

# Synthesis of polystyrene beads loaded with dual luminophors for self-referenced oxygen sensing

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## Abstract

Dispersion polymerization has been successfully applied to synthesize monodisperse polystyrene beads loaded with SiOEP and PtOEP for self-referenced oxygen sensing. The polystyrene beads became larger in size as the concentration of initiator was increased due to the reduction of primary particles precipitated from the polymerization medium. The dual luminophors showed similar absorption spectra but two distinctive emission spectra with peaks at 580 and 650 nm for SiOEP and PtOEP, respectively. While the emission of SiOEP exhibited no response to oxygen, the luminescence intensity of PtOEP was monotonically dependent on the concentration of oxygen. From the Stern–Volmer plot, we observed a linear correlation between the intensity ratio of SiOEP at 580 nm to PtOEP at 650 nm and the concentration of oxygen, which could be used to reliably monitor the partial pressure of oxygen in a system.

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## 1. Introduction

Colloidal particles derivatized with luminescent dyes have been exploited for monitoring the concentration of dissolved oxygen in biomedical applications because of their fast response to localized oxygen [1,2]. Recently, Abe et al. have also demonstrated that air-born microspheres loaded with pressure-sensitive dyes could be used to simultaneously acquire the images of both velocity and pressure fields because these particles were sufficiently small to accurately follow the fluid flow and showed the potential for monitoring a two-dimensional pressure field [3]. In spite of these proof-of-concept demonstrations, the reliability of these optical sensing techniques still needs to be improved before they can find use in practical applications. For instance, it has been shown that the detected luminescent signal was strongly dependent on experimental parameters that include the tem-

perature, the light source, the schemes for both illumination and detection, the index of refraction of the medium, and the concentration of dye. These problems can, in principle, be solved by incorporating two different types of luminophors into the colloidal particles, with one serving as the reference and the other for sensing oxygen [1]. In an ideal system, the luminescent dyes should be selected such that both of them have similar response to the experimental parameters (e.g., temperature) while the reference dye will not be quenched by oxygen and the sensing dye will strongly respond to the change of oxygen concentration [4].

To date, oxygen-sensitive luminophors have been mixed with binders and mainly fabricated in the form of thin films or porous films on the surfaces of certain objects in order to measure the concentration of oxygen [5]. For example Rosenzweig et al. incorporated a ruthenium complex in liposomes and explored their use for noninvasive oxygen sensing [2]. Abe et al. have reported on the synthesis of porous silica particles soaked with another ruthenium complex as the oxygen sensor albeit their particles were not uniform in size [3]. From the viewpoint of applications, it would be

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advantageous to introduce dual luminophors into monodisperse polymer latexes. For instance, such a particle can serve as a micrometer-sized sensor for oxygen detection by capturing the luminescence image with a CCD camera. Such particles can also be dispersed in space to simultaneously monitor the oxygen changes at different locations. Here we report the synthesis of such colloidal particles by incorporating octaethylporphyrin (SiOEP) and platinum octaethylporphyrin (PtOEP) (both are chemically stable) into polystyrene (PS) beads during dispersion polymerization. When loaded with dual luminophors, the PS beads could still be prepared as monodisperse samples and their diameters could be readily varied from 0.5 to 2.6  $\mu\text{m}$  by adjusting the concentration of initiator from 6 to 24 mM.

## 2. Experimental

### 2.1. Synthesis of monodisperse PS beads loaded with dual luminophors

In a typical synthesis, 45 mL of ethanol and 5 mL of deionized water (18 M $\Omega$ ) were placed in a three-neck flask (100 mL) equipped with a condenser. The solution was heated at 80 °C for 30 min and then 0.4 g of poly(vinyl pyrrolidone) (PVP, M.W.  $\approx$  55,000, Aldrich, the steric stabilizer), 0.009 g of SiOEP (Frontier Scientific), 0.031 g of PtOEP (Frontier Scientific), 5 mL of styrene (Aldrich, the monomer), and 0.1 g (12 mM) of 2,2'-azobisisobutyronitrile (AIBN, Aldrich, the initiator) were sequentially added to the solution. The polymerization was allowed to proceed for 24 h at 80 °C and magnetic stirring was applied during the entire synthesis. Finally, the suspension of PS beads was cooled down to room temperature. The monodisperse polymer beads loaded with SiOEP and PtOEP were collected via centrifugation at 3900 rpm for 2 min, followed by washing with ethanol three times. To vary the size of PS beads loaded with dual luminophors, we altered the amount of AIBN from 0.1 to 0.05 g (6 mM) and 0.2 g (24 mM), respectively, while other conditions were maintained the same.

### 2.2. Characterization of polymer beads

Samples for SEM studies were prepared by dropping suspensions of the beads on a piece of silicon wafer, followed by drying in a fume hood. SEM images were taken using a field emission scanning electron microscope (FEI-SEM, Sirion XL) operated at an accelerating voltage of 5 kV. Optical micrographs of the PS beads were obtained using a Zeiss Axiovert 200 inverted microscope. The fluorescent images were captured with a Panasonic Industrial Color CCD camera (model number GP-KR222) by acquiring the luminescent light passing through a cutoff filter of 455 nm. The PS beads were excited by a 100-W mercury short arc lamp equipped a band pass filter centered at 405 nm and a line width of 40 nm. The oxygen sensitivities of the PS beads were measured using

the set-up (the PMT survey apparatus) described by Harris [6]. Both PtOEP and SiOEP were excited by the light passing through a band pass filter of 400 nm and the emission spectra were recorded from the light passing through a band pass filter of 650 nm for PtOEP and 580 nm for SiOEP, respectively. The samples were surrounded by a gaseous environment whose oxygen concentration was varied from 0 (pure nitrogen) to 21% (air).

## 3. Results and discussion

For dispersion polymerization, the size of particles is strongly dependent on a number of parameters that include the concentration of initiator, steric stabilizer, or monomer; the polarity of reaction medium; and the polymerization temperature. Among all these parameters, it is most convenient and effective to control the size of particles by adjusting the concentration of initiator or steric stabilizer while maintaining the other variables. In the present study, we controlled the size of PS beads loaded with dual luminophors by varying the concentration of AIBN exclusively. AIBN is an initiator added to the polymerization medium along with the monomer. Fig. 1A shows a typical SEM image of PS beads loaded with SiOEP and PtOEP, which were synthesized with 6 mM AIBN. This image indicates that the PS beads were mainly characterized by two different diameters:  $\sim$ 560 nm (the majority, >90%) and  $\sim$ 200 nm (<10%). The small particles could be easily separated from the sample through centrifugation. The small particles seem to originate from a second round of nucleation of the unreacted monomers due to the presence of initiator at a relatively low concentration. To alter the size of PS beads, we increased the concentration of AIBN from 6 to 12 and 24 mM and typical SEM images of these products are given in Fig. 1B and C. These images clearly indicate that the diameters of resultant PS beads had increased to  $\sim$ 1 and  $\sim$ 2.6  $\mu\text{m}$ , respectively. The dependence of particle size on the concentration of AIBN is plotted in Fig. 1D, indicating that the PS beads were monotonically enlarged as the concentration of initiator was increased. Our explanation of this finding is as follows. The increase of initiator concentration led to the formation of more free radicals in the medium, which then resulted in shorter polymer chains that were more soluble in the polymerization medium. Because the number of insoluble, long chains was reduced, fewer primary particles were precipitated from the reaction medium and the precipitated particles could grow larger sizes by consuming all of the monomers [7–10]. As the PS bead became larger, their size distribution was also slightly broadened.

Fig. 2A shows a typical optical microscopy image of PS beads (1.0  $\mu\text{m}$  in diameter) containing dual luminophors. These monodisperse particles readily assembled into a hexagonal lattice when their suspension was dropped on the surface of a glass substrate and dried under ambient conditions. Fig. 2B gives a luminescence microscopy image clearly indi-

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