Highly Sensitive Oxygen Sensors Based on Cu(I) Complex/Polystyrene Composite Nanofibrous Membranes by Preparing Electrospinning

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Supporting Information

Fig. S1. UV-vis absorption spectra for (a) PS, (b) [Cu(POP)phencarz]BF_4 and (c) sample B in solid.

Fig. S2. UV-vis absorption spectra for (A) [Cu(POP)phencarz]BF_4, (B) ligand phencarz and (C) ligand POP in CH_2Cl_2 solution.

Fig. S3. Emission spectra of sample A, C and D under different oxygen concentrations. λ_{ex} = 365 nm.

Fig. S4. Response time and relative intensity change of sample B to alternate environments of 100% nitrogen and 100% oxygen.

Fig. S5. Emission spectra of continuous thin films preparing by different methods (a) spin coating, (b) dip coating and (c) casting under different oxygen concentrations. λ_{ex} = 365 nm.

Table S1: The response/recovery time of the [Cu(POP)phencarz]BF$_4$/PS composite nanofibrous membranes.

**Table S2:** The lifetimes of [Cu(POP)phencarz]BF$_4$ in thin films and in solution.

The procedure for electrospinning composite nanofibers.

An appropriate amount of PS (*Mw* = 100 000) was dissolved in *N, N*-dimethylformamide (DMF) at a concentration of 22 wt % at room temperature. After vigorous stirring, different amount of [Cu(POP)phencarz]BF$_4$ (1, 1.5, 2 and 3 wt % [Cu(POP)phencarz]BF$_4$ relative to PS) were added into the solution. Then the solution was put into a glass syringe and electrospun by applying 16 kV at an electrode distance of 16 cm. The fibers were collected on an aluminum frame.

The method for measuring the oxygen sensing properties of samples.

The oxygen sensing properties based on luminescence intensity quenching of the obtained samples were characterized using a Hitachi-4500 fluorescence spectrophotometer equipped with a xenon lamp (150 W) operating in the 200-900 nm range. The emission spectra of different samples were obtained under excitation wavelength at 365 nm. For the Stern-Volmer plots measurements, oxygen and nitrogen were mixed at different concentrations via gas-flow controllers and flowed

directly into the gas chamber sealed with a close fitting suba-seal rubber lid equipped

with two (in and out) tubes. We typically allowed 1 min between changes in the N_2/O_2

concentrations to ensure that a new equilibrium point had been established.

Equilibrium was evident when the luminescence intensity remained constant ($\pm 2\%$).

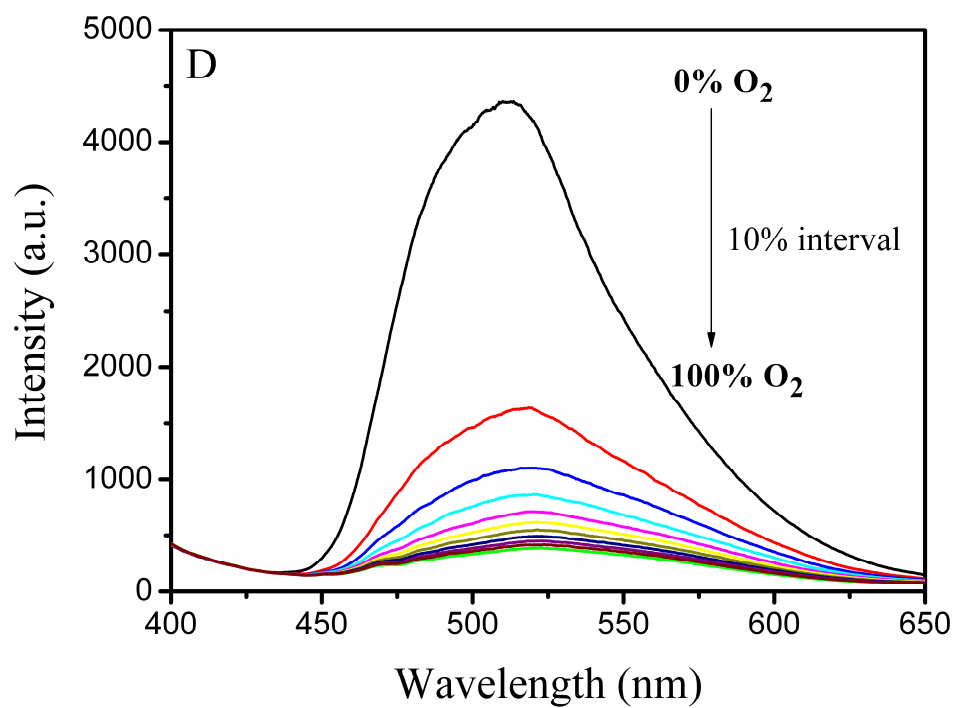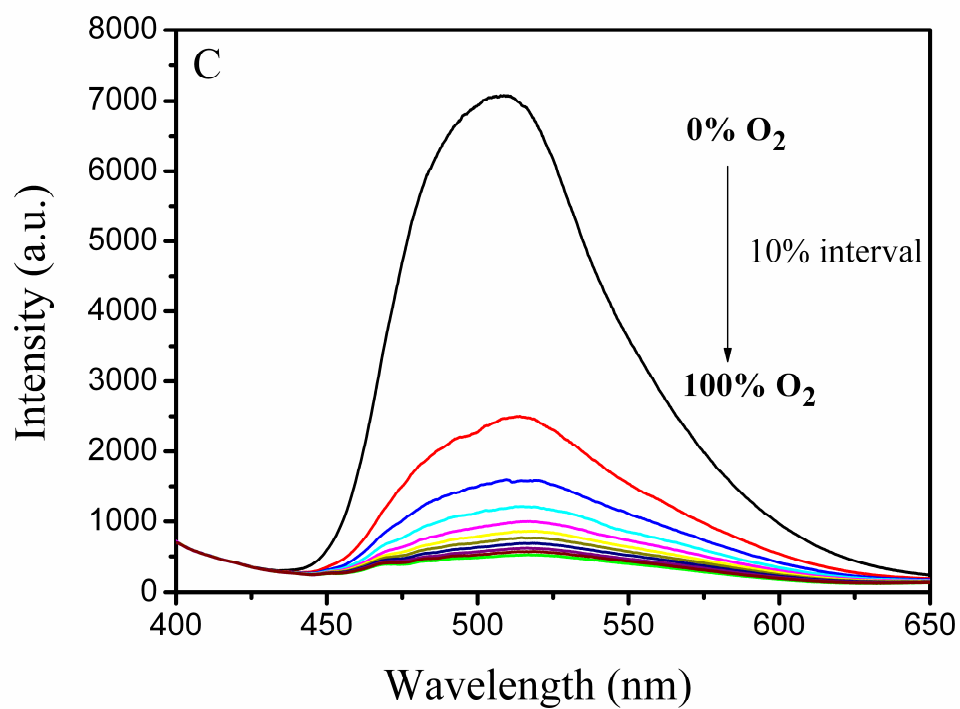The sensing response curves were obtained using the same instruments.
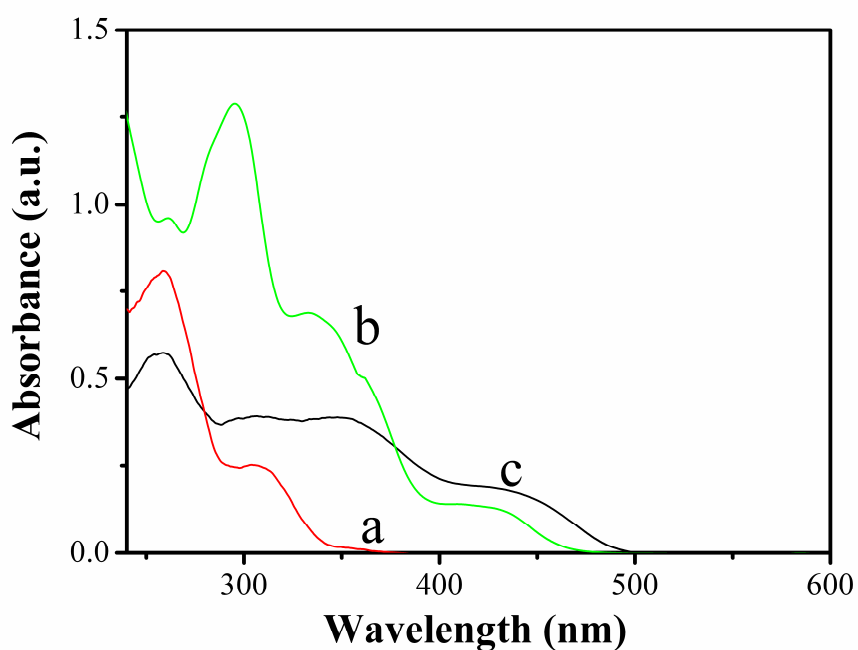
Fig. S1. UV-vis absorption spectra for (a) PS, (b) [Cu(POP)phencarz]BF$_4$, and (c)
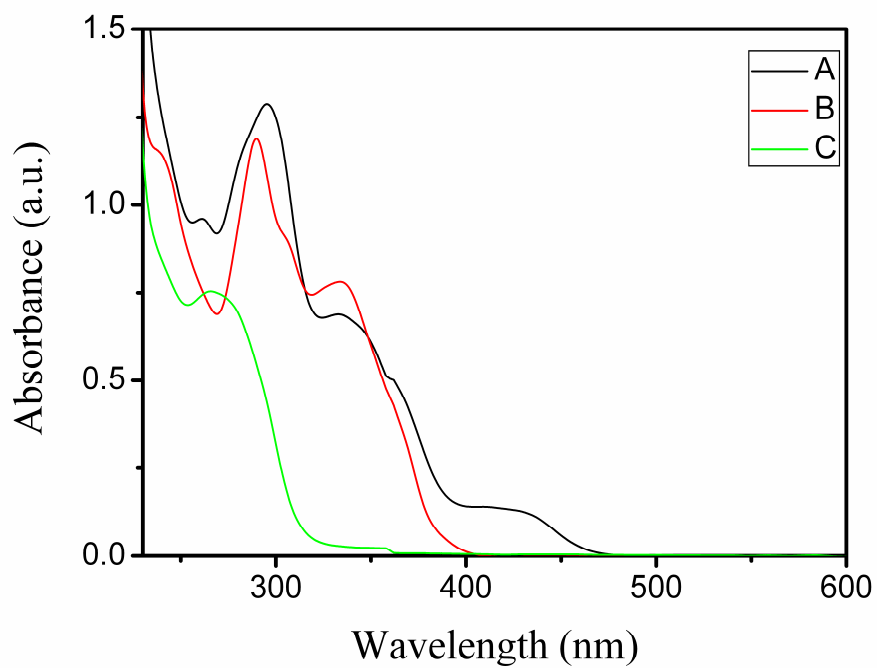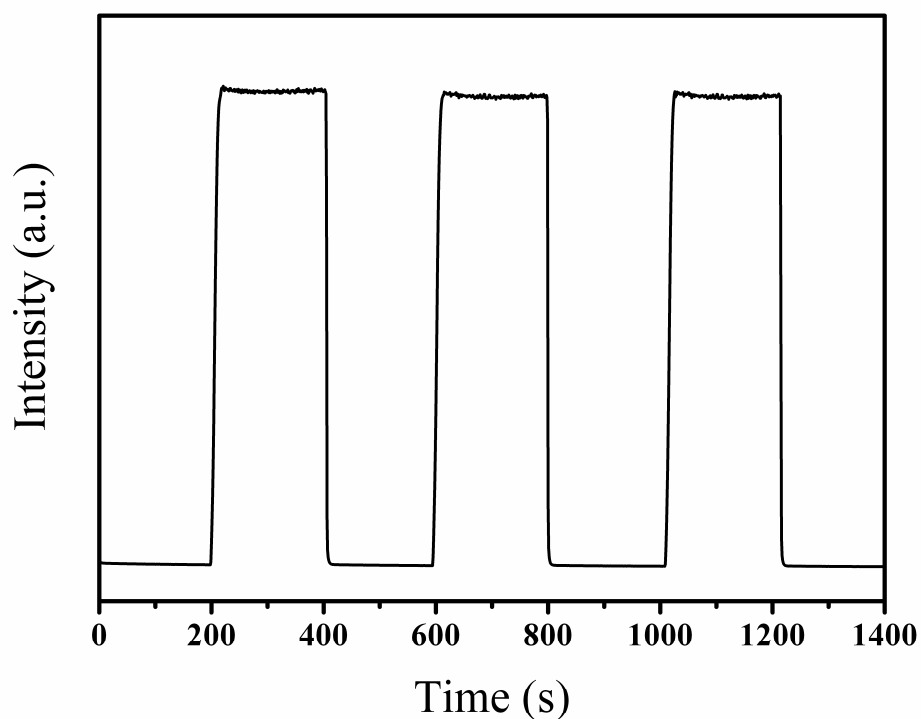
sample B in solid.

Fig. S2. UV-vis absorption spectra for (A) [Cu(POP)phencarz]BF$_4$, (B)ligand

phencarz and (C) ligand POP in CH$_2$Cl$_2$ solution.
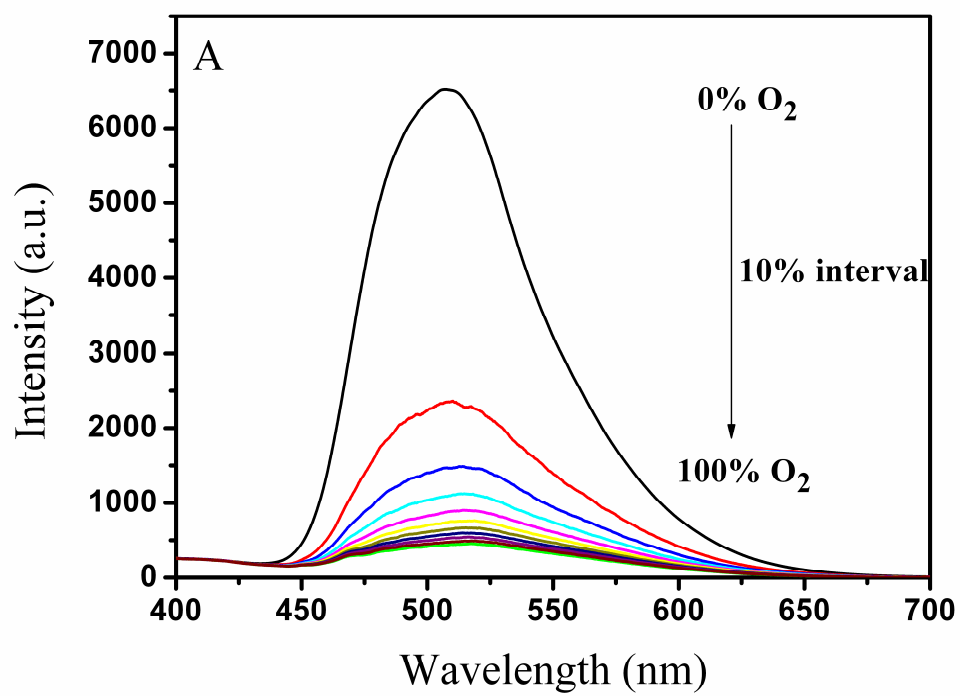
Fig. S3. Emission spectra of sample A, C and D under different oxygen

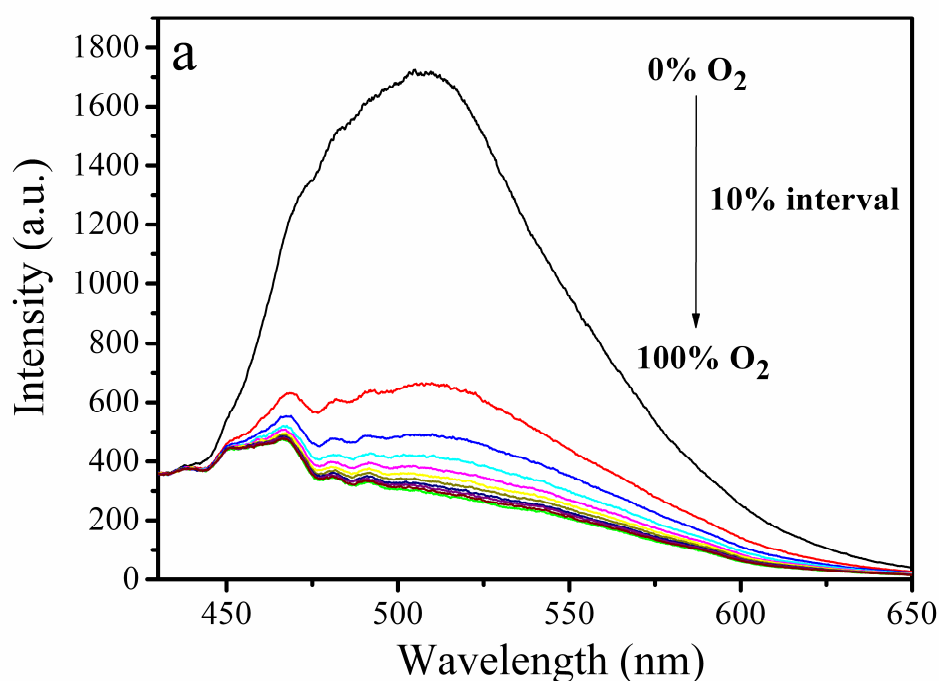concentrations. $\lambda_{ex} = 365$ nm.

Fig. S4. Response time and relative intensity change of sample B to alternate

environments of 100% nitrogen and 100% oxygen.

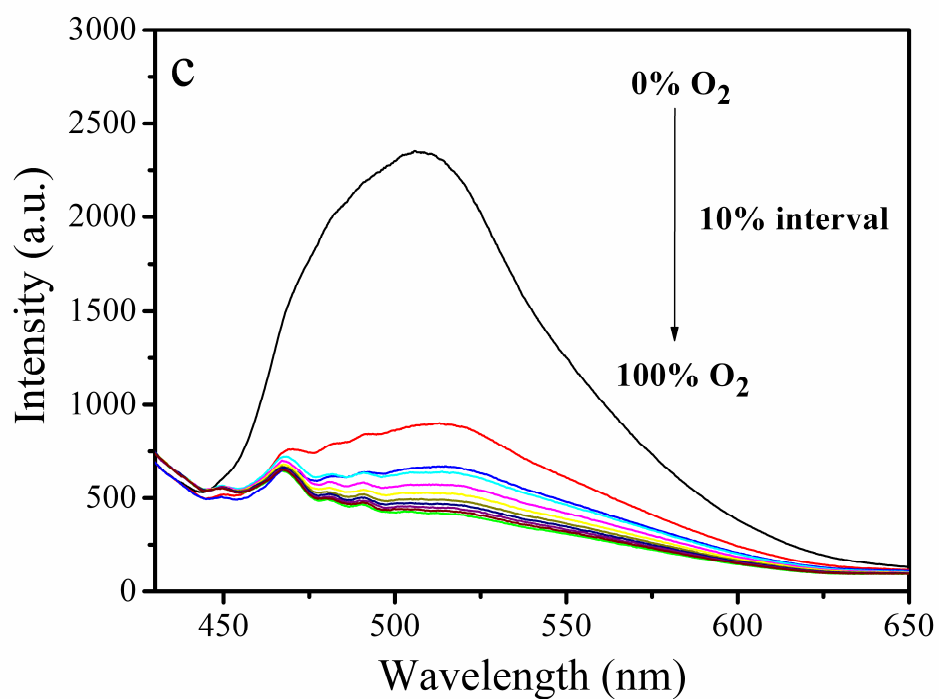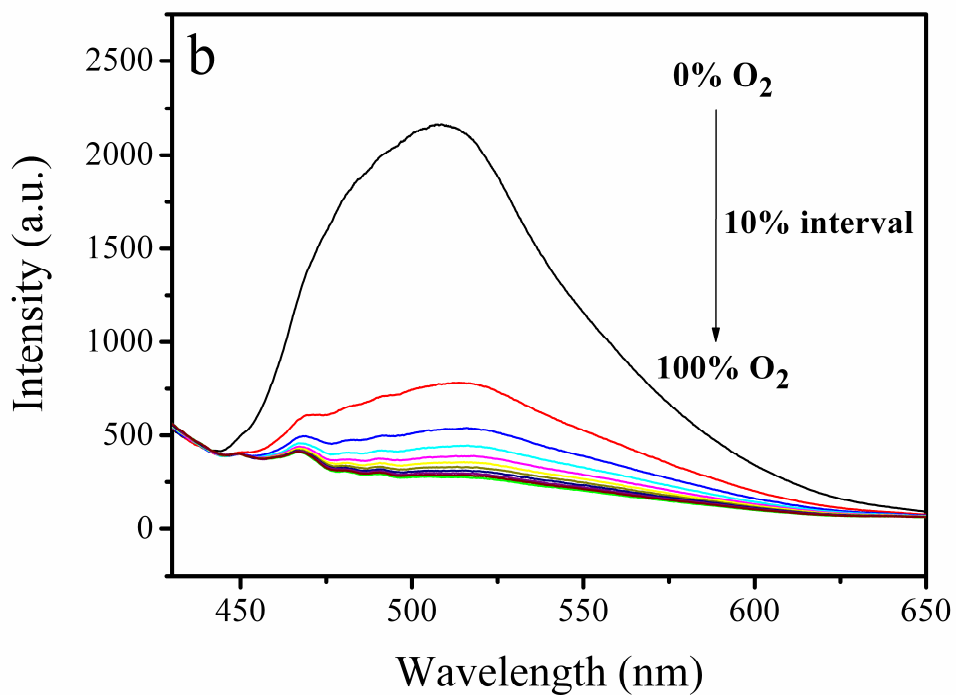**Table S1:** The response/recovery time of the [Cu(POP)phencarz]BF$_4$/PS composite

nanofibrous membranes.

sample	A	B	C	D
$t_\downarrow$ (s)	8	7	8	9
$t_\uparrow$ (s)	14	14	14	14

For an oxygen sensor, short response and recovery time are very important factors

in evaluating its feasibility of practical application. Generally, 95% response time,

i.e., $t_\downarrow$ (95%, N$_2$→O$_2$), is defined as the time required for the luminescent intensity to

decrease by 95% on changing from 100% N$_2$ to 100% O$_2$. Similarly, 95% recovery

time, i.e., $t_\uparrow$ (95%, $O_2 \rightarrow N_2$), means the time required for the luminescence intensity to reach the 95% of its initial value recorded under 100% N_2 on changing from 100% O_2 to 100% N_2. Fig.S4. shows the response property of sample B. Upon changing to pure O_2, the emission intensity of the samples drops very quickly, and increases and recovers to its initial value while upon changing to pure N_2. Although the samples are repeatedly exposed to an alternating atmosphere of nitrogen and oxygen, the sensors response are still stable and reversible. The response time $t_\downarrow$ and recovery time $t_\uparrow$ of sample B are 7s and 14s, respectively. To our knowledge, it is the shortest recovery time for oxygen sensors based on luminescent Cu(I) complexes. We ascribe the fast response and recovery to the fact that the porous structure of the electrospun membranes facilitates the high diffusion of oxygen.

Fig. S5. Emission spectra of continuous thin films preparing by different methods (a) spin coating, (b) dip coating and (c) casting under different oxygen concentrations. λ_{ex} = 365 nm.

Table S2：The lifetimes of [Cu(POP)phencarz]BF_4 in thin films and in solution.

samples	In thin film			In solution
	spin coating	dip coating	casting	solution
lifetime (μs)	8.14	9.21	8.43	0.37