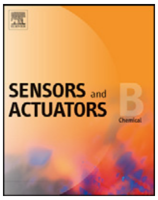
Sensors and Actuators B 171–172 (2012) 343–349

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb



A fast-response pressure sensor based on a dye-adsorbed silica nanoparticle film

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ARTICLE INFO

Article history:
Received 20 March 2011
Received in revised form 18 April 2012
Accepted 19 April 2012
Available online 3 May 2012

Keywords:
Optical sensor
Pressure-sensitive paint
Wind tunnel testing
Nanoparticle

ABSTRACT

An optical oxygen sensor was developed as a pressure-sensitive paint (PSP) to measure time-varying surface pressure in aerodynamic testing. A silica nanoparticle dispersion (slurry) was used as the binder for the sensor, with a pressure-sensitive dye dissolved in the slurry. The dye slurry was deposited onto arbitrary surfaces via spray coating. Thin porous silica films were successfully formed without any organic additives. The pressure and temperature sensitivity of common pressure-sensitive dyes platinum tetra(pentafluorophenyl)porphyrin (PtTFPP)and tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II)dichloride ($[Ru(dpp)_3]Cl_2$) with a silica/toluene slurry were tested, in addition to the temporal response. The pressure sensitivity was −0.94%/kPa for PtTFPP and −0.64%/kPa for $[Ru(dpp)_3]^{2+}$, which was comparable to the sensitivity of common PSPs. The sensor had good photostability, although it exhibited substantial temperature sensitivity (ca. 1.5%/°C). The response time was less than 0.1 ms for a step rise in pressure obtained using a shock tube.

1. Introduction

Optical oxygen sensors are widely used as pressure sensors for surface-pressure measurements in aerodynamic testing [1–8]. The optical oxygen sensor, which is frequently referred to as pressure-sensitive paint (PSP), is a thin film consisting of photoluminescent dyes (luminophores) and a supporting matrix (binder). The sensing mechanism is the energy exchange between oxygen molecules and luminophores. The emission rate from excited luminophores obeys the Stern–Volmer relation, which suggests that the emission rate is inversely proportional to the oxygen concentration in the film. In a quasi-equilibrium state, the concentration is proportional to the local gas pressure immediately above the film. Therefore, this type of oxygen sensor can be utilized as a pressure sensor.

A PSP is suitable for measuring time-varying pressure, because collisional quenching is a rapid process with a typical time scale of less than 0.1 ms. However, the *diffusion barrier* in a PSP film must be overcome to achieve a temporal response equivalent to the quenching. Oxygen molecules permeate into the film by a diffusion process; the characteristic time for diffusive transport is governed by two quantities of the film [9,10],

$$\tau = \frac{h^2}{D}, \qquad (1)$$

where h denotes the film thickness and D is the gas diffusivity.

Conventionally, the binder of the film is an oxygen permeable polymer such as silicone, organic glassy polymers including polystyrene and poly(methylmethacrylate), fluoropolymers, and cellulose derivatives (e.g. [11,12]). However, the time scale τ of the polymer film is long, in the order of seconds or tens of seconds, due to its low diffusivity (ca. 10^{-9} m^2 s^{-1}). This is much larger than the time scale of typical aerodynamic phenomena. Therefore, polymer-based PSPs are inadequate for the measurement of time-varying pressure, although a glassy-polymer PSP [13] has been reported with a relatively short response time of less than 1 s [14].

A *porous* material is an effective binder for improving the temporal response of a PSP, because it has much larger gas diffusivity than polymers. Various types of porous PSPs have been developed since the 1990s. Common materials now used as porous binder materials are commercial porous silica-gel thin-layer chromatography (TLC) plates [15], porous anodized aluminum (AA) [16–19], polymer/ceramic (PC) composites [20], and mesoporous silica particles [21,22]. All PSPs that employ these binders have sub-millisecond response times. However, some difficulties may be encountered in their practical application. The TLC plate is fragile and can only be applied to flat surfaces. AA is formed only on an aluminum surface through an electrochemical process. The polymer/ceramic composite has lower pressure sensitivity than the other materials. Mesoporous silica particles have typical diameters of 1 μm, so that special treatment such as layer-by-layer self-assembled film techniques [21] is required to adsorb them to the surface of the substrate.

In this paper, we present a novel method for the fabrication of a porous PSP using a silica nanoparticle slurry and luminophores.

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http://dx.doi.org/10.1016/j.snb.2012.04.049

Nanoparticles are high surface area particles with typical diameters of 10 nm, and nanoparticle deposits have a porous structure with nanoscale gaps; therefore, they could be suitable for use as the binder of porous PSPs.

Silica nanoparticles are applied in several fields such as photonics, solar energy, and fuel cells. Applications of silica nanoparticles in sensing devices, such as biomarkers (e.g. [23,24]), humidity sensors [25,26], a glucose sensor [27], and a pH sensor [28] have been proposed. However, as far as we know, this is the first attempt to apply silica nanoparticles as the binder for a PSP.

2. Experimental

2.1. Materials

Platinum tetra(pentafluorophenyl)porphyrin (PtTFPP, Frontier Science)and tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II)dichloride ($[Ru(dpp)_3]Cl_2$, GFS Chemical) were used as the pressure-sensitive dyes.

A commercial nanoparticle dispersion (Nanotek® slurry, C.I. Kasei[29]) was used as the binding matrix of the PSP. The slurry consists of 10 wt% ultrafine silica powder (average diameter 25 nm) in toluene.

Other materials used were of the highest grade available, obtained from Wako Pure Chemicals and Kanto Chemicals.

2.2. Sample preparation

A flat aluminum plate (20 mm × 20 mm) was used as the substrate for the performance test. The plate was firstly washed with NaOH aqueous solution (2 wt%) for 5 min, then with purified water, and then dried in a vacuum oven at 60 °C and 10 kPa for 24 h.

The dyes (PtTFPP or $[Ru(dpp)_3]^{2+}$) were dissolved in the silica/toluene slurry to provide a 0.3 mM solution. The solution was deposited onto the plate at room temperature using a spray gun (Olympos, HP-83C, 0.3 mm nozzle diameter) with compressed dry air (50 kPa). The coated plate was then dried in a vacuum oven at 60 °C for 24 h.

The thickness of the PSP film was adjusted to 5 μm, which was measured using an eddy current thickness tester. In the temporal response test, samples with a different thickness (10 μm) were also used.

2.3. Surface characterization

The surface of the prepared samples was observed using a commercial grade digital camera. Then it was characterized using field emission scanning electron microscopy (FE-SEM; Hitachi S-4700). Morphology of the prepared samples was observed using transmission electron microscope (TEM; model JEM-2010 from JEOL Inc.) and UV–vis absorption spectroscopy.

2.4. Performance test

2.4.1. Spectroscopic measurement

Steady-state fluorescence spectra and excitation spectra were measured for the samples using a fluorescence spectrophotometer (Hitachi High-Technologies F-7000) with a 150 W Xe lamp as an excitation light source. Excitation and emission bandpasses were 10 nm.

2.4.2. Pressure and temperature sensitivity

The pressure and temperature sensitivity of the samples were measured using the same optical setup used for practical PSP measurements in aerodynamic testing, as shown in Fig. 1. A pressure-vacuum chamber was used to obtain the luminescence intensity–pressure relationship at constant temperature and the luminescence intensity–temperature relationship at constant pressure. The sample was mounted on a thermoelectric (Péltier) module in the pressure-vacuum chamber to maintain a constant sample temperature. Dry air was used as the test gas. A precision pressure controller (GE Sensing DPI520) was used to set the pressure level in the chamber.

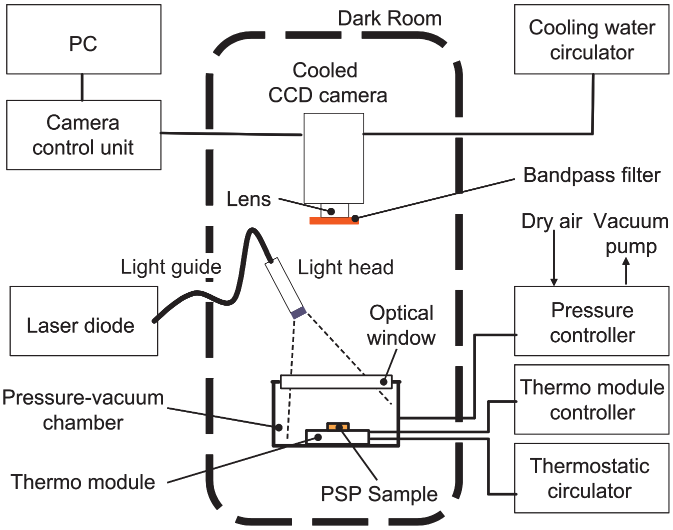

Fig. 1. Schematic diagram of the pressure-vacuum chamber.

The sample was illuminated from outside of the chamber via an optical glass window. The light source was a violet laser diode (Ricoh RV-1000, wavelength 400–410 nm, maximum output 1 W). The luminescence from the sample under a constant illumination was detected by a cooled charge-coupled device (CCD) camera (Hamamatsu Photonics C4880, intensity resolution 14 bit). An optical bandpass filter (transmission wavelength: 620 ± 50 nm) was mounted at the lens front to eliminate light except the luminescence.

2.4.3. Photostability

The photostability of the samples was evaluated using the same experimental setup for the pressure- and temperature-sensitivity measurements. The luminescence intensity was measured for samples exposed to continuous illumination for 1 h, during which the chamber was kept at constant pressure (100 kPa) and temperature (20 °C).

2.4.4. Temporal response

The temporal response was measured for a step rise in pressure using a shock tube (Fig. 2). The shock tube was separated into high- and low-pressure sections, and a thin plastic diaphragm was placed between these sections. The low-pressure section was evacuated at 10 kPa. A shock wave was generated in the low-pressure section by an abrupt break of the diaphragm. The end part of the low-pressure section consisted of a transparent acrylic resin for optical access to the sample.

The sample was placed on the end of the low-pressure section. The violet laser diode was used as the light source. Emission from the sample was detected using a photomultiplier tube (PMT; Hamamatsu Photonics C6780). The output current of the PMT was converted into voltage by a preamplifier unit (Hamamatsu Photonics C7319, frequency range: DC-200 kHz (−3dB)), and the voltage signal was stored in a 16-bit high-speed digital data recorder (Keyence GR-7000) at 1 MHz sampling.