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## PtOEP/PS composite particles based on fluorescent sensor for dissolved oxygen detection

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## ARTICLE INFO

## Article history:

Received 3 November 2015

Received in revised form

28 January 2016

Accepted 23 February 2016

Available online 27 February 2016

## Keywords:

Dissolved oxygen

PtOEP/PS fluorescent spheres

Stern-Volmer equation

Photo-stability

## ABSTRACT

Mono-dispersed platinum octaethylporphyrin/polystyrene (PtOEP/PS) fluorescent spheres were synthesized by a soap-free emulsion polymerization for the detection of dissolved oxygen (DO), in which hydrophobic PtOEP as indicator is embedded in PS spheres during the synthesis procedure. The performance of the PtOEP/PS spheres-based optical oxygen sensor was evaluated by recording their fluorescence intensities in different oxygen (O<sub>2</sub>) environments. Results suggest that PtOEP/PS spheres exhibit good oxygen sensing properties with fast response time and reliable photo-stability after several months of storage.

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## 1. Introduction

Monitoring dissolved oxygen (DO) concentration has a significant meaning in various fields, such as environmental monitoring, food and fermentation industry, and medical diagnosis as well as analytical chemistry. The iodometry method [1] is a traditional measurement method for DO, which is time-consuming, cumbersome and unable to fulfill the requirements of on-line measurement. On the other hand, the Clark electrode method [2] is applied for DO detection by measuring the diffusion rate of oxygen molecules through the membrane based on electrochemical techniques. Nevertheless, oxygen is consumed by the electrode during the redox reaction, leading to certain restrictions in application [3,4].

Nowadays, people pay special attention to the photochemical oxygen sensing technology for DO detection because of its high sensitivity, zero oxygen consumption and easy operation (on-line measurement) [5,6]. It is based on quenching of the luminescence of indicators entrapped in a matrix, which has been studied extensively [7]. Recently, Im et al. [8] loaded PtOEP and SiOEP into the polystyrene beads as the self-reference oxygen sensor by a dispersion polymerization, in which the luminescence intensity of PtOEP is linearly dependent on the concentration of oxygen and SiOEP shows no response to oxygen. Borisov et al. [9]

stained tetrakis pentafluorophenylporphyrin tetrakis pentafluorophenylporphyrine (PtTFPP) into poly(styrene-block-vinylpyrrolidone) beads to prepare oxygen nanosensors, finding that they are suitable to be used for monitoring fast processes due to their small size. Soap-free emulsion polymerization is a widely used method for preparation of nano-sized particles in the absence of surfactant, in which the stable latex can be gained by anionic initiators such as potassium persulfate (KPS) [10] and ammonium persulfate (APS) [11]. In this study, mono-dispersed PtOEP/PS fluorescent spheres were synthesized via a soap-free emulsion polymerization, 384 nm was chosen as a typical particle size and its emulsion acted as an optical oxygen sensor for DO detection. Physical characteristics and oxygen sensing properties of PtOEP/PS fluorescent spheres were investigated.

## 2. Experimental

Platinum octaethylporphyrin (PtOEP) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> were purchased from J&K Chemical Company Limited and Alfa Aesar, respectively. Styrene (Tianjin Yongda Chemical Reagent Company Limited) was washed by 5% NaOH to remove the inhibitor before use.

The experiment was carried out as the following steps: firstly, 20 ml of ultra pure water was added into the reactor, followed by the atmosphere of nitrogen for 30 min under mechanical stirring of 400 rpm. Then, 10 mg PtOEP and 3 ml polystyrene were

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successively added into water under the continued stirring for 15 min. Finally, an initiator of  $K_2S_2O_8$  aqueous solution (8 ml) was added into the reactor, and the reflux reaction was carried out at 70 °C for 24 h to obtain the PS fluorescent microspheres.

Morphology of the PS fluorescent microspheres was examined by field-emission scanning electron microscope (FE-SEM; S1800, Hitachi, Japan). The optical properties were measured using the fluorescence spectrometer (LS55, Perkin Elmer, America) equipped with a self-regulating gas mixture device which consists of  $N_2/O_2$  inlet part, a flow control part and a mixing part. PS fluorescent microspheres emulsion was diluted with ultra pure water in a quartz cuvette, and then placed on the test frame of the fluorescence spectrometer. The optical properties were measured when a certain proportion of the nitrogen-oxygen gas mixture was passed into the cuvette for several minutes until the gas was saturated. PtOEP/PS fluorescent spheres were excited by a mercury lamp equipped a filter centered at 380 nm and the emission spectra were recorded from the light of 650 nm. In addition, fluorescence lifetime was studied by time-resolved luminescence spectroscopy.

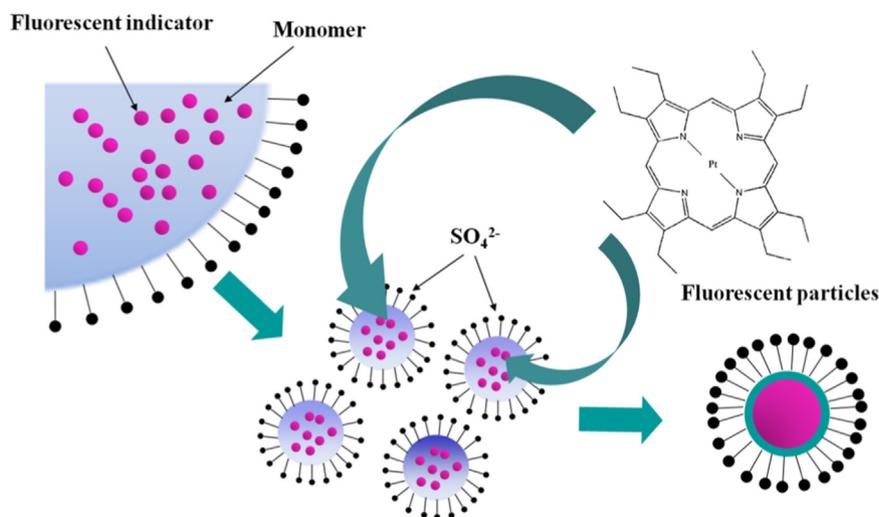
### 3. Results and discussion

The schematic diagram of preparation of PtOEP/PS fluorescent spheres via soap-free emulsion polymerization is shown in Fig. 1. Firstly, PtOEP molecules were well dispersed in styrene monomer solution stabilizing by the initiator of  $K_2S_2O_8$ , and then they are spontaneously embedded in the inner of particles with increasing the polymer chain to form the fluorescent particles. Finally, the product can be kept not only in aqueous solution but also as a powder state.

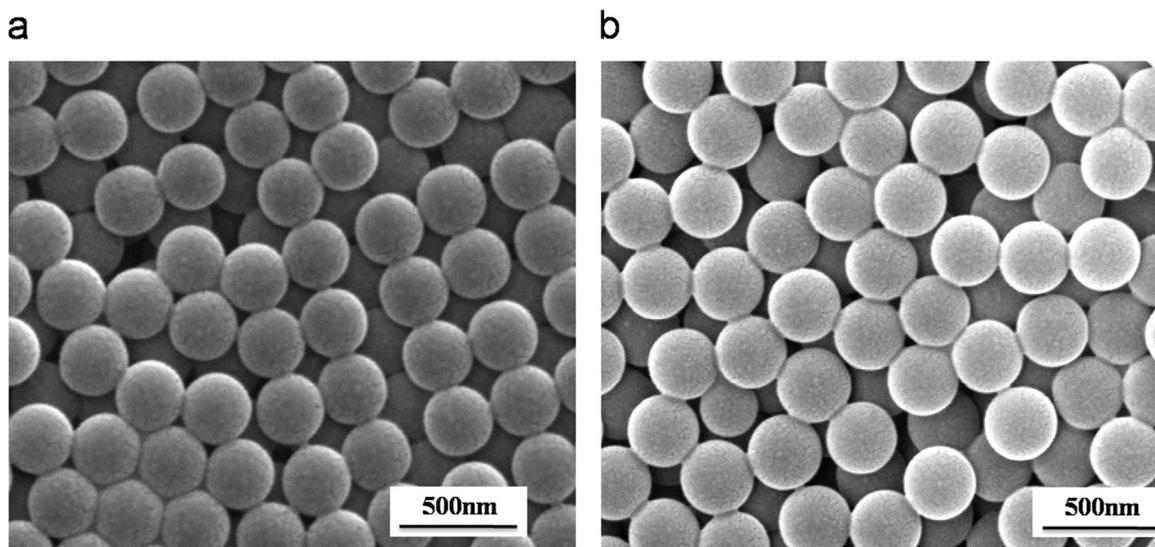
Fig. 2 shows typical SEM images of pure PS (Fig. 2a) and PtOEP/PS spheres (Fig. 2b). Both of them have well monodispersity and smooth surface as well as low PDI (Table 1). The average diameter

**Table 1**  
Particle size and distribution of pure PS and PtOEP/PS particles.

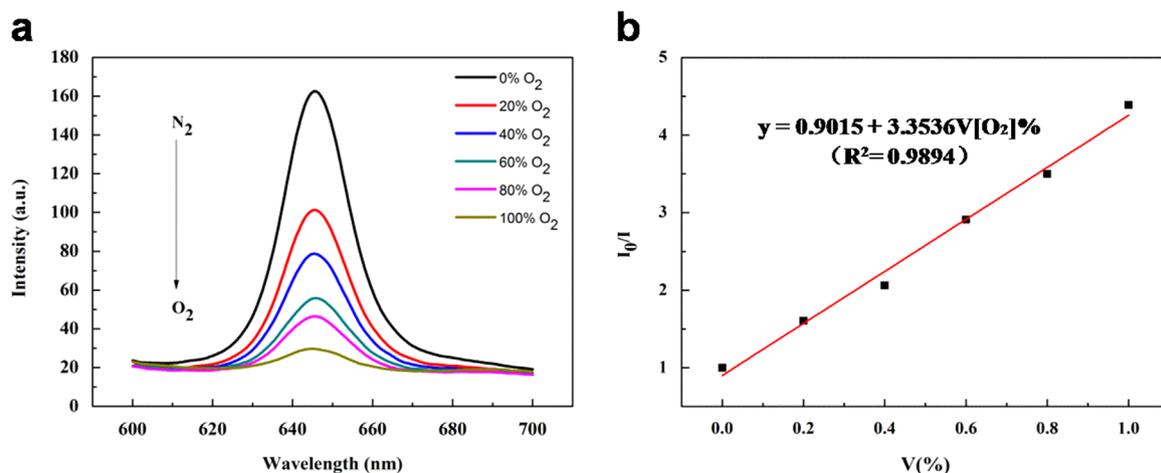
Sample	Mean diameter(nm)	Standard deviation(nm)	PDI(%)
PS	250.92	6.27	2.5
PS/PtOEP	383.96	12.28	3.2



**Fig. 1.** The schematic diagram of preparation of PtOEP/PS fluorescent spheres.



**Fig. 2.** SEM images of pure PS (a) and PtOEP/PS particles (b).

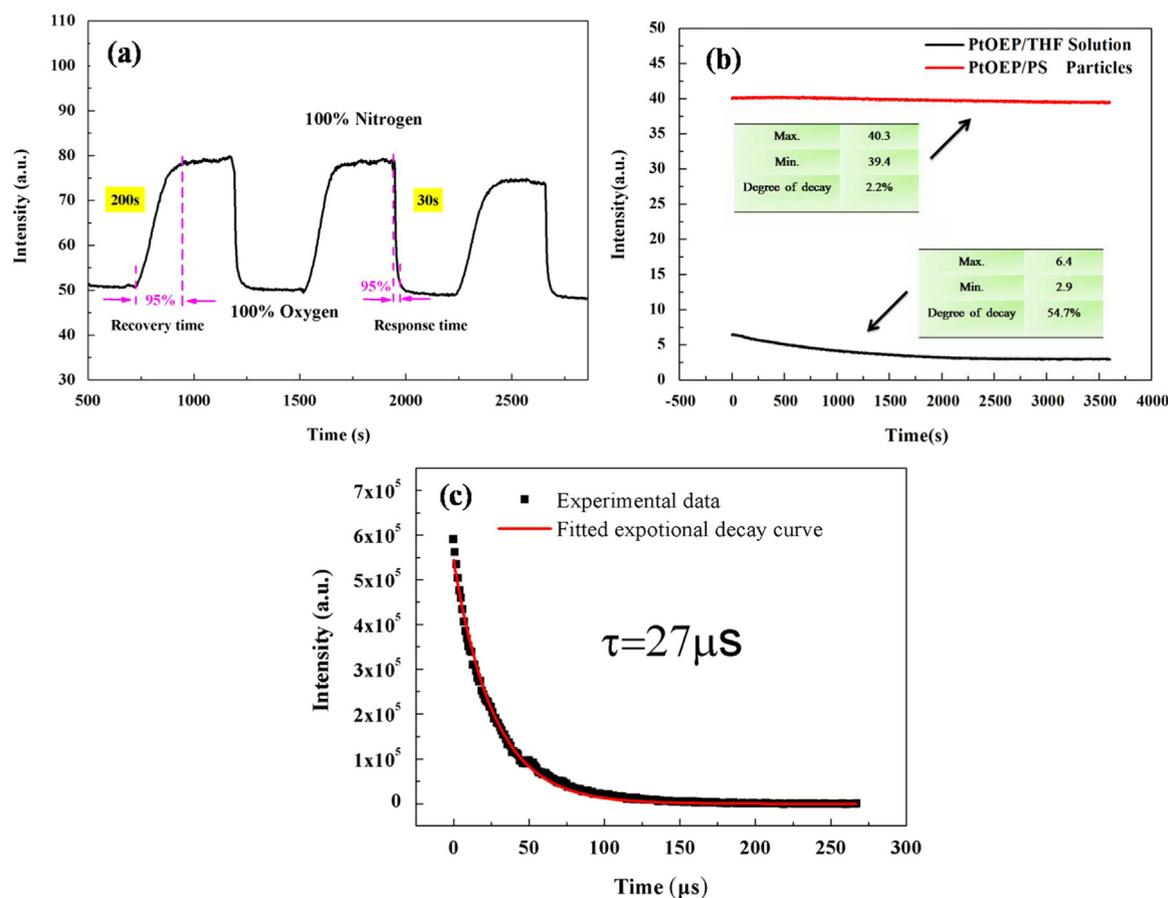


**Fig. 3.** Fluorescent properties of PS/PtOEP particles: the fluorescence emission intensity of PS/PtOEP particles with changes in different gas atmospheres (a); Stern-Volmer curves of PS/PtOEP particles (b).

of pure PS and PtOEP/PS particles is about 251 nm and 384 nm, respectively. It indicates that the indicator PtOEP is successfully embedded into the PS particles along with the chain propagation, resulting in the larger diameter than that of pure PS particles [8]. From the Zeta measurement, the surface potential of PtOEP/PS spheres is found to be  $-36.04$  mV, which is attributed to the  $\text{SO}_4^{2-}$  groups existing around the sphere to maintain the emulsion stable in the water.

The response of the oxygen sensor for dissolved oxygen was

investigated as given in Fig. 3. Fig. 3a shows the emission change of the oxygen sensor in the gas atmosphere with different  $\text{N}_2/\text{O}_2$  ratios. The intensity of fluorescence significantly decrease with the increase of dissolved oxygen content because PS latex particles have a highly porous structure, therefore dissolved oxygen can easily interact with PtOEP molecules to quench the sensor's emission [12]. This illustrates that PtOEP/PS spheres have excellent oxygen permeability and could be employed as an oxygen sensor for the measurement of DO.



**Fig. 4.** Stability test of PS/PtOEP particles: response time, relative intensity change and reproducibility of PtOEP/PS particles on alternated nitrogen and oxygen under the excitation wavelength of 380 nm (a); the photo-stability of fluorescent PtOEP/PS particles and PtOEP/THF solution (b); the decay curve of fluorescence intensity varies with time (c).

The amount of dissolved oxygen is quantitatively monitored via the Stern-Volmer equation:

$$I_0/I = 1 + K_{SV}V[O_2]\% \quad (1)$$

where  $I_0$  is the intensity of fluorescence measured in the aqueous solution containing saturated nitrogen;  $I$  is the intensity of fluorescence measured in different dissolved oxygen solutions.  $I_0$  and  $I$  are all steady-state luminescence signals obtained at 650 nm.  $I_0/I$  represents the quenching ratio and  $K_{SV}$  is the Stern-Volmer quenching constant which depends on the properties of the matrix and indicator.  $V[O_2]\%$  is the volume fraction concentration of dissolved oxygen. The partial pressure [13] can also be used in the Stern-Volmer equation instead of the volume fraction concentration. The intensity ratio ( $I_0/I$ ) versus  $V[O_2]\%$  is fitted with the Stern-Volmer equation (Fig. 3b). It shows that the response signal exists a good linear relationship with dissolved  $V[O_2]\%$  concentration, and gradually reduce with the increase of oxygen concentration in the measured range. Generally, the slope of the linear regression equation is bigger, indicating that the oxygen sensor sensitivity is good [14]. However, in many cases, non-linear Stern-Volmer plots are obtained due to an inhomogeneous dye distribution in the polymer matrix [15].

Fig. 4a shows the recycle stability of the oxygen sensor. The emission intensity signal of the saturated solution was measured at room temperature by blowing the alternated pure oxygen and nitrogen, respectively [16,17]. Note that the fluorescence intensity instantly decreased when altered from 100% nitrogen to 100% oxygen. The quenching time is about 30 s and the recovery time is about 200 s, suggesting that the fluorescent PS spheres synthesized via soap-free emulsion polymerization could be effectively quenched by oxygen in a short time, while the recovery time is much longer than quenching time due to the solubility of oxygen in water being larger than that of nitrogen [18]. In addition, indicator PtOEP is only sensitive to oxygen, incurring a larger response time when altered from oxygen to nitrogen. The photostability of the fluorescent PS spheres is observed under irradiation at 380 nm for 1 h after placed 3 months (Fig. 4b). Decay degree of intensity is just 2.2%, which is much better than that of the PtOEP/THF solution.

The fluorescence intensity varies with time  $t$  is shown as follows [19]:

$$I = I_0 \exp(-t/\tau) \quad (2)$$

where  $I_0$  is the initial fluorescence intensity,  $\tau$  is the fluorescence lifetime. Compared with the results of the steady-state, Fig. 4c exhibits the result of the time-resolved measurements of fluorescence lifetime under ambient condition. The measured lifetime  $\tau$  is estimated to be 27  $\mu$ s. It indicates that the fluorescent microspheres have a short residence time in the excited state, and quenching phenomena are easily triggered between PtOEP and  $O_2$ ,

which will improve the sensitivity of the sensor.

#### 4. Conclusions

Well-dispersed fluorescent PtOEP/PS spheres were successfully synthesized by a soap-free emulsion polymerization. For loading of PtOEP indicator, the size of PS spheres is varied from about 251–384 nm. Fluorescence intensity of PtOEP/PS spheres is strongly dependent on the concentration of oxygen, exhibiting good stability, linear relation, high sensitivity, and fast response time. In view of this, it is believed that soap-free emulsion polymerization is a feasible method to effectively entrap PtOEP in PS spheres to weaken the environmental interference and improve its stability. This work can be expanded in preparing other fluorescent spheres for real-time sensing of DO in different fields.

#### Acknowledgements

This work was supported by the Fundamental Research Funds for the Central Universities (Grant no. HIT.NSRIF.2014047), Heilongjiang Postdoctoral Science Foundation Funded Project (LBH-Z13106), China Postdoctoral Science Foundation Funded Project (Grant no.2014M561360) and 2015 Scientific Research Foundation for the Returned Overseas Chinese Scholars.

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