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Fast-response oxygen sensitive transparent coating for inner pressure ratiometric optical mapping†

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In this work, dual-luminophore self-referenced pressure sensitive paint (PSP) was prepared with siloxane precursors by using copolymerizable silane-functionalized carbon dots (SiCDs) as a reference probe and a newly synthesized silane-modified ruthenium complex (Ru-silane) as the sensitive probe respectively. The PSP is fully sprayable in the preparation of bi-layer thin coatings *via* a sol-gel process, by which a SiCD copolymerized silicone base layer was firstly constructed and subsequently covered by a Ru-silane grafted top layer. The resultant optical sensor is transparent, having a transmittance as high as 80%, besides the chemical bonding of the probes had favorably improved the stability of the luminescence properties. Based on the oxygen quenching mechanism, such transparent PSP coatings allowed efficient determination of the sudden changes of surface pressure in an inner flow channel with a time response of 1.3 ms, while the measurement can be performed from either the front side or the reverse side of the coating. Furthermore, the 2D pressure map can be quantified by calculating the intensity ratio of SiCDs to Ru-silane photoluminescence and thereby improved the accuracy of the measurement. We thus expect the transparent PSP coatings to be a useful tool in remote pressure and oxygen sensing in various fields, such as aircraft design and healthcare.

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Introduction

Remote monitoring of surface pressure distribution is of importance in various fields such as industrial manufacture, healthcare and especially aircraft design.^{1–3} Compared to the measurements based on the induced change in resistance, capacitance or piezoresistivity,^{2,4} where it requires the inclusion of an electrode, optical methods attract more attention because of the easy processability, cost-effective fabrication and moreover, the option of performing non-invasive measurements.^{5,6} In addition, optical sensing of pressure also allows a swift mapping of the distribution on a surface, without limitation to the topology.^{7,8} Among the

optical systems, the pressure-sensitive paint (PSP) technique was developed for getting a coating consisting of an oxygen sensitive probe in an oxygen-permeable polymer matrix, namely the binder, and was applied for full-field pressure measurement in aerospace research on aircraft model surfaces by the mechanism of oxygen quenching of photoluminescence.^{9–12} Meanwhile, such coatings have also been utilized for oxygen sensing.^{5,13,14} For observation, it is common and easy to have both the excitation light source and the imaging devices placed in the front of the sensor layer. Nonetheless, there are also many application scenarios, like the measurement of inner flows¹⁵ or the test of oxygen concentration in a package,^{16,17} which require that the observation equipment are arranged on the back side, indicating that in these cases, the sensor layer, as well as the substrate, should be at least transparent. However, this was rarely achieved owing to the low transmittance of most of the oxygen/pressure sensitive coatings.¹⁵

Meanwhile, in order to decrease the response time of PSP, such as to suit the needs of unsteady aerodynamics investigation,³ fast PSPs were prepared most commonly by the addition of ceramic nanoparticles into the polymer matrix, or by the fabrication of electrospun films, under the strategy of reducing the distance between the probe molecules and the solid-air interface to favour the penetration of oxygen to meet the luminophores.^{13,18}

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Such a strategy actually infers that the measurement will gain the fastest response if the probe molecules are anchored directly onto the substrate surface, so that the oxygen molecules can collide with the luminophores without any delay.^{13,19} However, to date, the construction of a homogeneous mono-layer of probe on a smooth substrate has been a challenge *via* physical absorption routes, especially on a surface with complex geometries.²⁰ The low specific surface area and weak interaction hampered the loading of dye molecules with high and uniform density to gain acceptable emission strength for the imaging. An alternative attempt is the application of semi-transparent porous substrates. Peng *et al.* tested the utility of anodized aluminumoxide membranes, having a thickness of 50 μm , to prepare PSP by the absorption of an oxygen sensitive ruthenium complex as the probe. However, the PSP membranes exhibited only 30% to 70% of transmittance from 400 to 700 nm.¹⁵ On the other hand, the increase of surface roughness might cause a notable difference to the pressure distribution during an aerodynamic measurement.²¹ Therefore, the development of PSP coatings that have both smooth and transparent characteristics becomes a key issue for exploiting the application of the PSP technique, in particular to the applications on inner surface pressure measurements. Compared to physical adsorption, by which the migration and aggregation of the luminophores will frequently happen, chemical grafting of dye molecules directly to a substrate thus has potential to achieve more homogeneous and stable distribution of the probes.^{20,22}

While multiple fluorescent sensing is of interest for monitoring samples under complex conditions,^{23–25} self-referenced dual-luminophore PSPs were developed, such as by the inclusion of an insensitive luminophore, *i.e.* the reference probe, in addition to the sensitive probe, for the quantification of pressure value by comparing the intensity ratio.²⁶ This is because the occurrence of inevitable movement or bending of the substrate will affect the record of luminescence strength in addition to the oxygen quenching, and thus will induce an error.²⁷ In a previous work, we have used silane-functionalized carbon dots (SiCDs) to build a polysiloxane reference layer, as a substrate to support a conventional silicone/ceramic PSP coating.²⁸ Despite the fact that it is not transparent, the coating can monitor the change of surface pressure distribution within sub-millisecond timing *via* ratiometric imaging.^{29–31} In this work, our aim is to develop fast-response optical pressure sensors particularly with high transmittance. To this end, we synthesized a new reactive oxygen sensitive dye, *i.e.* silane-functionalized ruthenium complex (Ru-silane), and used SiCDs to prepare fully sprayable dual-luminophore PSP. The silane modification can let the probes form molecular linkers with any silica, silicate, organosilicon or polymer substrates, and consequently achieve well-controlled and stable distribution of the probes. Herein, a transparent silicone coating with micrometer-scaled thickness was harvested to embed SiCDs which was subsequently grafted by Ru-silane on the surface. The characteristics of transparency, dual-luminophore and surface dye distribution of the as-prepared bi-layer coating contributed the ability for monitoring the surface pressure in

2D in an inner channel by the ratiometric method within a short response time.

Experimental

Materials

Ruthenium(III) chloride hydrate and 2,2'-bipyridine-4,4'-dicarboxylic acid were purchased from J&K Chemical Ltd (Beijing, China). 4,7-Diphenyl-1,10-phenanthroline, thionyl chloride, triethylamine, 3-(aminopropyl)triethoxysilane (APTES), methyltriethoxysilane (MTES) and tetraethoxysilane (TEOS) were purchased from Maiklin Biochemical Co., Ltd (Shanghai, China). Silane-modified CDs (SiCDs) were synthesized according to previously published literature.³² Solvents and other compounds were purchased from Beijing Chemical Reagents Company (China) and used without further purification.

Characterizations

Fourier transform infrared (FTIR) spectra were recorded on a Thermo scientific Nicolet 6700 FT-IR spectrometer in KBr pellets. Nuclear magnetic resonance (¹H NMR) was carried out on a JEOL JNM-ECZ400S spectrometer (400 MHz) at 298 K. Surface and section morphologies of the coatings were observed using scanning electron microscopy (SEM, Hitachi SU8010) operating at 5 kV. The samples for SEM were prepared on a silicon wafer. To view the section of the coatings, a freeze-fracture method was applied by immersing the coating covered wafer in liquid nitrogen. Transmittance of the coatings was characterized using a Hitachi U-4100 spectrophotometer on a glass substrate.

Preparation of di(4,7-diphenyl-1,10-phenanthroline) 2,2'-bipyridine-4,4'-dicarboxylic acid dichlororuthenium(II) (RuP₂d)

Typically RuCl₃ (256 mg, 0.98 mmol) and 4,7-diphenyl-1,10-phenanthroline (651 mg, 1.96 mmol) were dispersed in 18 mL of deionized water and heated to reflux for 12 h. After that, the mixture was transferred to a hydrothermal kettle and mixed with 2,2'-bipyridine-4,4'-dicarboxylic acid (240 mg, 0.98 mmol) for hydrothermal reaction in nitrogen at 160 °C. The reaction mixture was then filtered and red powder was obtained after evaporation of the solvent using a rotary at 80 °C. The product was purified by silica-gel chromatography. The first band was washed down by a mixed solvent of dichloromethane and methanol (1:4, v/v), and the second band was washed down by methanol, collected and dried. MALDI/TOF-MS, $m/z = 1010.2$ (M^{2+}) (calcd 1010.22).

Preparation of 3-(aminopropyl)triethoxysilane (APTES)-functionalized RuP₂d (Ru-silane)

RuP₂d (60 mg, 0.056 mmol) was dissolved in SOCl₂ (8 mL) and refluxed for 4 h in the dark. After that, SOCl₂ was eliminated by evaporation from the claret solution. APTES (24 mg, 0.1 mmol) was dissolved in dichloromethane (8 mL) containing triethylamine (11.2 mg, 0.11 mmol). The acyl chlorinated RuP₂d was added dropwise to the above mixed solution and stirred in an ice bath for 4 h, protected against the exposure to light. The

dark red precipitate was obtained by precipitation with diethyl ether, followed by natural drying.

Preparation of transparent bi-layer PSP coating

The dual-luminophore pressure sensitive paint (PSP) has two components, *i.e.* a reference base paint and a sensitive cover paint. The base paint is composed of desired amount of SiCDs, MTES and TEOS in a mixed solvent of ethanol and water (1 : 4 v/v). And the volume ratio of the siloxane precursors to the solvent was fixed at 1 : 2. The cover paint was made by dissolving Ru-silane in a mixed solvent of dichloromethane (DCM) and methanol (1 : 1, v/v). The bi-layer coating was prepared first by adjusting the pH of the reference base paint to 5.0 using acetic acid. Then the base paint was sprayed onto a glass slide or a piece of plastic film using a spray gun (F-3, Sheng-Tian, China) with a nozzle diameter of 0.8 mm. After a silicene film was formed, the sensitive cover paint was sprayed onto its surface using the same apparatus.

Fluorescence spectrophotometry

The fluorescence spectra were recorded using a FL970 fluorescence spectrophotometer (Techcomp, China). The glass sample plate was cut into a size of 13 × 27 mm, and was placed in a quartz cuvette diagonally. Mixed gas of nitrogen and oxygen in different fractions was purged into the quartz cuvette sealed with parafilm for at least 5 min.

For monitoring the photostability, the time scanning mode was used. The samples were continuously irradiated by an excitation of 470 nm, while the emission at 600 nm was recorded.

Pressure sensitivity and dynamic performance of transparent PSP coating

Pressure sensitivity of the transparent coatings on glass slides was conducted in a calibration chamber at 25 °C with pressure ranging from 10 kPa to 101 kPa. A LED lamp (SJUV 4D-104, SJMAEA, China) was used to excite the coating at 365 nm, the image of the coating was captured by a CCD camera (Nikon D810, Japan) through a 50 mm lens (AF-S 50 mm f/1.4 G, Nikon, Japan) with a long wavepass filter (LP410, Geng Xu, China) in front.

For determining the response time of the transparent coatings and imaging the inner surface pressure distribution, a shock tube with a square section of 84 × 84 mm, a long driver section of 0.5 m and a long low pressure section of 2.2 m was established (Scheme S1, ESI[†]). A quartz window with a diameter of 60 mm was placed on the vertical wall of the tube at 0.8 m from the low pressure section, on which a sample plate (50 × 25 × 1.2 mm) was pasted with the coating surface towards the inner section, leaving an attack angle of 0°. Outside the quartz window, an LED array ($\lambda_{\text{ex}} = 365 \text{ nm}$) and a high-speed CCD camera (FASTCAM Mini AX 200, Japan) equipped with a 410 nm filter were placed. The camera was connected to a trigger (DG535, USA) and set at a recording speed of 10 000 Hz (0.1 ms per picture) with a resolution of 1024 × 672 pixels. The experiments were started at ambient temperature, *i.e.* 25 °C, when the low pressure section was filled with air at an initial pressure of 20 kPa. The temperature variation during the test was around 3 °C in the shock tube.

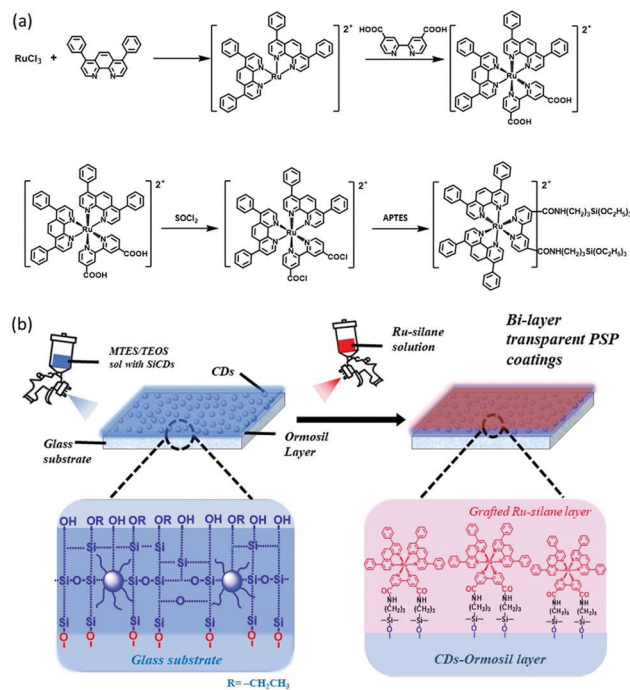
After the tests, the collected images were analysed using Image-Pro Plus 6.0 software for dividing and comparing the intensity in the blue and red channels by following the software's introduction.

Results and discussion

Preparation of transparent dual-luminophore PSP coating

The preparation of the transparent PSP is illustrated in Scheme 1. SiCDs were synthesized according to our previous work.^{32,33} And the silane-functionalized oxygen sensitive ruthenium complex, *i.e.* di(4,7-diphenyl-1,10-phenanthroline) 2,2'-bipyridine 4,4'-riethoxysilyl formamide dichlororuthenium(II) (Ru-silane), was synthesized in this work *via* a two-step procedure (Scheme 1a). The structure of Ru-silane was confirmed by ¹H NMR and FTIR (Fig. S1, ESI[†]).

Using SiCDs and Ru-silane as probes, two-component dual-luminophore pressure sensitive paint (PSP) was obtained for preparing bi-layer transparent coatings by first spraying the acid-catalyzed reference paint containing SiCDs onto a transparent substrate, for example, a glass slide or a piece of plastic film, to allow for a sol-gel process by which SiCDs were copolymerized with the siloxane precursors and then distributed inside the matrix. Subsequently the sensitive paint was sprayed onto the SiCDs base layer to graft the Ru-silane molecules on the surface *via* silica condensation (Scheme 1b). SEM images reveal the formation of a flat coating film on the glass substrate, with a thickness less than 5 μm (Fig. 1a and b).



Scheme 1 Schematic illustration of the synthesis of silane-functionalized ruthenium complex (a) and the subsequent preparation of dual-luminophore bi-layer hybrid coating (b).

Energy dispersive X-ray spectroscopy (EDX) further demonstrates the distribution of Si, O, C and Ru elements on the section of the coating, which indicates the formation of a bi-layer structure, that is, ruthenium rich materials over a silica rich film (Fig. 1c).

It can be recognized that the spraying procedures for preparing the bi-layer coatings are facile and with preferable applicability on substrates with complex surface geometry. Upon the sol-gel process, SiCDs can be uniformly dispersed inside the silicone matrix for efficient solid-state luminescence,³⁴ besides the matrix also has an ideal affinity to the glass substrate with the exposed hydroxyl groups through the formation of siloxane bonds, while on the other side, the residue hydroxyl groups existing on the silicone surface enable further immobilization of the Ru-silane molecules. The inclusion of MTES as a main component in the binder improved the flexibility of the reference layer since the formation of a siloxane network is more ductile compared to a rigid pure silica network, which avoided significant shrinkage and cracks in the matrix during the evaporation of solvent, and hence ensures the transparency of the coating. As shown in Fig. 2a and b, the PSPs, no matter whether they contain two luminophores or only an individual luminophore, have produced uniform films on beakers, a curved glass surface, and even on a flexible plastic membrane (*i.e.* polyethylene). Notably, the PSP patterns can be bent with the polymer membrane without causing any crack (Fig. 2b). The transmittance of the luminophore-containing coatings was revealed using UV spectrophotometer, showing values of higher than 80% within the visible light range, *i.e.* 400–700 nm (Fig. 2e), which is attributed to the homogeneous dispersion of the luminophores, especially the particulate SiCDs,³⁵ with a size in the nanometer scale,^{33,34} without gathering into larger clusters, owing to the copolymerization with the siloxanes. Besides, it is seen that the absorbance of SiCDs is mainly in the ultraviolet wavelength (Fig. 2e). This also benefits the transparency of the coating, but meanwhile limits the excitation of the probe within the UV band.

It is found that the Ru-silane on the film has a maximum absorption at 470 nm, which overlaps the CDs emission (Fig. 2c).

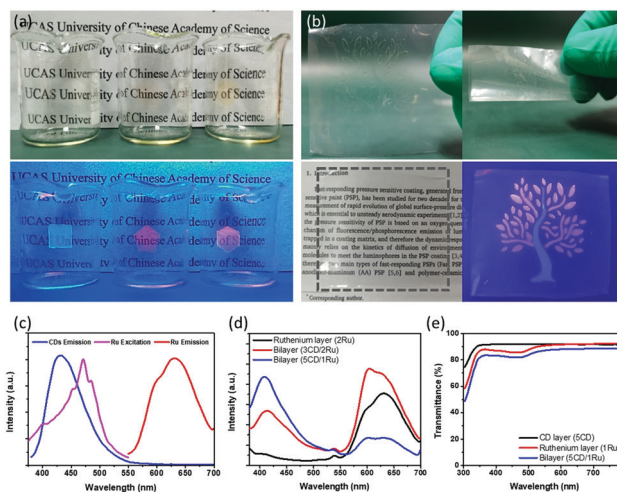


Fig. 2 (a) Photographs of the transparent coatings containing SiCDs (left), Ru-silane (middle) and both of the probes (dual-luminophore and bi-layer, right) respectively on beakers under visible light (upper) and UV light (bottom). (b) Photographs of a polyethylene membrane painted by the coatings containing either SiCDs or dual-luminophore (bi-layer) in the pattern under visible light or UV light. (c) Fluorescence spectra of SiCD emission, Ru-silane excitation and Ru-silane emission from a bi-layer coating on glass substrate (λ_{ex} was 365 nm for CDs and 470 nm for Ru-silane). (d) Emission spectra of bi-layer coatings with different chemical composition. xCDyRu represents that the composition of SiCDs and Ru-silane was x mg mL⁻¹ and y mg mL⁻¹ in the reference paint and the sensitive paint for making the coating respectively. The excitation wavelength was 365 nm. (e) Transmittance of SiCDs base coating (5 mg mL⁻¹ in the paint), bi-layer coating without the inclusion of SiCDs in the reference layer (0 mg mL⁻¹ of CDs and 1 mg mL⁻¹ of ruthenium complex in the paint) and the dual-luminophore bi-layer coating (5 mg mL⁻¹ of CDs and 1 mg mL⁻¹ of ruthenium complex in the paint).

Meanwhile, the emission of Ru-silane centres at 630 nm (Fig. 2c). With such a relationship, the two luminophores can be excited by a single light source suitable to CDs, *i.e.* under UV irradiation for example at a wavelength of 365 nm, leading to a fluorescence resonance energy transfer of CDs emission to excite the ruthenium complex. Furthermore, the emission gap between CDs and the

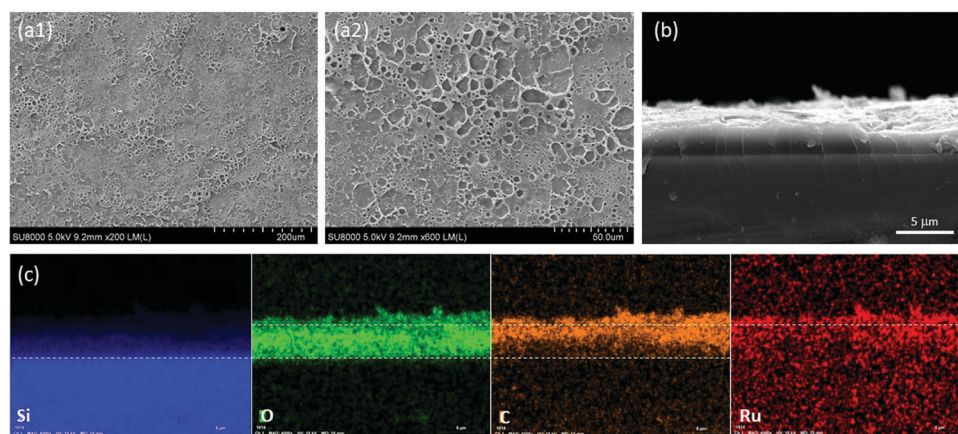


Fig. 1 (a) SEM images on the surface of the bi-layer coating prepared from PSP composed of 3 mg mL⁻¹ SiCDs and 2 mg mL⁻¹ of Ru-silane. (b) Section view of the coating by SEM. (c) Elemental maps (EDX) of the coating.

ruthenium complex is as large as 200 nm (Fig. 2d), favourable to the spectroscopic separation of the photoluminescence in blue and red channels, and hence the calculation of emission intensity ratio of the two probes. Moreover, the colour of luminescence from the coating can be tuned by adjusting the amount of the luminophores (Fig. 2a, b and d). It is known that CDs have upconversion ability, meaning that the coating is potentially excited by near-infrared (NIR) irradiation,²⁹ which provides the possibility for the regime to cooperate with other NIR imaging techniques that have familiarly studied for biomedical applications.^{36,37}

Stability of the transparent dual-luminophore PSP coating

To gain PSP coating with fast-responsibility, it is essential to allocate the sensitive dye molecules close to the surface of the substrate, as the response time is in proportion to the square of the distance for oxygen travel in the polymer matrix before it reaches the sensitive probe.³⁸ However, in practice, thinner matrix, or thinner binder, normally have problems immobilizing the sensitive dyes stably by only physical interactions. Migration of the dye molecules especially for those distributed at the solid–air interface would not be avoided.³⁹ Herein, we have tried to graft the ruthenium complex through the formation of siloxane bonds which has significantly improved the stability of the ruthenium complex on the coating surface. According to Fig. 3a and b, compared to the physical absorption of a commercial available dye, *i.e.* tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) (Ru(dpp)₃), the fluorescence intensity of the Ru-silane-grafted coating shows a minor difference ($\Delta I \sim 0$) before and after the coating was washed using dichloromethane, a solvent of the compound, whilst an obvious decrease of intensity is observed from the Ru(dpp)₃ loaded coating. Meanwhile,

negligible fluorescence is revealed from the leach liquor of the Ru-silane coating, in marked contrast to the strong emission from the washout solvent of the Ru(dpp)₃ coating (Fig. 3c), confirming the stable bonding of Ru-silane onto the silicone substrate.

In addition to the grafting stability, it is interesting to see that the photobleaching of the ruthenium complex becomes less serious in the case where it was chemically grafted on the substrate (Fig. 3d). Photodegradation of the dye molecules used to be a major issue to deal with in the PSP technology, especially so far when prolonged experiment time and high power excitation light are more frequently applied.¹⁵ The above results imply that compared to the physical entrapment, the photolysis of the ruthenium complex was seriously inhibited after the molecules were anchored onto the silicone surface.

Since the photoluminescence of the ruthenium complex is sensitive to oxygen partial pressure, the influence of chemical grafting on the responsibility of the probe molecule was also investigated. Fig. 3b displays that a solvent washing process on the coating would not affect the sensitivity of Ru-silane, showing a similar intensity ratio of the emission in nitrogen to that in air (I_0/I), despite the prolongation of washing period. Furthermore, in a comprehensive test by alternating the nitrogen and oxygen gas environments on the Ru-silane grafted coating together with a continuous light exploration, it reveals that the luminescent intensity under both of the atmospheres was rather stable within the tested cycles (Fig. S2, ESI†). Therefore, we have actually demonstrated the advantage of the chemical bonding in making a photoluminescent device, when compared to the common physical doping route, that is, the chemically grafted dye molecules are not only topologically more stable, but also photochemically more stable.

Oxygen sensitivity of the PSP coating

The oxygen sensitivity of the dual-luminophore transparent coating on the glass slide was tested by checking the fluorescence emission, with an λ_{ex} of 365 nm, under a mixed atmosphere with predetermined amount of oxygen and nitrogen. The spectra are shown in Fig. 4. The weakening of Ru-silane emission can be clearly seen with increase of oxygen fraction, while the intensity of CDs emission has only minimum change throughout the variation of oxygen concentration from 0% (full nitrogen gas) to 100% (full oxygen gas), no matter if the spectra were collected from the front side or the back side of the coating (Fig. 4a and b). Moreover, by quantifying the intensity as a function of oxygen concentration, one can see a well-fitted linear relationship between I_0/I of the ruthenium complex and the oxygen concentration, *i.e.* [O₂], which strictly follows the Stern–Volmer relation,

$$\frac{I_0}{I} = 1 + K_{\text{SV}}[\text{O}_2] = 1 + K'_{\text{SV}} \frac{P}{P_0}$$

where K_{SV} is the Stern–Volmer quenching constant, representing the sensitivity of the regime.⁴⁰ The linear relationship within the whole oxygen concentration range implies favourable property of the coatings for the surface pressure measurement in aerodynamic research. Meanwhile, it is also noted that the ruthenium luminescence collected from each side of the glass slide

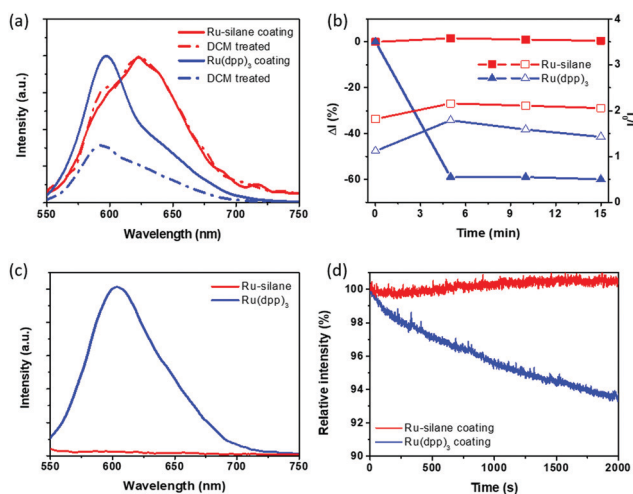


Fig. 3 Tests on the stability of the chemically grafted Ru-silane on the base layer surface, in comparison with physically absorbed Ru(dpp)₃ on the substrate, through washing the coating with DCM for different periods ($t = 0$, before wasting), followed by (a) checking the variation of fluorescence spectra, (b) comparing the change of emission intensity (filled symbols) and oxygen sensitivity (open symbols) and (c) examining the fluorescence of the leach liquor. (d) The photostability of Ru-silane and Ru(dpp)₃ was monitored by recording the emission of the luminophores at 620 nm upon excitation at 470 nm (d).

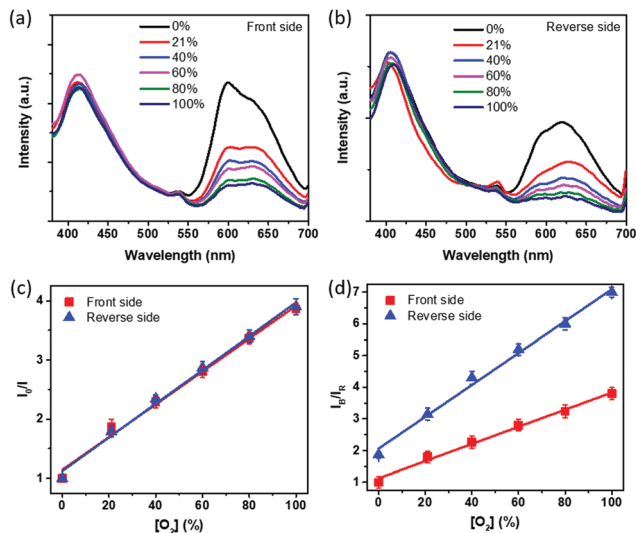


Fig. 4 Reflection fluorescence spectra ($\lambda_{\text{ex}} = 365 \text{ nm}$) of the bi-layer coating (2CD/1Ru) on the glass slide taken from the front (a) and reverse (b) side respectively under an atmosphere containing the desired amount of oxygen (% v/v), and the subsequent fitting of the intensity change (I_0/I where I_0 is the intensity at 0% of oxygen) (c) and intensity ratio (I_B/I_R where I_B is the intensity measured at 430 nm and I_R is the intensity measured at 630 nm) (d).

resulted in firmly overlapped I_0/I curves, which is very reasonable because the fluorescence was emitted from the same probe (Fig. 3c). This phenomenon absolutely infers that the as-prepared PSP coating is capable for the determination of oxygen concentration and furthermore the surface pressure loaded on the coating surface *via* an observation from the reverse side of the coating through a transparent substrate, and without losing the responsibility.

Furthermore, it is also noticed that when using the CDs emission as a reference, the intensity ratio of CDs emission (430 nm, blue) and Ru-silane emission (630 nm, red), *i.e.* I_B/I_R , demonstrates an expected difference on the values, so as to the slope of the fitted curves as a function of $[\text{O}_2]$, between the data collected from the front side and those from the reverse side (Fig. 4d), because in this case, if taking a back view, the red emission needs to penetrate the CDs containing film before it reaches the detector, which makes the red emission become a little bit weaker in comparison with that being observed from the front side. The phenomenon can be viewed by reviewing the relative fluorescence intensity between the CDs and the ruthenium in Fig. 4a and b.

Static pressure sensing

The pressure sensitivity of the transparent coating on the glass slide was evaluated in a pressure calibration chamber. Visible images of the excited coatings were taken by an optical camera and then the blue and red colours were separated at each pixel for the determination of the emission strength of either CDs or the ruthenium complex, and subsequently for the calculation of 2D distribution of the intensity ratio. In Fig. 5a and b, it is worth mentioning that the colour change caused by the

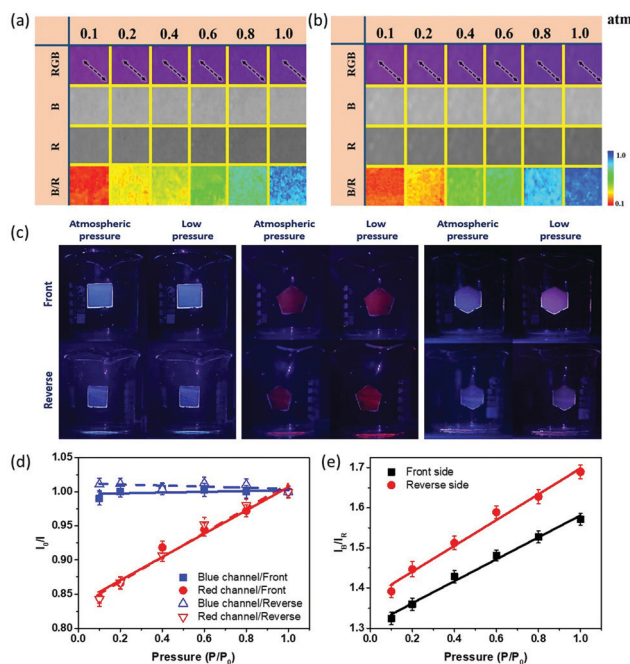


Fig. 5 (a and b) 2D images of surface pressure distribution, derived from optical pictures taken from the front side (a) and the reverse side (b) of the coatings under predetermined pressure values followed by processing the photos to separate RGB channels for the generation of pseudo-color. (c) Demonstration of photoluminescence under different pressure from the SiCDs monolayer coating (left), Ru-silane grafted silicone coating (middle) and the dual-luminophore coating (5CD1Ru, right). (d) Sensitivity of CDs and Ru-silane within a pressure range of 0.1–1.0 atm from the front view or back view. I_0 is the intensity at 1 atm (P_0). (e) The change of intensity ratio of blue emission (I_B) to red emission (I_R) as a function of surface pressure.

variation of local pressure on the coatings can be distinguished from the visible images (RGB pictures), no matter whether from front or reverse side, indicating the ideal responsibility of the coatings especially the sensitivity of the grafted Ru-silane molecules. From the sprayed patterns on the beakers, one can more conveniently compare the luminescence intensity of CDs and Ru-silane under normal pressure and in vacuum ($\sim 0.1 \text{ atm}$) respectively (Fig. 5c). While an increase of the red light strength from the Ru-silane monolayer coating can be distinguished in the picture taken under lower pressure conditions (middle image), the unchangeable blue light strength from the CDs coating is seen (left image). Altogether, this led to the colour change of the bi-layer coating (right image). Compared to the observation of the brightness, *i.e.* emission intensity, the colour change is more conspicuous, *i.e.* from blue to purple (Fig. 5c). Therefore, the coatings containing two luminophores should be able to benefit the qualitative monitoring of the surface pressure due to the self-reference feature.

In addition to a gross view, the quantitative calibration on the sensitivity of the coatings was assessed from the digitalized pictures and the results are plotted in Fig. 5d and e. Therein, the change of averaged integral intensity in the blue channel and red channel shows a similar relationship as in the fluorescence spectra of CDs and Ru-silane's peaks (Fig. 4), observed

from both the front side and the reverse side of the coating, demonstrating nearly constant I_0/I in the blue channel and linear enhancement I_0/I of the red channel as a function of P/P_0 , where I_0 and P_0 are the intensity and the pressure under atmospheric conditions (Fig. 5d). Meanwhile, the averaged intensity ratio of the two channels, *i.e.* I_B/I_R , also changes linearly within the pressure range from 0.1 to 1.0 atm, and has a higher slope from the back view than that from the front view (Fig. 5e), in good agreement with the regulation of the oxygen responsibility (Fig. 4). Therefore, the Stern–Volmer equation is still applicable to correlate the environmental pressure with the chrominance of the digital images taken from the luminous coating.

Moreover, we also tested the influence of chemical composition, in particular, the amount of luminophores, on the sensitivity of the coatings. The results imply that the sensitivity mainly relates to the ruthenium grafting density, *i.e.* the amount of Ru-silane grafted on the surface (Fig. S3, ESI†). Less density of the sensitive probes on the coating surface resulted in higher sensitivity, up to 3% kPa⁻¹, attributed to a lower possibility of the occurrence of aggregation caused quenching. However, fewer probe molecules would also

result in lowering the absolute intensity of fluorescence, which will affect the quality of the imaging. Compared to the measurement of ruthenium fluorescence, the slopes of the intensity ratio are less influenced by the chemical composition (Fig. S3, ESI†), inferring that the ratio measurement may help to balance the relationship between the properties of sensitivity and emission strength. In addition, it must be mentioned that the spray skills are also important during the preparation of the coatings. As well as spraying, other painting methods, *e.g.* spin-coating and dipping techniques, can also be included in the coating fabrication, especially on a planar substrate.

Application of the transparent PSP in unsteady aerodynamic testing

In addition to the oxygen and pressure sensing abilities, the pressure mapping performance and the response time of the transparent coating were evaluated using a shock tube (Scheme S1, ESI†). Through a quartz window, a high-speed CCD camera recorded the colour change of the coating on a glass slide during the wind-on process from the back side, which was excited at 365 nm from the back side as well. In the process, the

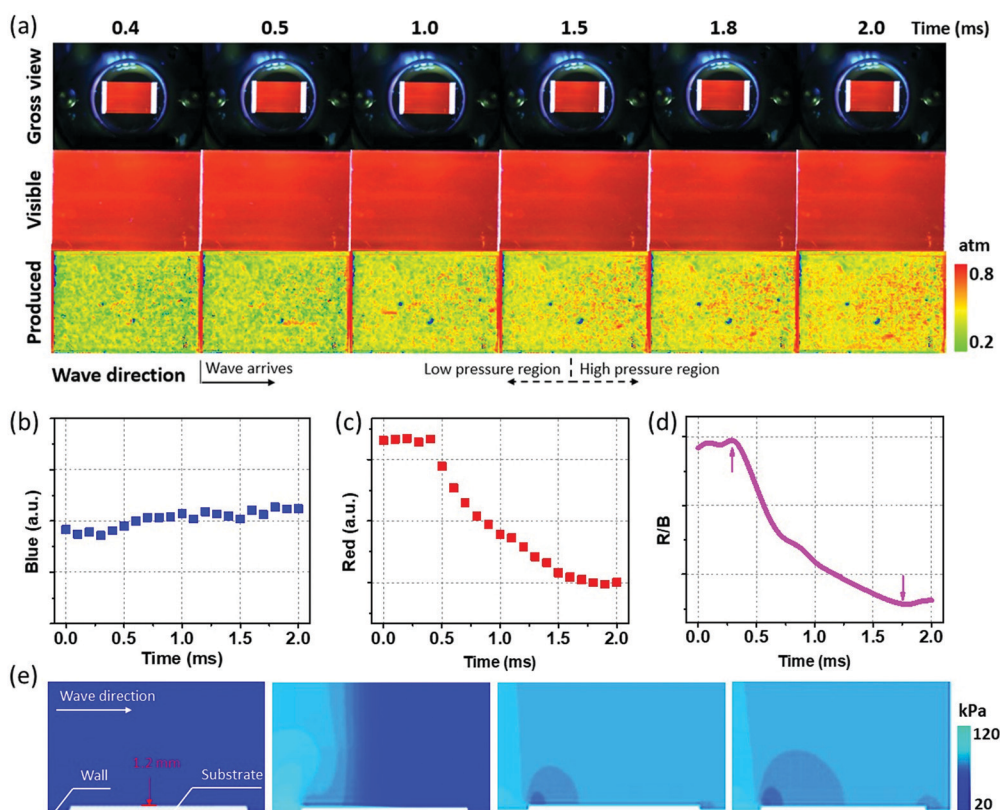


Fig. 6 (a) Visible and produced photographs of the PSP coating on the glass slide recorded by the high-speed camera from the reverse side of the coating at given time points. Top line: Gross view of the coating through the quartz window. Middle line: Optical images of the coating. Bottom line: Produced images, through separating the blue colour and red colour and then comparing the ratio of the two channels in a wind-on state with that in the wind-off state taken at 0.2 atm. The size of the coating on glass is 25 × 50 mm. (b) Blue colour intensity and (c) red colour intensity averaged from a vertical section of the wind-on images as a function of the experiment time. (d) Calculated intensity ratio of the red channel and blue channel as a function of the experiment time. Arrows indicate the time points for the PSP coating in response to the shock wave. (e) Numerical simulation on the effect of a bulge on the surface pressure. Whenever a shock wave arrives, the protrusion of the substrate will induce separated flow which then expands to the downstream area of the bulge.

optical photographs taken by every 0.1 ms reveal a chromatic aberration occurred at the time point between 0.5 to 1.0 ms after the pressure release (Fig. 6a), very close to the calculated time for the shock to arrive at the coating surface, *ca.* 0.5 ms. As the camera was operated with a very short exposure, the observation of distinguishable chromatic difference within sub-millisecond interval in the visible pictures indeed suggests a gratifying emission strength of the luminophores from a coating with a rather smooth surface, in comparison with the nanoparticle doped rough coatings, which once again confirms the benefits of the chemical immobilization of the ruthenium complex, that is, to get stable, uniform and relatively high density of the dye molecules on the substrate.

Furthermore, for pressure calculation, it should be noted that the photoluminescence of ruthenium complex is not only oxygen sensitive but also responsive to the environmental temperature.^{23,41,42} Nevertheless, since the shock tube features short flow duration, the first shock wave passes through the coating in the order of several milliseconds. In such case, the temperature change is normally less than 5 °C.⁴³ The difference in the emission intensity of the bi-layer coating is smaller than 2% within this temperature interval (Fig. S4, ESI†). Thus, the temperature effects to the PSP coating are considered negligible.^{38,43} Besides, the data also demonstrate that by grafting the ruthenium complex, the temperature dependence is less serious for the chemically immobilized Ru-silane when compared to physically absorbed Ru(dpp)₃ (Fig. S4, ESI†). Even so, the probe may not be suitable for the steady experiments in the wind channel.

Fig. 6b and c show the quantified amplitude of the intensity change from the blue and red channels respectively. As expected, which minor variation on the strength of the photoluminescence is viewed from CDs within the experimental time-course, a sudden change of the red emission was found, starting at 0.5 ms and reached an equilibrium at around 1.6 ms. Hence, the intensity ratio of the two channels gains a response time of *ca.* 1.3 ms for the coating (Fig. 6d). It needs to be pointed out that the response was determined from the grayscale value of the images,²⁸ rather than measuring the 90% rise time of signal from a photomultiplier.^{15,40} Nonetheless, the response time is not so fast as that of the reported polymer/ceramic PSP coatings,^{28,40} although it can support the fast PSP applications.^{27,35} The main reason is attributed to the grafting chemistry. A transparent coating requires a smooth surface. Thus, in order to have a reasonable luminescence for getting better imaging quality, a relatively high level of the dye molecules was loaded onto the coating surface. Although the possibility of dynamic aggregation of the dyes has been diminished by chemical bonding of the dyes, the stacking among neighbouring ruthenium complexes cannot be completely avoided and thus caused the delay of oxygen penetration. Besides, compared to the imaging of a rough surface, the camera condition is less favourable because the emission light is from a planar emission source. The effect of reflection and refraction must be faced, especially for the imaging from the back side, due to the existence of multiple interfaces. Future work is warranted to improve the designation of an optical system in order to get better correlation between the imaging requirements and the

responsibility of the transparent PSP film. Nevertheless, the presented data still prompts the practicability of a transparent PSP coating for the investigation of the surface pressure in an inner flow channel.

To more clearly show the pressure distribution on the coating surface, the optical pictures were produced to get pseudo-colour maps (Fig. 6a). While it displays a homogeneous low pressure distribution before the approach of the shock wave, *e.g.* at 0.4 ms, the pressure increases are more clearly recognized from the pseudo-colour pictures, *i.e.* 1.0–2.0 ms. One can discover that after the wave arrives, the distribution of pressure on the surface becomes inhomogeneous, divided into a low pressure region in the near-end together and a high pressure region in the far-end to the wind direction, which can be understood since there is a 1.2 mm step between the sample substrate and the wall of the shock tube (Fig. 6e and Scheme S1, ESI†), which will cause the disturbance of the flow.⁴⁴ The phenomenon is not just correlated to the numerical simulation (Fig. 6e), but also realizes the observation of the radial distribution of pressure along the flow direction, caused by the long edges of the glass slide (Fig. 6a). Thus the experimental results suggest the effectiveness of the bi-layer PSP coating for monitoring an unsteady aerodynamic process.

Conclusions

In summary, we developed a fast-response transparent optical pressure sensor by the preparation of dual-luminophore sprayable PSP and hence the construction of the luminophore-copolymerized silicone bi-layer coatings. Ru-silane was synthesized for grafting onto the silicone substrate, while SiCDs were favourably embedded in the silicone matrix. The chemical bonding gained better distribution and stability of the probes. Besides, the inclusion of two luminophores enabled the determination of oxygen concentration or surface pressure through the measurement of emission intensity ratio, besides the surface grafting strategy also led to rapid contact of the surrounding oxygen molecules to the sensitive probes, and therefore contributed a fast response time of 1.3 ms to a shock wave. By using the polymerizable silane-functionalized luminophores, this work actually suggests a facile but efficient approach for the preparation of photoluminescent materials for various optical sensing aims. Future work will focus on further improving the responsibility and the optimization of optical conditions for longer excitation wavelength and more efficient capture of luminescence from a transparent coating.

Author contributions

D. Yang: data curation, formal analysis, investigation, methodology, writing – original draft. J. Li: data curation, formal analysis, investigation, methodology, writing – original draft. J. Ren: data curation, formal analysis, investigation. Q. Wang: data curation, formal analysis, investigation. S. Zhou: supervision, writing – review & editing. Z. Xie: conceptualization, funding acquisition, supervision, validation, writing – review & editing. Q. Wang: conceptualization,

methodology, project administration, supervision, visualization, writing – original draft, writing – review & editing. X. Qu: conceptualization, funding acquisition, methodology, supervision, visualization, writing – original draft, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

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