon cloth could not only be used for fast oxygen level estimation, but also for quantitative oxygen determination using analysis instruments. The stilbene dye had no response to oxygen, which could be taken as a reference signal for quantitative ratiometric oxygen determination, and further eliminate the influences of light-source and transmission intensity fluctuation, spatial distance induced signal attenuation, photodecomposition of probes, inhomogeneous dye distribution and scattered light.[18,19] The prepared chameleon cloth showed a very good linear relationship between I_0/I (where I_0 is the fluorescence intensity of PtOEP in oxygen free environment, I is the fluorescence intensity at different oxygen concentrations) and oxygen concentration, which fitted well with the Stern–Volmer equation from 0 to 100% oxygen partial pressure (Figure S4†).

Conclusions

In summary, we have fabricated a colour-changing chameleon cloth with a reversible colour change for oxygen monitoring and imaging. The oxygen-sensitive chameleon cloth presents bright luminescence, vivid colour, fast response, good photostability, and high physical stability. Oxygen concentration could be easily and directly read using the naked eye without any assistance from optics. The bright emission also enabled quantitative oxygen monitoring and imaging based on ratiometric[18,19] or photographic methods.[12–15] Owing to the lightness, softness and flexibility of the cotton cloth, this chameleon cloth could be easily attached to clothes or moulded into different shapes for fast positioning or real-time monitoring of oxygen-deficient and oxygen-free regions. Furthermore, it is also possible to use simpler devices (such as mobile phones,[20] web cameras[21] and even CCTV systems) for real-time monitoring of oxygen-deficient regions to warn of any potential danger.

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