View Online / Journal Homepage / Table of Contents for this issue

Downloaded by Changchun Institute of Optics, Fine Mechanics and Physics, CAS on 05 September 2012
Published on 12 August 2009 on http://pubs.rsc.org | doi:10.1039/B910305H

Highly sensitive oxygen sensors based on Cu(I) complex–polystyrene composite nanofibrous membranes prepared by electrospinning†

Yinghui Wang,[ab] Bin Li,*[a] Yanhong Liu,[ab] Liming Zhang,[ab] Qinghui Zuo,[ab] Linfang Shi[ab] and Zhongmin Su*[c]

Received (in Cambridge, UK) 27th May 2009, Accepted 20th July 2009
First published as an Advance Article on the web 12th August 2009
DOI: 10.1039/b910305h

The first optical oxygen sensor based on Cu(I) complex–polystyrene composite nanofibrous membranes, showing high sensitivity (I_0/I_{100} = 15.56), good linear Stern–Volmer characteristics (R^2 = 0.9966) and short response/recovery time ($t_\downarrow$ (s) = 7 and $t_\uparrow$ (s) = 14), has been prepared; these results represent the best values reported for oxygen sensors based on Cu(I) complexes.

Over the past decades, the development of oxygen sensors has been extensively pushed because the determination of molecular oxygen content in gas and liquid phases is very important in many different fields, such as oceanography, meteorology, biology, environmental science and life science.[1] Commonly, optical oxygen sensors are based on noble metal complexes, *e.g.*, Pt(II), Ru(II), Au(I), Ir(III) and Re(I) complexes.[2] However, their wide utilization is largely limited due to their extremely high cost. Recently, luminescent Cu(I) complexes have attracted great attention owing to their highly emissive metal-to-ligand-charge-transfer (MLCT) state, long luminescence lifetimes, large Stokes shift and low cost. Nevertheless, few oxygen sensors based on Cu(I) complexes have been reported.[3]

For optical oxygen sensing devices, it is necessary to incorporate the luminescent complexes into a solid matrix, such as sol–gel-derived silica-based materials,[4] mesoporous silicas[5] and polymers.[6] Recently, nanofibers prepared by electrospinning have been proved to be excellent host materials for developing functional materials because of their large surface area-to-volume ratio, the unique nanoscale architecture, and the simple and cost-effective preparation method.[7] Electrospun nanofibrous membranes have approximately one to two orders of magnitude more surface area than that found in continuous thin films.[7d] It is expected that the large amount of available surface area of electrospun nanofibrous membranes is helpful to improve oxygen sensor performances. However, up to now, there has been no report on oxygen sensors based on polymer nanofibers by electrospinning as the matrix.

In this contribution, [Cu(POP)phencarz]BF_4 (POP = bis[2-(diphenylphosphino)phenyl]ether; phencarz = 2-(*N*-ethyl-carbazole-yl-4)imidazo[4,5-*f*]1,10-phenanthroline) was incorporated into polystyrene (PS) matrices, and electrospun into composite nanofibrous membranes. The optical oxygen sensing properties of [Cu(POP)phencarz]BF_4–PS composite nanofibrous membranes were investigated. High sensitivity (I_0/I_{100} = 15.56), good linear Stern–Volmer characteristics (R^2 = 0.9966) and short response/recovery time ($t_\downarrow$ (s) = 7 and $t_\uparrow$ (s) = 14) were obtained. A performance comparison shown in Table 1 between this work and literature values suggests that [Cu(POP)phencarz]BF_4–PS composite nanofibrous membranes represent the best oxygen sensing performances reported for oxygen sensors based on Cu(I) complexes. Phencarz and [Cu(POP)phencarz]BF_4 were prepared according to literature methods[8] and the structure of [Cu(POP)phencarz]BF_4 is depicted in Fig. 1 (I). The typical procedure for electrospinning composite nanofibers can be found in the ESI.† In the following text, [Cu(POP)phencarz]-BF_4–PS composite nanofibrous membranes electrospun from 1, 1.5, 2 and 3 wt% concentrations relative to PS in *N*,*N*-dimethylformamide solution are labelled as samples A, B, C and D, respectively.

The scanning electron microscope (SEM) image and fluorescence microscopy image of sample B are shown in Fig. 1. It is observed that the obtained electrospun nanofibers are smooth, uniform, and evenly distributed on the substrate with a random orientation. The diameter for the composite fibers is 500–700 nm. The fluorescence photography of sample B shows bright green emission of [Cu(POP)phencarz]BF_4 arising from the MLCT excited state, suggesting that

Table 1 Representative examples of reported I_0/I_{100} values of optical oxygen sensors based on Cu(I) complexes

Sensor materials	I_0/I_{100}	Linear relationship	Ref.
[Cu(POP)phencarz]BF_4–PS	15.56	Near-linear	This work
[Cu(dbp)(dmp)](PF_6)–PS	1.70	Near-linear	3*a*
[Cu(POP)(PTZ)]BF_4–MCM-41	11.16	Non-linear	3*b*
[Cu(dpephos)(pip)]BF_4–SBA-15	7.44	Non-linear	3*c*
[Cu(dpephos)(epip)]BF_4–SBA-15	5.68	Non-linear	3*c*
[Cu(dpephos)(nip)]BF_4–SBA-15	5.51	Non-linear	3*c*
[Cu(dpephos)(enip)]BF_4–MCM-41	5.95	Non-linear	3*c*

---

[a] *Key Laboratory of Excited State Physics, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 3888 Eastern South-Lake Road, Changchun 130033, P. R. China. E-mail: lib020@yahoo.cn; Fax: +86 431-86176935; Tel: +86 431-86176935*
[b] *Graduate School of the Chinese Academy of Sciences, Chinese Academy of Sciences, Beijing, 100039, P. R. China*
[c] *Department of Chemistry, Northeast Normal University, Changchun 130024, P. R. China. E-mail: zmsu@nenu.edu.cn*

† Electronic supplementary information (ESI) available: UV-vis absorption spectra, emission spectra of samples A, C, D and continuous thin films under different oxygen concentrations, and response time and relative intensity change of sample B to alternate atmosphere. See DOI: 10.1039/b910305h

This journal is © The Royal Society of Chemistry 2009

Downloaded by Changchun Institute of Optics, Fine Mechanics and Physics, CAS on 05 September 2012
Published on 12 August 2009 on http://pubs.rsc.org | doi:10.1039/B910305H

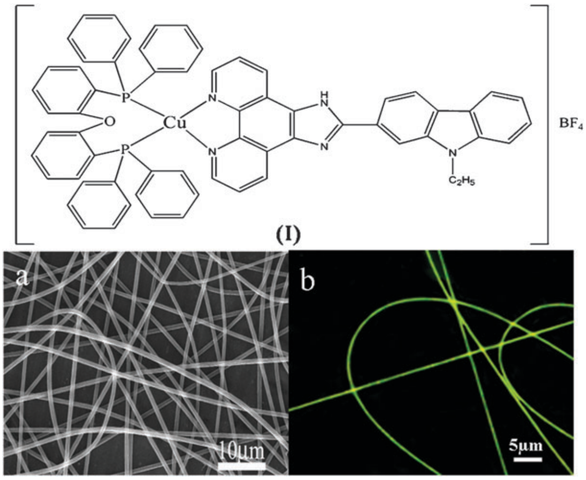

Fig. 1 (I) The molecular structure of [Cu(POP)phencarz]BF_4; (a) scanning electron microscope (SEM) image and (b) fluorescence microscopy image of sample B.

[Cu(POP)phencarz]BF_4 was successfully electrospun into composite nanofibrous membranes.

UV-vis absorption spectra of [Cu(POP)phencarz]BF_4, PS and sample B are given in Fig. S1 of the ESI.† As for [Cu(POP)phencarz]BF_4, the absorption bands located around 260, 290 and 330 nm are attributed to spin-allowed ligand-centered transitions. The absorption band from 360 to 480 nm is experimentally assigned to MLCT [dπ(Cu)–π*(phencarz)] transition compared with the absorption spectra of POP and phencarz (see ESI, Fig. S2†).[3b] Two absorption bands exist, located around 258 and 309 nm in pure PS fibers. All the absorption bands aforesaid are found in the spectrum of sample B, confirming that [Cu(POP)phencarz]BF_4 is successfully incorporated into PS matrices.

In order to test the oxygen sensing performances of [Cu(POP)phencarz]BF_4–PS composite nanofibrous membranes, emission spectra of samples A, B, C and D were recorded under different oxygen concentrations at room temperature (see ESI, Fig. S3†) and that of sample B is presented in Fig. 2. The emission peaks centered at about 510 nm originate from MLCT transition. Upon excitation by light in a pure nitrogen atmosphere, the Cu(I) complex transitions from the ground state to a higher energy state (excited state), and when returning to ground state, it emits light. As oxygen molecules enter, bimolecular collisions between the excited Cu(I) complex molecules and the ground state (triplet) oxygen relax the luminophore nonradiatively, resulting in singlet oxygen (excited state). Thus, a quenching process occurs. The corresponding sensing mechanism can be described as:

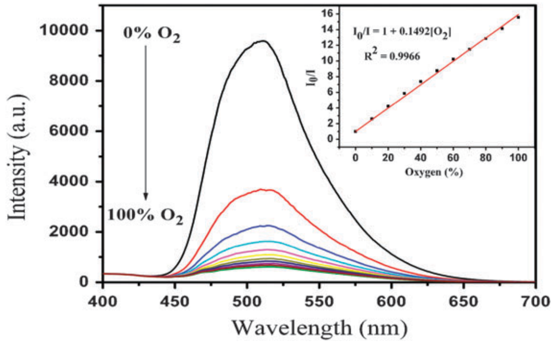

Fig. 2 Emission spectra of sample B under different oxygen concentrations. Inset: Stern–Volmer plot for sample B under different oxygen concentrations. $\lambda_{ex} = 365$ nm.

$$\mathrm{Cu(I)^*} + \mathrm{O_2} \rightarrow \mathrm{Cu(I)} + \mathrm{O_2^*}$$

where Cu(I) denotes the [Cu(POP)phencarz]BF_4 molecule and "*" is the excited state. The relative luminescence intensities of samples A, B, C and D decrease by 92.6, 93.0, 92.0 and 90.9%, respectively, upon changing from pure nitrogen to pure oxygen. Sample B (1.5 wt%) is not only more sensitive compared with other samples, but also shows the strongest emission intensity. We speculate that the reason for this is as follows: when the doping concentration is low (1 wt%), emission from the probe is comparatively weak, which results in the low sensitivity; when it is too high (2 and 3 wt%), aggregation between probe molecules may become serious, resulting in low emission intensity. As a result, 1.5 wt% [Cu(POP)phencarz]BF_4 relative to PS is the optimum level.

Oxygen quenching is diffusion-limited and can be described by the Stern–Volmer relationship[9] in the simplest scenario of a luminophore in a homogeneous microenvironment:

$$I_0/I = 1 + K_{SV}[O_2] = 1 + k_q\tau_0[O_2]$$

where I is the steady-state luminescence intensity of luminophore, the subscript 0 denotes the absence of oxygen, τ_0 is the excited-state luminescence lifetime in the absence of oxygen, K_{SV} is the Stern–Volmer constant, k_q is the bimolecular rate constant describing the efficiency of the collisional encounters between the luminophore and the quencher, and $[O_2]$ is the oxygen concentration. For this ideal case, a plot of I_0/I *vs.* $[O_2]$ will be linear with a slope equal to K_{SV} and an intercept of unity, allowing a simple single-point sensor calibration. The lifetime decay of the luminophore in homogeneous media can be described by a single-exponential equation:[10]

$$I(t) = \alpha \exp(-t/\tau)$$

where $I(t)$ is the luminescence intensity at time t, and α is the pre-exponential factor.

The Stern–Volmer plot of sample B exhibits good linearity ($R^2 = 0.9966$) over the full oxygen concentration range studied (0–100% O_2) as shown in Fig. 2, suggesting that all [Cu(POP)phencarz]BF_4 molecules are in very similar microenvironments within the composite nanofibrous membranes. Nonlinear Stern–Volmer plots arise when luminophores are distributed simultaneously between two or more sites, in which one site is more heavily quenched than the other. Consequently, the microheterogenous sites exhibit different quenching constants K_{SV} and unquenched lifetime τ_0 values. Fig. 3 presents the time-resolved intensity–decay curve of sample B in the absence of oxygen (pure N_2). A single exponential decay law best described the observed intensity decay, which is consistent with the Stern–Volmer plot shown in Fig. 2. All these data confirm that [Cu(POP)phencarz]BF_4 molecules are distributed homogeneously within the composite nanofibrous

Downloaded by Changchun Institute of Optics, Fine Mechanics and Physics, CAS on 05 September 2012
Published on 12 August 2009 on http://pubs.rsc.org | doi:10.1039/B910305H

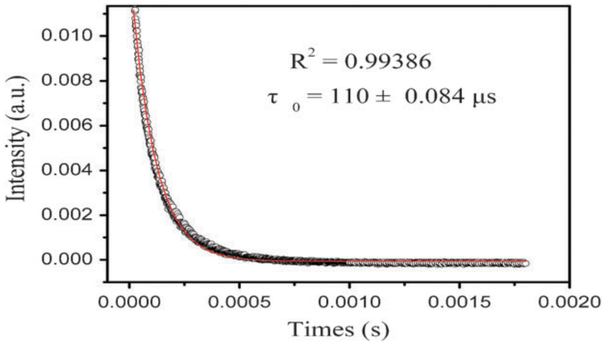

Fig. 3 Time-resolved intensity–decay curve of sample B in the absence of oxygen (pure N_2). The fit to a single-exponential decay model is shown (solid line).

Table 2 Oxygen-sensing properties of the [Cu(POP)phencarz]BF_4–PS composite nanofibrous membranes and the PS thin films with 1.5 wt% [Cu(POP)phencarz]BF_4 prepared by different methods

Sample	A	B	C	D
I_0/I_{100}	14.38	15.56	13.46	11.62
Ksv ($O_2\%^{-1}$)	0.1394	0.1492	0.1312	0.1138

Sample	Spin coating[a]	Dip coating[a]	Casting[a]
I_0/I_{100}	5.82	7.84	5.53
Ksv_1 ($O_2\%^{-1}$)	0.2606	0.2543	0.3886
Ksv_2 ($O_2\%^{-1}$)	0.0005	0.0006	0.0038

[a] Demas "two-site" model is used to fitting the PS thin films with 1.5 wt% [Cu(POP)phencarz]BF_4 prepared by different methods.

membranes. The oxygen sensing properties of all samples are summarized in Table 2. A sensor with I_0/I_{100} more than 3.0 is a suitable oxygen sensing device.[2a] The value of I_0/I_{100} of sample B achieves 15.56, and this is by far the highest value for optical oxygen sensors based on luminescent non-noble metal complexes. For comparison, the PS continuous thin films with 1.5 wt% [Cu(POP)phencarz]BF_4 are prepared by spin coating, dip coating and casting, respectively. Inspection of these data shows that the sensitivity (I_0/I_{100}) ranges from 5.53 to 7.84, indicating that the oxygen sensing performances of the electrospun nanofibrous membranes are superior to those of continuous thin films. We attribute these results to three factors. Firstly, the excited-state lifetime of [Cu(POP)phencarz]BF_4–PS nanofibrous membrane is quite long (up to 110 μs), offering enough time for bimolecular collision between [Cu(POP)phencarz]BF_4 and oxygen molecules. Correspondingly, the [Cu(POP)phencarz]BF_4 lifetimes in thin films and in solution are less than 10 μs (see ESI, Table S2†). Secondly, PS is an excellent host material since it is oxygen permeable. Last, but most important, the porous structure of the electrospun membranes not only provides a large surface area-to-volume ratio, but also facilitates the oxygen entry and diffusion.[11] At the same time, we obtain the shortest recovery time for oxygen sensors based on luminescent Cu(I) complexes (see the ESI†). We ascribe the fast response/recovery to the fact that the porous structure of the electrospun membranes facilitates the high diffusion of oxygen. The obtained oxygen-sensing performances of [Cu(POP)phencarz]BF_4–PS nanofibrous membranes indicate that they are superior to the commonly used Clark-type electrode in some aspects, *e.g.*, the stability of signals, response time, interferences and cost.

In summary, composite nanofibrous membranes as optical oxygen sensors based on low-cost Cu(I) complexes were successfully prepared by electrospinning, exhibiting the highest sensitivity among optical oxygen sensors based on Cu(I) complexes, near-linear Stern–Volmer characteristics, and short response/recovery time. The excellent performances can be explained by the fact that the porous structure of the electrospun membranes with large surface area-to-volume favors the oxygen diffusion, the PS is an outstanding host material owing to its good oxygen permeating ability, and the excited-state lifetime of [Cu(POP)phencarz]BF_4–PS composite nanofibrous membranes is long enough for bimolecular collision between [Cu(POP)phencarz]BF_4 and oxygen molecules. The outstanding performances, the simple and versatile preparation method, and economical attraction endow this kind of composite nanofibrous membrane with the potential for commercial application in oxygen sensors.

The authors gratefully thank the financial supports of the National Natural Science Foundations of China (Grant No. 50872130).

Notes and references

1 (*a*) Y. Amao, *Microchim. Acta*, 2003, **143**, 1; (*b*) B. T. Glazer, A. G. Marsh, K. Stierhoff and G. W. Luther, *Anal. Chim. Acta*, 2004, **518**, 93; (*c*) H. Hasumoto, T. Imazu, T. Miura and K. Kogure, *J. Oceanogr.*, 2006, **62**, 99; (*d*) Y. Amao, T. Miyashita and I. Okura, *Anal. Chim. Acta*, 2000, **421**, 167; (*e*) K. Mitsubayashi, Y. Wakabayashi and D. Murotomi, *Sens. Actuators, B*, 2003, **95**, 373.

2 (*a*) C. Huo, H. D. Zhang, H. Y. Zhang, H. Y. Zhang, B. Yang, P. Zhang and Y. Wang, *Inorg. Chem.*, 2006, **45**, 4735; (*b*) B. Lei, B. Li, H. Zhang, Sh. Lu, Z. Zheng, W. Li and Y. Wang, *Adv. Funct. Mater.*, 2006, **16**, 1883; (*c*) A. Mills, A. Lepre, B. R. C. Theobald, E. Slade and B. A. Murrer, *Anal. Chem.*, 1997, **69**, 2842; (*d*) M. C. DeRosa, P. J. Mosher, G. P. A. Yap, K.- S. Focsaneanu, R. J. Crutchley and C. E. B. Evans, *Inorg. Chem.*, 2003, **42**, 4864; (*e*) L. Huynh, Z. Wang, J. Yang, V. Stoeva, A. Lough, I. Manners and M. A. Winnik, *Chem. Mater.*, 2005, **17**, 4765.

3 (*a*) M. T. Miller and T. B. Karpishin, *Sens. Actuators, B*, 1999, **61**, 222; (*b*) L. F. Shi, B. Li, S. M. Yue and D. Fan, *Sens. Actuators, B*, 2009, **137**, 386; (*c*) L. F. Shi and B. Li, *Eur. J. Inorg. Chem.*, 2009, 2294.

4 R. M. Bukowski, R. Ciriminna, M. Pagliaro and F. V. Bright, *Anal. Chem.*, 2005, **77**, 2670.

5 (*a*) H. B. Han, I. Manners and M. A. Winnik, *Chem. Mater.*, 2005, **17**, 3160; (*b*) B. F. Lei, B. Li, H. R. Zhang, L. M. Zhang and W. L. Li, *J. Phys. Chem. C*, 2007, **111**, 11291.

6 (*a*) Z. Wang, A. R. McWilliams, C. E. B. Evans, X. Lu, S. Chung, M. A. Winnik and I. Manners, *Adv. Funct. Mater.*, 2002, **12**, 415; (*b*) A. Mills, C. Tommons, R. T. Bailey, M. C. Tedford and P. J. Crilly, *Analyst*, 2006, **131**, 495.

7 (*a*) J. Yoon, S. K. Cha and J. M. Kim, *J. Am. Chem. Soc.*, 2007, **129**, 3038; (*b*) J. Jang, J. Ha and J. Cho, *Adv. Mater.*, 2007, **19**, 1772; (*c*) S. K. Chae, H. Park, J. Yoon, C. H. Lee, D. J. Ahn and J. M. Kim, *Adv. Mater.*, 2007, **19**, 521; (*d*) X. Wang, C. Drew, S. H. Lee, K. J. Senecal, J. Kumar and L. A. Samuelson, *Nano Lett.*, 2002, **2**, 1273.

8 (*a*) H. Xin, F. Y. Li, M. Guan, C. H. Huang, M. Sun, K. Z. Wang, Y. A. Zhang and L. P. Jin, *J. Appl. Phys.*, 2003, **94**, 4729; (*b*) S. Kuang, D. G. Cuttell, D. R. McMillin, P. E. Fanwick and R. A. Walton, *Inorg. Chem.*, 2002, **41**, 3313.

9 C. Malins, S. Fanni, H. G. Glever, J. G. Vos and B. D. MacCraith, *Anal. Commun.*, 1999, **36**, 3.

10 (*a*) E. R. Carraway, J. N. Demas, B. A. DeGraff and J. R. Bacon, *Anal. Chem.*, 1991, **63**, 337; (*b*) M. T. Murtagh, M. R. Shahriari and M. Krihak, *Chem. Mater.*, 1998, **10**, 3862.

11 Y. Amao, K. Miyakawa and I. Okura, *J. Mater. Chem.*, 2000, **10**, 305.

This journal is © The Royal Society of Chemistry 2009