

Silica Nanoparticles Coated with Smaller Au Nanoparticles for the Enhancement of Optical Oxygen Sensing

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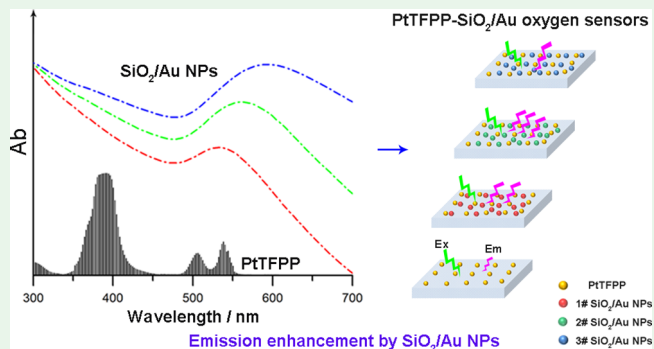
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Supporting Information

ABSTRACT: In the vicinity of metal nanostructures, phosphorescent intensity can be greatly enhanced through the localized surface plasmon resonance (LSPR). The enhancement of phosphorescence intensity in noble-metal nanoparticle (NP) systems is highly dependent on the overlap of the absorbance peak of a noble metal with that of phosphorescent dyes. When the peak of the NPs' absorption spectra has a maximum overlap with that of these dyes, the phosphorescence enhancement is the largest. Here, we use a seeded growth method to synthesize SiO₂/Au NPs with tunable plasmonic resonance and compare their phosphorescence enhancement for an oxygen range of 0–21%. The measurement sensitivity of oxygen is strongly dependent on the enhancement of phosphorescence. When used with PtTFPP, when the absorbance peak of the SiO₂/Au NPs has a maximum overlap with that of PtTFPP, the phosphorescence enhancement factor is as high as 7; the sensitivity of oxygen concentration is as high as 75. Moreover, we also optimize the performance by varying the number of NPs to eliminate the nonradiative energy-transfer (NRET) process and self-quenching.

KEYWORDS: metal-enhanced luminescence, luminescence enhancement, tunable plasmonic resonance peak, sensitivity, oxygen sensors, nanoparticles



1. INTRODUCTION

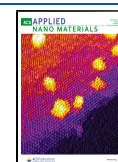
Optical oxygen sensors based on the quenching of luminescence emitted from dyes have experienced increasing success in the past decades since their introduction to detecting oxygen.^{1,2} These optical oxygen sensors exhibit several advantages such as unmatched sensitivity, remote sensing capabilities via fiber optics, noninvasiveness, and low toxicity,^{3–6} which have been successfully used both in scientific and commercial terms.^{7–9} However, the response of optical oxygen sensors always faces many problems in actuality when the dye displays weak emission intensity to variations of oxygen concentrations.¹⁰ While, in the vicinity of metal nanostructures, plasmon excitation providing enhanced optical fields can greatly enhance the emission intensity.^{11–15} Metal-enhanced luminescence (MEL) can not only provide enhanced emissions but also expand the field of dyes by incorporating weak quantum emitters, which has been proved to be an efficient method to increase luminescence sensitivity and intensity in optical oxygen sensors.^{16–18} Chu's group fabricated a metal-enhanced optical oxygen sensor. This sensor comprises an optical fiber that was coated at one end with platinum(II) meso-tetrakis (pentafluorophenyl) porphyrin (PtTFPP) and silver-coated silica nanoparticles (NPs) in an n-octyltriethoxysilane (octyl-triEOS)/tetraethylorthosilane (TEOS) composite xerogel.¹⁶ With metal NPs, the Pt(II)-doped oxygen

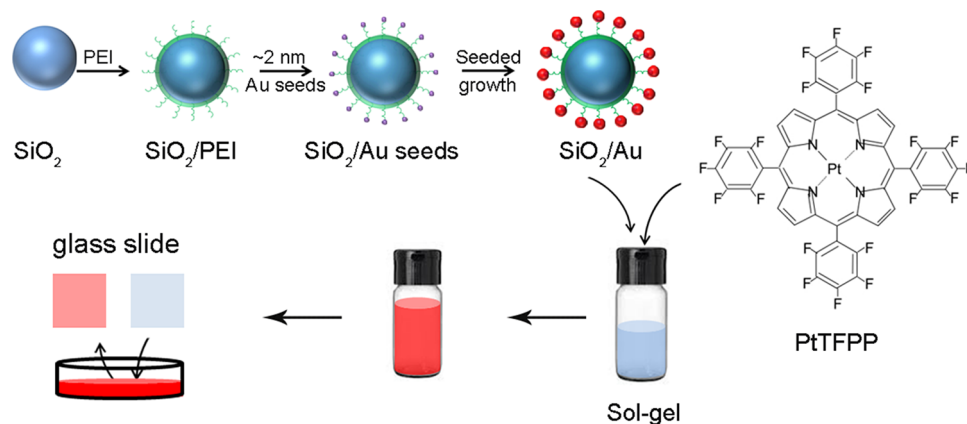
sensors' sensitivity was eight times higher than that of Pt(II)-doped oxygen sensors. Yin et al. added silica-coated Ag NPs to PtTFPP dyes in pressure-sensitive paints to enhance the luminescence intensity. In an ethanol solution, the luminescence intensity-enhanced factor is 3.¹⁸ Our group prepared a series of SiO₂@Ag with tunable plasmonic resonance and embedded in silica gels containing PtTFPP dyes to measure its variation with respect to oxygen concentration. The SiO₂@Ag-Pt(II)-doped oxygen sensors exhibit high sensitivity, 7.7 times higher than that of Pt(II)-doped oxygen sensors.¹⁹ The higher enhancement and sensitivity of the emission intensity of the metal-based oxygen sensors can be attributed to the augmented emission, resulting from the local field enhancement effects and increased emission rate by surface plasmon coupled emission; this can increase both the fluorescence intensity and the quantum yield. The sensitivity and intensity in metal-based oxygen sensors are affected by many parameters, for example, morphologies and sizes of the dyes

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Scheme 1. Fabrication of PtTFPP-SiO₂/Au NP-Based Oxygen Sensors

and metal NPs, especially spectra overlap of the metal localized surface plasmon resonance (LSPR) with the excitation spectra. Our results of SiO₂@Ag with tunable plasmon resonance in oxygen sensors have clearly indicated that the emission intensity of MEL-based optical oxygen sensors is strongly correlated with the degree of the spectral overlap between the plasmon resonance of the noble-metal NPs and the absorption peak of luminescence dyes.^{19–23} The greatly enhanced intensity will result in more accurate measurements at lower O₂ concentrations, demonstrating that MEL-based oxygen sensors will highly contribute to the field of optical oxygen sensors.

Among various metal materials, silver nanostructures produce the strongest plasmon resonance. It has long been recognized that the use of silver may lead to more sensitive surface plasmonic resonance (SPR)-sensing devices than any other noble-metal materials.^{24–27} However, poor chemical and structural stability of silver nanostructures have become the main issue that prevents broad use of silver in SPR sensing.^{28–31} In silver-based optical oxygen sensors, the same problem associated with poor stability also exists, which limits the long-term use of silver-based oxygen sensors. Compared with silver, gold displays much weaker LSPR but excellent stability. Thus, Au-based oxygen sensors can be a good alternative compared with Ag-based oxygen sensors. To explore this potential, we first use the same seeded growth method for SiO₂/Ag NPs to synthesize SiO₂/Au NPs.³² Second, we further make full use of the samples' tunable plasmonic resonance and show its application in an oxygen sensor to amplify the phosphorescence intensity and sensitivity.

2. RESULTS AND DISCUSSION

The seeded growth method is typically used to synthesize SiO₂/Au NPs. This is composed of two steps. The first step is to deposit nucleus seeds on the functionalized SiO₂ surface, and the second step is to grow Au shells over these nucleus seeds.³³ In our work, we focus on investigating how to enhance the emission intensity and sensitivity in MEL-based oxygen sensors. The seeded growth method is just one of the preparation methods for SiO₂/Au NPs. The method is advantageous for preparing nanostructures that have narrow size distributions. In general, the SiO₂ NPs' surface must be functionalized with various organosilanes containing amino (-NH₂) or mercapto (-SH) groups. This will allow for the deposition or adsorption of metal seeds on SiO₂ NPs before

following up with growing Au shells.³⁴ The full surface group modification of SiO₂ NPs is the key to achieving uniform and complete Au shell coating. This is obtained using a slow-growth approach using multiple or slow addition of HAuClO₄ to the seed-coated SiO₂ NP suspensions that contain reducing agents.^{35,36} In this work, we used polyethyleneimine (PEI) to easily adsorb dense Au seeds on the surface of silica and sequentially add growth solutions containing HAuClO₄ for growing Au shells on the SiO₂ NPs, as shown in Scheme 1. This is the most convenient synthesis route for preparing SiO₂/Au NPs with good dispersibility, controllable Au shell, and fast preparation.³⁷

The synthesis procedure for obtaining monodisperse SiO₂/Au NPs is as follows: we prepared SiO₂ with 300 nm diameter NPs (Figure 1b) using a modified Stöber method.³⁸ We treated the SiO₂ NPs ultrasonically with PEI solution, which resulted in PEI-coated SiO₂ NPs. We prepared the SiO₂/Au seeds by adsorbing Au NPs on the PEI layer of SiO₂ NPs using

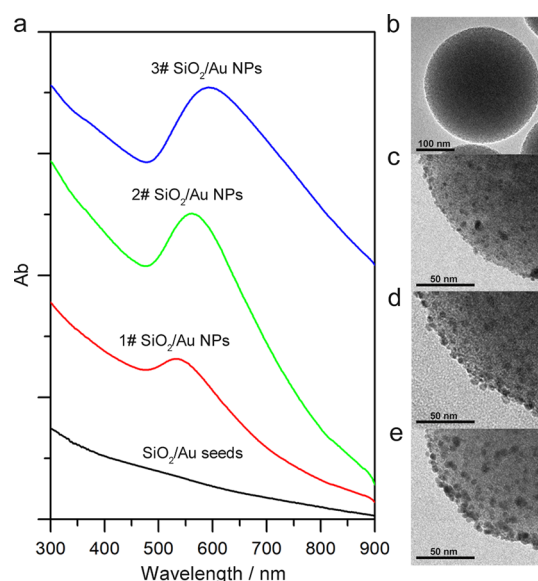


Figure 1. (a) UV-vis spectra of SiO₂/Au prepared by SiO₂-THPC-Au seeds reacted with 0 mL (SiO₂/Au seeds), 20 mL (1# SiO₂/Au), 60 mL (2# SiO₂/Au), and 100 mL (3# SiO₂/Au) of growth solution containing HAuClO₄; (b) SiO₂ TEM images; (c) 1# SiO₂/Au TEM images; (d) 2# SiO₂/Au TEM images; and (e) 3# SiO₂/Au NPs TEM images.

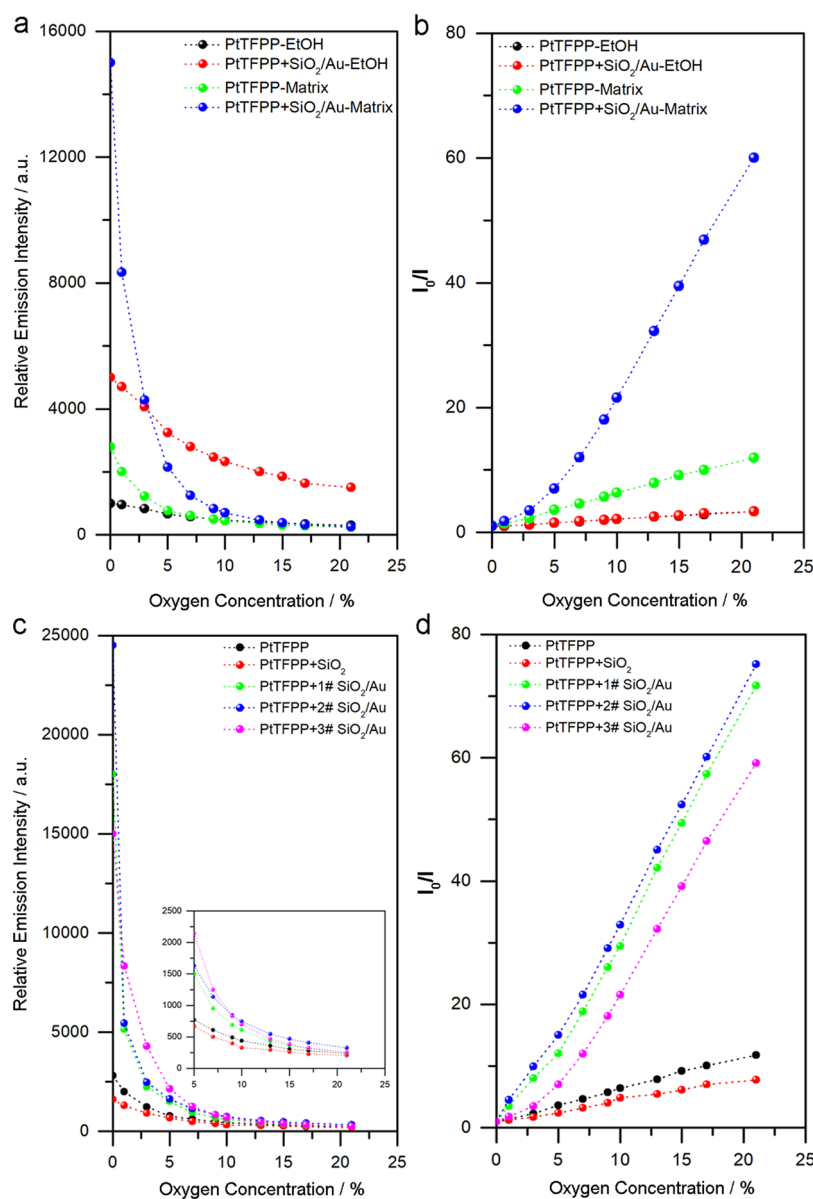


Figure 2. (a) Emission intensity at different oxygen concentrations; (b) Stern–Volmer plots for PtTFPP-based oxygen sensors and PtTFPP and MEP-oxygen sensors mixed with 3# SiO₂/Au NPs in different matrices, in the sol–gel matrix or ethanol, at different oxygen concentrations (0–21%); (c) emission intensity at different oxygen concentrations; (d) Stern–Volmer plots of the Pt-based oxygen sensor and SiO₂/Au-Pt-based oxygen sensors at different oxygen concentrations.

electrostatic attraction between the Au NPs and the $-\text{NH}_2$ groups of PEI, as stated in the literature.³⁷ Finally, by reducing the plating solution using formaldehyde (0.05 mL, 37%) under the stabilization of sodium citrate (0.2 mL, 0.1 M), the SiO₂/Au NPs were rapidly developed. The plating solution was first prepared by adding 7.5 mL of 25 mM HAuCl₄ in 500 mL of 1.8 mM K₂CO₃ aqueous solution and stored for a minimum of 24 h before use.³⁷ We formed the uniform Au shells on the exterior of the SiO₂ NPs using the isotropic growth of all Au seeds under sonication. This was achieved in 5 min. In order to obtain SiO₂/Au NPs with a controllable plasmonic peak in a wide range, we vary the plating solution from 20 mL (1# SiO₂/Au) and 60 mL (2# SiO₂/Au) to 100 mL (3# SiO₂/Au). Figure 1 shows the ultraviolet–visible (UV–vis) spectra of these products with different volumes of growth solution dispersed in deionized (DI) water. As shown in Figure 1a, there is no peak of SiO₂/Au seeds without HAuClO₄ growth

solution. After the injection of 20 mL of growth solution and the reduction reagent of 0.05 mL of formaldehyde (37%) into 1 mL of SiO₂/Au seed (0.1 mg/mL) suspension, the reduction of Au³⁺ was initiated. The absorbance peak located at 530 nm (1# SiO₂/Au NPs) appears, which indicates the formation of Au NPs on the SiO₂ surface.³⁷ As the volume of the growth solution increases to 60 (2# SiO₂/Au) and 100 mL (3# SiO₂/Au), the absorbance peaks red-shifted to 600 nm, and the intensity increased significantly. The main reason for the different plasmonic peaks of SiO₂/Au samples prepared with different amounts of growth solution was that as the growth solution increases, the size of Au NPs increases; the interparticle distance was shortened, thereby enhancing plasmonic coupling. Both the increased size of Au NPs and plasmonic coupling lead to the redshift and broad absorption of incident visible light. In this work, the SiO₂ nanospheres we prepared were 300 nm (Figure 1b). As the SiO₂/Au

nanospheres prepared with the growth solution increases from 20 to 100 mL (Figure 1c–e), the size of Au NPs on the SiO₂ surface is estimated to be 8 nm (1# SiO₂/Au), 10 nm (2# SiO₂/Au), and 12 nm (3# SiO₂/Au), separately. The amount of Au NPs on SiO₂ nanospheres also increases. Thus, the nanogap between Au NPs on the surface of SiO₂ nanospheres decreased. Using this method, the Au NPs coating on the SiO₂ NPs can be varied from the sparse coating of small Au NPs (Figure 1c) to densely coated and uniform Au NPs (Figure 1e).

The fabrication of oxygen sensors is as shown in the scheme: the prepared SiO₂/Au NPs were uniformly mixed with PtTFPP dyes and composite sol–gel solution; then, the glass slides were immersed in the mixture and dried. There are many good polymer matrices used in oxygen sensors, including polydimethylsiloxane,³⁹ ethyl cellulose,⁴⁰ and hydroxymethyl cellulose.^{6,41–43} We just selected the sol–gel in Chu's report to fabricate PtTFPP-based oxygen sensors and investigate the emission enhancement of SiO₂/Au NPs. Oxygen sensors without matrices were prepared with ethanol instead of the sol–gel solution. As shown in Figure 2a, the Pt-based oxygen sensors' emission intensity with EtOH is around three times lower than that of the sensors with the sol–gel matrix at 0% O₂, which indicates that the sol–gel matrix is beneficial for the measurement of oxygen at lower concentrations in the system. With the addition of SiO₂/Au NPs (3# SiO₂/Au) in the oxygen sensors, the intensity of the Pt-NPs based oxygen sensors in EtOH is around 5 times higher than that of the Pt-based oxygen sensors in EtOH throughout the 0–21% O₂ range. In the sol–gel matrix, the luminescence intensity of Pt-NP-based oxygen sensors is five times higher than that of Pt-based oxygen sensors at 0% O₂ and almost the same at 21% O₂. These data show that the emission intensity of oxygen sensors can be greatly enhanced by the SiO₂/Au NPs. The different intensity enhancement of NPs in the matrix and EtOH at different concentrations of O₂ might be caused by the diffusion rate of oxygen in the sol–gel solution and EtOH. The enhancement factor (I_0/I_{O_2} : the ratio of intensity at 0% via different oxygen concentrations) of the Pt-based oxygen sensors, with and without NPs, in ethanol solution is almost the same (Figure 2b); the intensity of Pt-based oxygen sensors with NPs within the matrix is five times higher than that without NPs. These data further indicate that the sol–gel is beneficial for the performance of Pt-based oxygen sensors.

The performance of Pt-based oxygen sensors mixed with 1#, 2#, and 3# SiO₂/Au samples were tested and compared. The performance of Pt-based oxygen sensors without NPs was also tested as a comparison. Figure 2c shows that the oxygen sensors' relative phosphorescence intensities decrease as the oxygen concentration increases. In addition, the phosphorescence intensities of Pt-SiO₂/Au-based oxygen sensors are higher than those of Pt-based oxygen sensors at the same concentrations of oxygen because of the metal-enhanced phosphorescence of SiO₂/Au. Among these SiO₂/Au samples, the phosphorescence intensity of the 2# SiO₂/Au-Pt-based oxygen sensor, which is prepared with 60 mL of HAuClO₄ growth solution at 0.0% O₂, is the highest than the other SiO₂/Au samples, while the intensity of the oxygen sensors with these SiO₂/Au samples is closer in value at 21% O₂. In order to obtain a clear insight into the difference in the oxygen sensors, we increase the emission intensity at 5–21%. As shown in the inset of Figure 2a, at 5–10%, the emission intensity decreases in the order 3# > 2# > 1#; at 10–21%, and the emission

intensity of 2# is higher than those of 3# and 1#. The emission of the oxygen sensors with SiO₂/Au is observed to be still brighter than that of the oxygen sensors at a higher concentration of oxygen. As a comparison, we also fabricate oxygen sensors just mixed with SiO₂. The PtTFPP-SiO₂ oxygen sensors' intensity is much weaker than that of the PtTFPP-oxygen sensors; this further shows that the oxygen sensors' enhancement is attributed to the metal-enhanced phosphorescence of Au.

The slope of the Stern–Volmer plot, K_{sv} , based on the ratio of $I_0/I_{[O_2]}$ divided by the oxygen concentration provides a measure for the relative sensitivity of the oxygen sensors. At 0–5% O₂, the plots of Pt-NP-based oxygen sensors are nonlinear. From 7–21% O₂ concentrations, the slopes are constant, ranging from 3.36 for 3# and 3.77 for 1# to 3.83 for 2#. Compared with the slope of the Pt-based oxygen sensor, 0.51, this shows a 6.6–7.5-fold increase in sensitivity. The maximum (I_0/I) for the enhanced curves range from 59–75, which when compared with the maximum (I_0/I) of the Pt-based oxygen sensor, 11, shows a 5.3–6.8-fold increase in the maximum attainable I_0/I . The different sensitivities of these samples can be predominantly attributed to the different phosphorescence intensity profiles of the PtTFPP-SiO₂/Au-based oxygen sensors, that is, to say, higher intensities at 0% O₂ (I_0) and almost the same intensities at 21% O₂ will lead to larger slopes and therefore higher sensitivities. The different enhancement of phosphorescence intensities is caused by the different absorbance peaks of different SiO₂/Au NPs, resulting in different overlap between the excitation spectra of the dyes and the LSPR of the SiO₂/Au NPs. The dominant excitation of PtTFPP is at 392 nm, and compared with the UV–vis spectra of these SiO₂/Au samples, the 2# sample has the maximum overlap and thus the highest enhancement factor. These data further support experimental evidence that the intensity of dyes enhanced by the SiO₂/Au NPs relies strongly on the overlap between the excitation spectra properties of the dye with the LSPR of the NP, which is consistent with our previous findings using the seeded growth of SiO₂@Ag with tunable plasmon resonances.¹⁸ Compared with that of the PtTFPP-SiO₂/Ag-based oxygen sensors, the sensitivity of PtTFPP-SiO₂/Au-based oxygen sensors is slightly lower at low concentrations (0–5%) but almost the same at 5–21% (Figure S2). The difference can be explained as follows: the absorption spectrum of the PtTFPP has a Soret band (S_0 to S_2 transition) at 392 nm and two Q bands (S_0 to S_1 transition) at 508 and 541 nm, respectively. The absorbance peak of SiO₂@Ag is mainly localized at 450 nm, while the absorbance peak of SiO₂/Au is mainly localized at 550 nm. It can be seen that the absorbance peak of SiO₂@Ag is more overlapped with that of PtTFPP dyes. Furthermore, the silver NPs display stronger LSPR with higher plasmon energy and more intense local electric field enhancement than gold NPs. In addition, the SiO₂@Ag NPs are more easily oxidized at higher concentrations of oxygen, and the diffusion of oxygen in the sol–gel system will lead to the surface oxidation of SiO₂@Ag, finally resulting in the weakened emission intensity at higher concentrations of oxygen. While at higher concentrations of oxygen, the SiO₂/Au NPs are stable, the SiO₂/Au NP-based oxygen sensors can emit brighter luminescence. Based on these results, both the LSPR of the NPs matched well with the excitation spectra of the dyes, and the stability of NPs is crucial to the intensity enhancement in oxygen sensors. That is to say, in addition to the PtTFPP dye, the intensity of other dyes

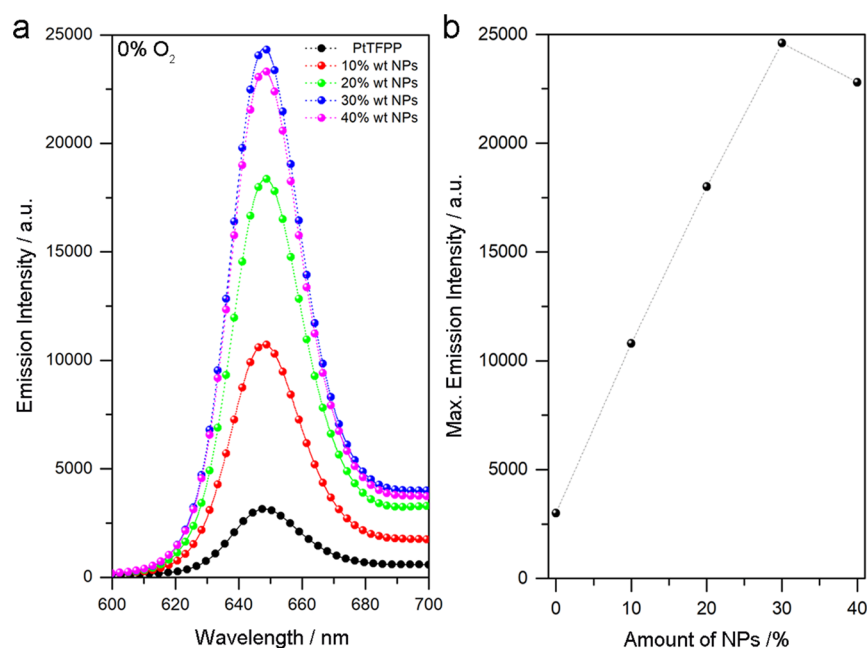


Figure 3. (a) Phosphorescence intensity; (b) maximum phosphorescence intensity of PtTFPP at different volumes of 2# SiO₂/Au measured at 0% oxygen concentration.

including fluorescent dyes can also be enhanced with matched NPs. The role of SiO₂ NPs is to prepare NPs with a wide absorbance peak in visible light.

To optimize the performance of SiO₂/Au-Pt-based oxygen sensors, we further investigate the dependence of phosphorescence intensity on the number of SiO₂/Au NPs. As shown in Figure 3a, the peak phosphorescence intensity of Pt-based oxygen sensors (fixed volume of 0.2 mg/mL PtTFPP at 0.2 mL) at 0% oxygen concentration is around 3000. As the volume of SiO₂/Au increases from 10 to 30% wt, the peak intensity increases from 11,000 to 24,000; while the number of SiO₂/Au further increases to 40%, the peak intensity decreases to 23,000. Figure 3b shows that this trend can be clearly seen in the maximum phosphorescence intensity plot. These data show that the phosphorescence intensity of SiO₂/Au-Pt-based oxygen sensors is highly dependent on the number of SiO₂/Au NPs. In the fluorescein system, there are resonance energy transfer between fluorescein molecules (homo RET), which is called self-quenching and nonradiative energy transfer (NRET) to the NPs.³⁹ In our SiO₂/Au-PtTFPP systems, if the PtTFPP molecules are too close to each other, self-quenching will occur. In addition, if the PtTFPP molecules are too close to the SiO₂/Au NPs, there will be NRET to the NPs. Both the self-quenching (RET) and NRET will weaken the emission from the dyes. Only when these distances are optimized, these losses can be eliminated so that the phosphorescence emission under the effect of the electromagnetic field of NPs can be significantly enhanced. In this case, when the volume of NPs is less than 30%, the number of NPs is not enough to accomplish this: the dyes are surrounded by more dye and less NPs, leading to more self-quenching and therefore less MEL. At 30% NPs, the dyes are mostly surrounded by NPs, the MEL is strongest, and thus the intensity is the brightest. When the volume of NPs is further increased to 40%, the NRET is dominated by the NPs, resulting in a decrease in phosphorescence intensity. There-

fore, 30 wt % NPs by volume is the optimal amount for the SiO₂/Au-PtTFPP-based oxygen sensors.

The photostability of Pt-based oxygen sensors was tested by irradiation of the oxygen sensors with 405 nm laser at room temperature for 5 h, as shown in Figure 4. After illumination

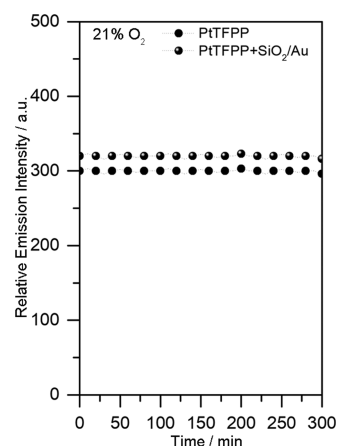


Figure 4. Photostability of PtTFPP-based oxygen sensors.

for 5 h, the relative phosphorescence intensity of the Pt-based oxygen sensor and the 1# SiO₂/Au-Pt-based oxygen sensor at 21% O₂ remains stable at 300 and 320, respectively, with no signs of decay. This is because the fluorophenyl groups of the PtTFPP (PtTFPP has four fluorophenyl groups that are connected to its porphyrin) are impervious to oxidation/reduction, thereby making the PtTFPP molecules stable against photo-oxidation/reduction. In addition, the SiO₂/Au is also very stable; this, therefore, increases the photostability of Pt-based oxygen sensors.

3. CONCLUSIONS

In this work, we fabricated PtTFPP-based oxygen sensors with SiO₂/Au NPs. Under the MEL effect of NPs, both the

sensitivity and intensity of oxygen sensors can be greatly enhanced in a wide range of oxygen concentrations. The intensity of dyes enhanced by the NPs relies strongly on the overlap between the LSPR of the NPs with the excitation spectra properties of the dye. If one were to use other dyes that are often used in luminescent oxygen sensing (e.g., PtOEP), it would be important to design and fabricate NPs to maximize the overlap between the NPs' LSPR and the dye's excitation spectra. There are some inherent limitations from solution processing, such as the need to control the space/distance between Au NPs and to prevent them from aggregation. Because of such current material processing challenges, we believe the sensitivities achieved in this work are far from the maximum value. This new type of noble-metal-based oxygen sensors and the approach for use with other luminescent oxygen sensors offer us accurate measurements ranging from a low oxygen concentration (0%) to atmospheric oxygen concentrations (21%), which is a great milestone in the development of ultrasensitive oxygen sensors.

4. EXPERIMENTAL SECTION

4.1. Synthesis of SiO₂ Nanospheres. The synthesis of SiO₂ nanospheres was performed, as described in our previous publication.¹⁸

4.2. Synthesis of SiO₂/Au. The synthesis of SiO₂/Ag described in our previous publication¹⁸ was adjusted for the use of Au. Here, we dispersed 0.6 g of SiO₂ in 60 mL of PEI (1 wt %) solution, and then, the solution was stirred for 4 h. The SiO₂ nanospheres from the previous step were washed three times with water and then placed in 6 mL of water (0.1 g/mL). The sample (1 mL) was then pipetted to 10 mL of tetrakis-(hydroxymethyl) phosphonium chloride (THPC)-Au seed solution and sonified for 1 h and then stirred overnight. The solution was then centrifuged and dispersed in water. Baiker's method was used to synthesize the THPC-Au seeds: 41 mL of water, 1.35 mL of NaOH (0.2 M), and 0.90 mL of THPC aqueous solution (1.2 mM) were mixed and stirred for 10 min, after which 1.80 mL of the aqueous solution of chloroauric acid (25 mM) was quickly added. Then, the resulting solution was aged for a minimum of 2 weeks at 4 °C before it was used.

The seed-mediated growth was then carried out to deposit Au onto the Au seeds attached to the SiO₂ particles. A plating solution was first prepared by adding 7.5 mL of 25 mM HAuCl₄ in 500 mL of 1.8 mM K₂CO₃ aqueous solution and stored for at least 24 h before use. The above SiO₂/Au seed solution was added to 20 mL of the plating solution, stirred for 5 min, and mixed with 0.2 mL of 100 mM trimethyl sodium citrate and 0.05 mL of formaldehyde (37%), and then stirred for 10 min. Finally, we centrifuged the sample and then washed it with water three times. For the growth procedure, after centrifuging and washing, the prepared SiO₂/Au samples were added to 20 mL of plating solution and mixed with TSC and formaldehyde multiple times to prepare 1# (1 time), 2# (3 times), and 3# (5 times).

4.3. Fabrication of SiO₂/Au-Based Oxygen Sensors. Octyl-triEOS/TEOS composite sol-gel was used as the matrix material in the pressure-sensitive paint. The sol-gel was prepared by mixing 0.20 mL of octyl-triEOS and 4.0 mL of TEOS; this forms the precursor solution using Chu's method. We then added 1.25 mL of EtOH and 0.40 mL of HCl (0.1 M) to this solution, which catalyzed the ORMOSIL reaction. We then magnetically stirred the solution for 1 h at room temperature. We then added 0.10 mL of Triton-X-100 so that the silica sol's homogeneity would be improved. Next, we added 20 mg of SiO₂/Au to 0.50 mL of PtTFPP/EtOH (0.2 mg/mL), and the solution was stirred for 12 h. Next, we added 0.50 mL of the composite sol-gel solution to the dye solution. Lastly, we capped the solution and magnetically stirred it for another 12 h. Before testing the response of this formulation to varying oxygen concentrations, the glass slide (2 × 2 cm²) was immersed in the solution for 10 min and left to stabilize under ambient air conditions for 24 h.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsnm.1c03391>.

UV-vis absorption spectra of PtTFPP and 1–3# SiO₂/Au NPs (PDF)

Plot showing the wavelength of PtTFPP against Ab (TIF)

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Notes

The authors declare no competing financial interest.

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