Silver Nanowire-Induced Sensitivity Enhancement of Optical Oxygen Sensors Based on AgNWs–Palladium Octaethylporphine–Poly(methyl methacrylate) Microfiber Mats Prepared by Electrospinning

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ABSTRACT: Sensitivity enhancement of optical oxygen sensors is crucial for the characterization of nearly anoxic systems and oxygen quantification in trace amounts. In this work, for the first time we presented the introduction of silver nanowires (AgNWs) as a sensitivity booster for optical oxygen sensors based on AgNWs–palladium octaethylporphine–poly(methyl methacrylate) (AgNWs@PdOEP–PMMA) microfiber mats prepared by electrospinning. Herein, a series of sensing microfiber mats with different loading ratios of high aspect ratio AgNWs were fabricated, and the corresponding sensitivity enhancement was systematically investigated. With increasing incorporated ratios, the AgNWs@PdOEP–PMMA-sensing microfiber mats exhibited a swift response (approx. 1.8 s) and a dramatic sensitivity enhancement (by 243% for the range of oxygen concentration 0–10% and 235% for the range of oxygen concentration 0–100%) when compared to the pure PdOEP–PMMA microfiber mat. Additionally, the as-prepared sensing films were experimentally confirmed to be highly photostable and reproducible. The advantages of AgNW-induced sensitivity enhancement could be useful for the rational design and realization of revolutionary highly sensitive sensors and expected to be readily applicable to many other high-performance gas sensor devices.

1. INTRODUCTION

Oxygen is one of the most popular and important analytes on the earth and is vital for the survival of most living organisms.1–3 In addition, many industrial applications such as nitrogen generation, food packaging, industrial gas manufacturing, and industrial safety need to ensure oxygen is absent, even at trace levels.4 As we all know, sensitivity enhancement of optical oxygen sensors is the most crucial aspect for the characterization of nearly anoxic systems and oxygen quantification in trace amounts. Therefore, oxygen sensors that perform with high sensitivity have been widely developed, among which optical oxygen sensors based on the luminescence quenching principle have been of particular interest because of their unique advantages, such as excellent sensitivity, accurate detection, low detection limit, swift response/recovery, and so forth.5–7 Up to now, how to rationally design and realize revolutionary sensing films for improving the sensitivity of oxygen sensors is still a long-standing challenge.

In general, one alternative way to achieve high sensitivity is to use polymeric materials with high oxygen permeability such as a silicone matrix and fluorinated copolymers.6,9 Apart from the polymer matrix materials, the internal hierarchical structures and surface morphologies of the sensors also act as important factors to determine the sensitivity of the sensors.9,10 Distinct from many solid sensing films or coatings, porous-based sensing films potentially improve the sensitivity thanks to the high accessibility of gas molecules and free movement of the oxygen molecules in the sensing films.10,11 Thus, porous sensing films have attracted considerable attention and manufactured in various formats depending on their surface structures, such as particle assembly porous films,7 honeycomb porous films8,10,12 and microfiber films.13–15 In the past decades, oxygen sensor probes encapsulated in pure polymer matrixes...
were integrated into fibers via electrospinning and attracted much attention in the field of gas sensors. Thanks to the high specific surface area of fiber mats, a much larger analyte-sensing material interface can be realized, leading to improved sensitivity when compared to the solid sensing films. Importantly, unlike solid sensing films, the intrinsic superhydrophobic fiber mats can serve as a promising substrate for high-sensitive sensors because of their good water repellency and higher oxygen gas permeability. Therefore, the microfiber mats with superhydrophobic property is an efficient, highly versatile, and a promising substrate, which can be used for fabricating high-performance sensor devices.

Recently, precious metal particles have been successfully applied to the oxygen-sensing system owing to the capability to tune the emissive spectral properties of nearby fluorophores for simple sensitivity control. Plasmon resonance can induce enhanced local electromagnetic fields and modulate optical properties of nearby chromophores. For instance, Gryczynski et al. investigated the effects of metallic silver particles on the emission properties of [Ru(bpy)₃]²⁺ on silver island films. Roche et al. reported enhanced luminescence for the ruthenium dye in trimethoxysilane xerogel spin-coated on a gold surface, which exhibited high sensitivity to determine trace oxygen. Önal and co-workers investigated phosphorescence-based oxygen-sensing properties of metal porphyrins improved by silver nanoparticles. The results indicated that the offered sensing composites provided the advantages of fast response, enhanced sensitivity, reversibility and higher Stern–Volmer constants, and a low limit of detection for oxygen. Ozturk et al. also reported the utilization of silver nanoparticles in electrospun polymeric fibers for oxygen-sensing purposes with many advantages such as tunable sensitivity, a linear calibration plot for larger concentration ranges, and an increased surface area enhancement in all sensor dynamics. Above all, roles of precious metals in the sensitivity enhancement of oxygen sensors have garnered much attention. Although silver nanoparticles are used for the fabrication of optical oxygen sensors widely and act positively in sensitivity improve-

**2. RESULTS AND DISCUSSION**

AgNWs with a high aspect ratio were prepared through a typical polyol method. Figure 1A shows the UV–vis spectrum for AgNWs and the absorption peak centered at 370 nm.
nm that can be assigned to the typical longitudinal resonance of AgNWs, suggesting the final formation of AgNWs. Figure 1B is the high-magnification scanning electron microscopy (SEM) image of the as-prepared AgNWs, which reveals that the AgNWs are uniform in diameter with a mean value of 50 nm. Figure 1C,D shows the SEM images of AgNWs with a diameter of 50 nm and length of 100 μm before and after two cycles of selective precipitation and purification of AgNWs. From the SEM images, it is obvious that there is a dramatic decrease in the number of particles after the purification process. Figure S1 depicts the X-ray diffraction (XRD) pattern of the uniform AgNWs. All diffraction peaks can be indexed to the (111), (200), (220), (311), and (222) planes of a pure face-centered cubic silver crystal, which is consistent with the standard value according to JCPDS card no. 04-0783. Additionally, the peak in the (111) crystalline plane is much stronger (three times) than any of other peaks, indicating the enrichment of the (111) crystalline planes in the as-prepared AgNWs, resulting in the high aspect ratio AgNWs.

To understand the AgNW-induced sensitivity enhancement effect on oxygen-sensing properties of AgNWs, Figure S2 presented the SEM images (on cross sections) of all microfibers with different dosages of AgNWs. The neat PdOEP–PMMA microfiber without any additional AgNWs to a dosage of 0 wt % was also studied as a control. As found in Figure S2, AgNWs were embedded into the PMMA matrix, and the amounts of AgNWs increased as the loading increased. Additionally, Figure 2 showed that all microfiber mats interact across each other as a porous network, which could thus contribute to oxygen diffusion and quenching on the emissive sensor dye. Therefore, the highly hierarchical porous structure of the microfiber mats allows rapid gas exchange resulting in a swift sensor response/recovery. The optimized AgNW loading concentration in the microfiber mats was found to range from 1 to 2 wt %, which provides overall excellent performance, such as higher sensitivity and swift response/recovery properties. Moreover, thermal gravimetric analysis (TGA) was used to determine the loading of AgNWs, and the TGA curves of AgNWs@PdOEP–PMMA microfibers are shown in Figure S3. In addition, the TGA results are basically in agreement with the loading of AgNWs in the experiments.

The remarkable properties of the superhydrophobic surface of the sensing films have attracted much academic and industrial interest recently because of the potential use in various sensing device applications. Because of the superhydrophobic property of fiber mats, the mats serve as a promising substrate for high-sensitive sensors because of their good water repellency and higher oxygen gas permeability. Subsequently, the contact angles (CAs) of the microfiber mats were obtained on a CA tester. The CA values for PdOEP–PMMA and AgNWs@PdOEP–PMMA (1.0 wt %) microfibers
mats are as high as 140° (Figure 3). Moreover, with the increase of AgNW loading, the CA values decreased from 141° to 131°. Although the introduction of AgNWs into the microfiber mats resulted in a slight decrease of the CA values, the microfiber mats still maintain the hydrophobic properties with CA values above 130°. The surface wettabilities of the cast film and fiber mat based on the AgNWs@PdOEP–PMMA (1 wt %) sample were compared and displayed in Figure S4. For the cast film, the CA value is below 100° and exhibited poor hydrophobic properties. Finally, the water droplets with different colors rolled down on the mats without moistening the mat surface, indicating the excellent superhydrophobic property of microfiber mats loaded with AgNWs (Figure 3).

To further confirm the homogeneous dispersion of PdOEP in the PMMA matrix, the UV–vis absorption spectra and phosphorescence spectra of PdOEP and AgNWs@PdOEP–PMMA (1 wt %) were characterized at 23 °C, as shown in Figure S5. From the UV–vis absorption, PdOEP showed a band at 395 nm. After doping inside the AgNWs@PdOEP–PMMA (1 wt %) solutions, the bands of PdOEP also appear in the absorption spectrum of AgNWs@PdOEP–PMMA (1 wt %) solutions, indicating the uniform existence of PdOEP composition in the AgNWs@PdOEP–PMMA (1 wt %) composites (Figure S5). Additionally, the emission spectrum of PdOEP existed in the emission spectrum of the AgNWs@PdOEP–PMMA (1 wt %) microfiber mat, which also confirmed the existence of the PdOEP composition in the AgNWs@PdOEP–PMMA (1 wt %) microfiber mat. Figure 4 shows the phosphorescence images of the AgNWs@PdOEP–PMMA microfiber mats containing the luminescent oxygen.

Figure 3. CA images for the microfiber mats: PdOEP–PMMA (141 ± 1°), AgNWs@PdOEP–PMMA (1.0 wt %) (140 ± 1°), AgNWs@PdOEP–PMMA (1.5 wt %) (139 ± 1°), AgNWs@PdOEP–PMMA (2.0 wt %) (138 ± 1°), AgNWs@PdOEP–PMMA (2.5 wt %) (135 ± 1°), and AgNWs@PdOEP–PMMA (3.0 wt %) (131 ± 1°). Photographs of water droplets (50 μL) on the surface of microfiber mats.

Figure 4. Phosphorescence micrograph photos of AgNWs@PdOEP–PMMA microfiber mats (λex = 395 nm, λem = 663 nm).
sensor dye PdOEP. Uniform red emissions were observed for all AgNWs@PdOEP−PMMA microfibers under the laser excitation at 395 nm. All microfibers are distributed on the aluminum foil substrates randomly with clear phosphorescence emission. From above results, it is clearly demonstrated that the PdOEP sensor dye had been successfully and homogenously doped into the PMMA matrix.

The phosphorescence emission spectra of AgNWs@PdOEP−PMMA microfiber mats under different oxygen concentrations are shown in Figure 5A. Subsequently, the oxygen-sensing performances of the AgNWs@PdOEP−PMMA microfiber mats were investigated systematically based on the phosphorescence intensities. The relative phosphorescence intensities of the AgNWs@PdOEP−PMMA microfiber mats gradually decreased as the oxygen concentration varies from 0 to 100%. The distinct decrease of phosphorescence intensities is mainly attributed to the efficient quenching effect of the microfiber mats when exposed to oxygen. In other words, all microfiber mats align across each other, forming a highly hierarchical porous structure of the microfiber mats that allows rapid gas exchange resulting in a swift sensor response/recovery.28 Quenching of phosphorescence by oxygen was long known but not understood until Stern and Volmer derived their famous equation.33 In the optical oxygen sensors based on the quenching of luminescence, the relationship between the luminescence intensity and the oxygen concentration is reflected by the Stern−Volmer equation. In many oxygen-sensing cases, the intensity from the Stern−Volmer equation with dynamic quenching can be described by the formula 1

\[ I_0/I = 1 + k_{sv}[O_2] \]  

where \( I_0 \) is the value in the absence of the quencher, \( I \) is the phosphorescence intensity under different oxygen concentrations \([O_2]\), and \( k_{sv} \) is the Stern−Volmer constant.3 Generally, in an ideal quencher system, there is a linear relationship between \( I_0/I \) and the oxygen concentration, described as formula 1. However, many cases showed that downward Stern−Volmer plots (SVPs) originate from the heterogeneity of the microenvironment of the oxygen-sensing probes. It assumed that the sensor dye exists in two distinctly different environments: one being quenchable and the other either not being quenched at all or being quenched at a very different rate. Therefore, a two-site model was introduced to fit the SVPs, which has been widely used ever since.34,35 Generally, the nonlinear Stern−Volmer equation can be described as follows (eq 2)

\[ \frac{I_0}{I} = \frac{1}{1 + k_{sv1}[O_2] + \frac{f_2}{1 + k_{sv2}[O_2]}} \]  

where \( f_1 \) and \( f_2 \) the fractions of the total emission for each component (with \( f_1 + f_2 = 1 \)) and \( k_{sv1} \) and \( k_{sv2} \) are the Stern−Volmer constants for each component.2

The SVPs for phosphorescence intensity exhibited nonlinear behaviors for all AgNWs@PdOEP−PMMA microfiber mats, indicating heterogeneity in the microenvironment of PdOEP caused by the loading of AgNWs. Assuming localization of the dye at two different sites, the SVPs were fitted using a two-site model (eq 2).34,36 The calibration SVPs for all AgNWs@PdOEP−PMMA microfiber mats in the presence of oxygen from 0 to 100% are shown in Figure 5B, and the Stern−Volmer constants for sensing films are summarized in Table 1.
Interestingly, $k_{\text{on}}$ values are much higher than $k_{\text{off}}$ for all AgNWs@PdOEP–PMMA microfiber mats, and the fractional contribution of the component being quenched $f_I$ is higher than $f_2$. Therefore, a considerable linearity of SVPs and favorable homogeneity of oxygen-sensing microfiber mats were found at different oxygen concentrations between 0 and 10%.

Subsequently, the calibration SVPs for all AgNWs@PdOEP–PMMA microfiber mats in the presence of various oxygen concentrations from 0 to 10% are shown in Figure S3C, and the Stern–Volmer constants for sensing mats are summarized in Table 2. From the above results, the offered AgNWs@PdOEP–PMMA microfiber mat sensing films are highly sensitive in a low oxygen concentration and showed a linear relationship, which is in accordance with the previous research studies. Importantly, the sensitivity of the AgNWs@PdOEP–PMMA microfiber mats increased with increasing AgNW loading. The sensitivity enhancement of AgNWs@PdOEP–PMMA microfiber mats induced by AgNWs can also be observed clearly from the values of $I_P/I_{\text{I,100}}$ presented in Tables 1 and 2. AgNWs@PdOEP–PMMA microfiber mats showed an excellent sensitivity (increased by 243 and 235%) compared to the pure PdOEP–PMMA microfiber mat, performed under the oxygen concentration of 0–10 and 0–100%, respectively. However, because of the higher loading of

### Table 1. Comparison of the Key Parameter for the Oxygen Sensor Films (O$_2$ %: 0–100%)

| Sensor Films | $I_P/I_{\text{I,100}}$ | $k_{\text{on}}$ (O$_2$ %$^{-1}$) | $k_{\text{off}}$ (O$_2$ %$^{-1}$) | $f_I$ | $R^2$ | Mathematical Model |
|--------------|---------------------|-----------------|-----------------|------|------|------------------|
| AgNWs@PdOEP–PMMA (1.0 wt %) (cast film) | 2.23 | 0.08036 | −0.00119 | 0.99411 | 0.9934 | $I_P/I_{\text{I,100}} = \frac{0.099411}{1 + 0.00608[O_2]} + 0.00549$ |
| PdOEP–PMMA | 14.00 | 0.18314 | −0.0015 | 0.97951 | 0.9999 | $I_P/I_{\text{I,100}} = \frac{0.97951}{1 + 0.18314[O_2]} + 0.00249$ |
| AgNWs@PdOEP–PMMA (1.0 wt %) | 20.33 | 0.40365 | 0.00037 | 0.97356 | 0.9999 | $I_P/I_{\text{I,100}} = \frac{0.97356}{1 + 0.40365[O_2]} + 0.02541$ |
| AgNWs@PdOEP–PMMA (1.5 wt %) | 19.83 | 0.40374 | −0.00059 | 0.97459 | 0.9998 | $I_P/I_{\text{I,100}} = \frac{0.97459}{1 + 0.40374[O_2]} + 0.02561$ |
| AgNWs@PdOEP–PMMA (2.0 wt %) | 19.77 | 0.59218 | 0.00072 | 0.96294 | 0.9999 | $I_P/I_{\text{I,100}} = \frac{0.96294}{1 + 0.59218[O_2]} + 0.03706$ |
| AgNWs@PdOEP–PMMA (2.5 wt %) | 19.70 | 0.61321 | 0.00035 | 0.89636 | 0.9992 | $I_P/I_{\text{I,100}} = \frac{0.89636}{1 + 0.61321[O_2]} + 0.01304$ |
| AgNWs@PdOEP–PMMA (3.0 wt %) | 4.90 | 0.57435 | 0.00043 | 0.80316 | 0.9996 | $I_P/I_{\text{I,100}} = \frac{0.80316}{1 + 0.57435[O_2]} + 0.10604$ |

Equation $f_I + f_2 = 1$.

### Table 2. Comparison of the Key Parameter for the Oxygen Sensor Films (O$_2$ %: 0–10%)

| Sensor Films | $I_P/I_{\text{I,100}}$ | $k_{\text{on}}$ (O$_2$ %$^{-1}$) | $R^2$ | Mathematical Model |
|--------------|---------------------|-----------------|------|------------------|
| AgNWs@PdOEP–PMMA (1.0% wt) (cast film) | 1.41 | 0.08932 | 0.9972 | $I_P/I_{\text{I,100}} = 0.96133 + 0.08932[O_2]$ |
| PdOEP–PMMA | 2.45 | 0.14782 | 0.9978 | $I_P/I_{\text{I,100}} = 0.94767 + 0.14782[O_2]$ |
| AgNWs@PdOEP–PMMA (1.0 wt %) | 4.21 | 0.31972 | 1.0000 | $I_P/I_{\text{I,100}} = 1.00252 + 0.31972[O_2]$ |
| AgNWs@PdOEP–PMMA (1.5 wt %) | 4.25 | 0.32233 | 0.9981 | $I_P/I_{\text{I,100}} = 1.08442 + 0.32233[O_2]$ |
| AgNWs@PdOEP–PMMA (2.0 wt %) | 5.72 | 0.46462 | 0.9978 | $I_P/I_{\text{I,100}} = 1.14778 + 0.46462[O_2]$ |
| AgNWs@PdOEP–PMMA (2.5 wt %) | 6.17 | 0.50771 | 0.9981 | $I_P/I_{\text{I,100}} = 1.15483 + 0.50771[O_2]$ |
| AgNWs@PdOEP–PMMA (3.0 wt %) | 4.56 | $k_{\text{on}} = 0.7248, k_{\text{off}} = 0.0247; f_I = 0.8560$ | 1.0000 | $I_P/I_{\text{I,100}} = \frac{0.8560}{1 + 0.7248[O_2]} + 0.144$ |

Figure 6. Photographed charge-coupled device images of the AgNWs@PdOEP–PMMA microfiber mat sensor film under excitation at various $p\text{O}_2$s.

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AgNWs in the AgNWs@PdOEP–PMMA (3.0 wt %) microfiber mat, which resulted in the heterogeneity in the microenvironment of PdOEP, the SVPs exhibited a nonlinear relationship even in a low oxygen concentration, and the mathematical model is shown in Table 2. Figure 5D shows the response/recovery capabilities of the AgNWs@PdOEP–PMMA (1 wt %) microfiber mat with the applied oxygen concentration step changing between 0 and 100%. Quenching and swift recovery cycles were fully reversible, and the curves exhibited excellently stable optical signals in 31 cycles when the oxygen concentration was continuously switched within 21 min. The dynamic response and recovery of the other fiber mats were also systematically investigated in this work and presented in Figure S6. On the basis of the oxygen–nitrogen saturation method, it was found that the response times for all microfiber mats, $t_{95}$ (i.e., the time for 95% of the total change in phosphorescence intensities to occur), are about 3 s from the deoxygenated condition to the oxygenated condition. All response and recovery time are presented in Table S1. Moreover, the photostability of the AgNWs@PdOEP–PMMA (1 wt %) microfiber mat was also studied at ambient air conditions and exhibited high photostability with no obvious intensity decrease (Figure S7).

Pressure-sensitive paints (PSPs) are effective, noninvasive tools capable of mapping gas flows near complex surfaces. Optical chemical imaging by means of luminescence is a powerful technique for pressure measurement and has been applied to various aerodynamic researches, such as unsteady flow fields, short-duration wind tunnels, and so on. Particularly, imaging of oxygen partial pressure ($p_O_2$) is of high practical relevance. In this work, a simple oxygen imaging platform with the AgNWs@PdOEP–PMMA microfiber mat was demonstrated. A step change of $p_O_2$ was used to characterize the color-changing features of the mat sensing film. Figure 6 presented the performance of the AgNW@PdOEP–PMMA (1.0 wt %) microfiber mat sensor film for the PSP experiment. The PSP sensing film presented remarkable light intensity-changing features under different $p_O_2$s. As shown in Figure 6, ultrabright red emission can be observed by the naked eye when the sensing film was exposed to nearly 0% oxygen. The brightness of red emission increased obviously with decreased $p_O_2$ ($p_O_2$: 0.273 Pa). From Figure 6 we can confirm that the AgNWs@PdOEP–PMMA (1.0 wt %) microfiber mat sensor film provides remarkable light intensity-changing features under different $O_2$ partial pressures. Especially in the lower $p_O_2$, the red-colored emission from the AgNWs@PdOEP–PMMA (1.0 wt %) microfiber mat sensor film can be observed with ultrahigh brightness. The results herein indicated that the AgNWs@PdOEP–PMMA (1.0 wt %) microfiber mat sensor film has remarkable performance for the PSP test. Thus, the AgNWs@PdOEP–PMMA microfiber mats can be utilized for the easy identification of $O_2$ concentration by the naked eyes or monitoring of the unsteady pressure measurement and unsteady flow visualization.

3. CONCLUSIONS

In conclusion, for the first time, the authors demonstrated a novel AgNW-induced sensitivity enhancement of oxygen sensors based on AgNWs@PdOEP–PMMA microfiber mats prepared by electrospinning. The introduction of high aspect ratio AgNWs into the AgNWs@PdOEP–PMMA microfiber mats as oxygen sensing films can obviously enhance the sensitivity and swift response/recovery properties. A series of sensing microfiber mats with different loadings of AgNWs were fabricated, and the sensitivity enhancement induced by AgNWs was systematically investigated. The AgNWs@PdOEP–PMMA-sensing microfiber mats exhibit a swift response (approx. 1.8 s) and an exceptional improvement in sensitivity (increased by 243%) compared to the pure PdOEP–PMMA sensing microfiber mat under a low oxygen concentration. Additionally, the remarkable light intensity-changing characteristic of AgNWs@PdOEP–PMMA-sensing microfiber mats under a lower $p_O_2$ facilitates the convenient identification of oxygen concentration even with the naked eye. We believe that the advantages of AgNW-induced sensitivity enhancement can be potentially extended for the realization of revolutionary highly sensitive sensors which can be expected to be readily applicable to many other high-performance gas sensor devices.

4. EXPERIMENTAL SECTION

4.1. Synthesis of AgNWs. AgNWs with a high aspect ratio were synthesized and purified as described in the literatures. The synthesis process was performed as follows: first, 1.5 g of poly(vinylpyrrolidinone) (PVP) and AgNO₃ (1.0 g, 5.9 mmol) were dissolved in 250 mL of ethylene Glycol (EG). Then, FeCl₃ (0.5–25.0 μM) EG solution was added and stirred at room temperature. The obtained mixture was then transferred into a 300 mL Teflon thermal water kettle and reacted at 130 °C for 8 h till the reaction completed, and then, the reaction mixture was allowed to cool to room temperature. The process for the purification of AgNWs was performed as described in the literatures. The reaction mixture was diluted with 200 mL of deionized (DI) water. Acetone (200 mL) was slowly added into this solution with gentle mixing. During the mixing, the dispersion turned pale yellow, which indicated that the AgNWs aggregated. At this point, no additional acetone was added and the aggregates were let to settle to the bottom of the beaker, leaving the particles suspended in the solution. The supernatant was removed by a pipette. Subsequently, the aggregated AgNWs were redispersed in 100 mL of DI water containing 0.5 wt % PVP and then precipitated by 150 mL of acetone. The aggregates formed and settled within 10 min, and the supernatant was removed again. AgNWs with high purity can be obtained after repeating this procedure for repeated 2–4 times. Finally, the AgNWs were dispersed in ethyl alcohol and collected by centrifugation to remove the extra PVP. Finally, the AgNWs were dispersed in dimethylformamide (DMF) with 25 mg/mL concentration and used in the following.

4.2. Fabrication of AgNW@PdOEP–PMMA Microfiber Mats. The formulations of AgNW@PdOEP–PMMA microfiber mats with various AgNWs are listed in Table S1. The general procedure for the preparation of AgNW@PdOEP–PMMA composite solutions is described as follows: first, PdOEP and DMF were charged into the sealed ampoules and ultrasonically dispersed until PdOEP dispersed uniformly in the DMF solution. Then, PMMA was added into the mixture and stirred until PMMA was dissolved into DMF. Subsequently, the AgNW solution was added into the above mixture, and the new mixture was continued to stir at room temperature (23 °C) for 48 h. After that, the above viscous liquid solutions were used for the fabrication of AgNW@PdOEP–PMMA microfiber mats. The electrospinning setup consisted of a syringe pump delivering the AgNW@PdOEP–PMMA viscous liquid solutions to a metal capillary at a controlled flow rate of 5 μL/h. The applied voltage between the needle and the collector was
22 kV. The AgNW@PdOEP–PMMA microfibers were collected on aluminum foil to form fiber mats. All AgNW@PdOEP–PMMA microfiber mats were placed under vacuum overnight to fully remove any residual solvent and were stored in darkness prior to testing.42

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00115. Experimental details and additional figures; formulations of AgNWs@PdOEP–PMMA-sensing microfiber mats; XRD pattern for the prepared AgNWs; SEM images of the cross sections of microfibers; TGA curves; CA images; UV–vis absorption spectra and phosphorescence spectra of AgNWs@PdOEP–PMMA-sensing microfiber mats; the time response properties to oxygen and photosensitivity of microfiber mats (PDF)

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**Notes**
The authors declare no competing financial interest.

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