



Sol-gel matrix modified microstructured optical fibre towards a fluoride sensitive optical probe

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ABSTRACT

In this article, we report an optical fluoride probe based on microstructured polymer optical fibers (MPOFs) which is modified with morin-Al complex doped silica gel film. This probe is fabricated by sol-gel fluxion coating process. Sol solution doped with morin-Al is directly inhaled into array holes of MPOF and then forms morin-Al-gel matrix film in them. The sensing probe shows different fluorescence intensity to different fluoride ion concentrations in the aqueous solution. The range of response is 5–50 mmol/L, under the condition of pH 4.6.

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1. Introduction

Microstructured optical fibres (MOFs), whose properties are primarily determined by the air-holes in cladding region, have received increasing interests for their extensive potentials in broad applications [1–5]. Besides optical applications, air-holes of MOF open up new possibilities for exploiting the interaction of light with gases or liquids via evanescent fields in the holes [6,7]. The hole structure of MOF has a inherent advantage that it can hold small volume of fluid. Such small volume is very useful for micro-analysis and can simplify the experimental setup of optical fiber sensors. In the past several years, new types of optical fiber sensors based on MOF such as optoelectronic fibres functionalized with metals or semiconductors that allows both optical and electrical transport [8], MPOF chemical sensors based on evanescent wave probing for a gas or liquid phase analyte sensing [9–14] and surface modified fibres with thin metal or polymers layers for sensing have been developed [15]. Recently, great efforts have been made to investigate modification methodologies of MOF-based chemical sensor in our group [16,17]. A case in point is a new type of pH probe based on polymer sensing film modified MOF [17].

Among all the sensitive film fabricating methods, sol-gel technology is a very promising and extensively investigated strategy to fabricate the support for indicators of optical and chemical sensors [18–20]. Sol-gels have been extensively studied with respect to their applications to chemical sensing of analytes such as pH,

metal ions, gases and biomolecules [21–24]. In sol-gel process, a silica gel is made by hydrolysis of alkoxide precursor followed by condensation of silanol. It provides a low-temperature process to obtain porous silicate glass matrices to entrap organic reagents and molecular receptors easily. Several significant advantages over other methods of film deposition make it to be a preferred choice. They include chemical and thermal stability, chemical inertness, high purity, homogeneity and very high optical transparency in a broad wavelength range from ultraviolet to infrared [25,26]. Sol-gel sensing film is characterized by its unique feature of the highly porous three-dimensional network structure. Coupling agents can be tailored to no-leaching of the entrapped molecules from the matrix. Hydrophobicity, thickness, porosity, flexibility, reactivity and stability, can also be easily tailored by controlling the process conditions, the type and size of precursors and catalysis.

In this paper, we firstly introduce a new modification methodology of sol-gel technology to fabricate new type of MPOF chemical probes. It has been proved that the holes in MPOF could be easily used as substrate for coating thin silica gel layer which is doped with fluorescent molecules. Furthermore, we fabricate a convenient, highly selective and sensitive MPOF probe for fluoride analysis through functionalizing MPOF with morin-Al entrapped gel sensing film. The fluorescent characteristics of the probe are investigated with the change of concentration of fluoride ion in a buffer solution.

2. Preparation and morphology of morin-Al-gel-MPOF probe

Firstly, morin-Al chelate was prepared by dissolving 33.0 mg of morin and 31.0 mg of sodium nitrate in 1.0 ml of alcohol. An acid

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catalyzed sol solution was obtained by stepwise mixing 1.1 ml of tetraethoxysilane (TEOS), 1.0 ml of absolute ethanol, 1.9 ml of 2,3-epoxy propoxy propyltrimethoxysilane (Silane coupler, KH-560) and 1.2 ml of H₂O. The mixed solution was heated under water bath to 60 °C. Then 0.1 mol/L HCl was dropped into the solution to adjust the pH to 3. After stirring for 40 min, the mixture forms a homogeneous phase, which was followed by adding the morin-Al solution into the mixed solution. With the pre-hydrolysis and condensation polymerization of silane, the solution becomes viscous and the indicator molecules were entrapped within the sol-gel matrix. After continuous reaction for 1 h, the solution was cooled to room temperature and the sol was prepared.

The optical fibre adopted here is polymethyl methacrylate (PMMA) MPOF which is made by ourselves [5]. The MPOF contains 18 air-holes which distribute in two circles. The outer diameter of the MPOF is 800 μm and the hole diameter is 95 μm (Fig. 1a). Film coating was achieved by inhaling the above viscous sol into holes of MPOF under pressure of 0.03 Mpa. When the sol was inhaled, it immediately spread on the inner walls of holes in MPOF. Then the sol layer deposited in MPOF was kept for aging and drying under ambient conditions for 2 days to form morin-Al entrapped gel sensing film with three-dimensional network of silicon dioxide (SiO₂). Because one end face of the MPOF was coated with gel film due to immersing into the sol solution, and the other end was also coated by the outflow sol, the two ends were cut and the final length of fiber probe used for sensing was 4 cm.

The morphology of the gel film is observed by scanning-electron microscopy (SEM). Fig. 1b is obtained by cutting the sample in the inclined orientation. It is apparent from the insert that the morphology of morin-Al xerogel layer is very smooth, homogenous and compact. The sensing film with thickness of about 210 nm adheres to PMMA substrate compactly. This smooth morphology can effectively reduce the optical scattering of MPOF probe. With the co-crosslinkage of KH-560 and TEOS, the mechanical strength of the gel film is high and there is no crack on the film, which is proved by the tubular structure retains during cutting (Fig. 1b). The gel film modified MPOF presents golden color for the existence of morin-Al (Fig. 1c).

3. Response principle and setup of fluorescent analysis

The basic response principle of morin-Al molecules to fluoride quencher is demonstrated in Fig. 2. There exists a chemical relation between morin and morin-Al (Fig. 2a). Morin with flavone structure does not exhibit fluorescence under exciting, while the coordination of morin with Al³⁺ gives rise to the rigidity enhancement of morin structure and emits strong fluorescence [27]. Finally, when some anion such as F⁻ and PO₄³⁻ is added, they capture Al³⁺ from morin-Al and then its fluorescence is quenched (Fig. 2b). Simultaneously, the fluorescence quenching degree reveals the concentration of fluoride in sample solution.

Fig. 3 shows the setup for fluorescent analysis. To obtain high sensitivity, the exit source is collimated to emit a beam with diameter of 10 mm, and the beam is orthogonal to the cross-section of morin-Al-gel-MPOF [28]. Emitted fluorescence transmits through the evanescent field into the cross-section of the probe. Then the end faces of the analytes solution-contained probe and the end-fiber of detector are tightly connected in immobilized connector. The detector end-fiber is a commercial POF with large diameter of 1 mm and it is coaxial with morin-Al-gel-MPOF probe which ensures sufficient collection of the fluorescence from the whole probe end. The probe is placed in a dark chamber to prevent it from external light noise.

The absorption spectra of morin solution, morin-Al solution and morin-Al-gel free film are measured (Fig. 4) for choosing the excite source. Comparing with the main peak of morin at 350 nm, the main peak of morin-Al solution shifts to 420 nm. When morin-Al molecules are entrapped in gel matrix, the main peak of 420 nm exhibits no shift, and the second absorption peak at about 280 nm is enhanced against main absorption peak. This result shows strong interaction between morin-Al and silica matrix. Because the main absorption located at 420 nm, a higher power LED (1 W) at 405 nm is adopted as the excite source of the probe.

4. pH dependence of the morin-Al-gel-MPOF probe

Before investigate the response of the probe to fluoride, pH dependence is studied. It is inserted in a series of aqueous solution with different pH, and the fluorescent spectra are recorded as shown in Fig. 5. When pH is gradually increased from 1.0 to 5.8, the emission intensity decreased nonlinearly. If the aqueous solution is fully changed to basic, that pH value is above 7, Al³⁺ ion of morin-Al doped in the probe is captured by OH⁻, which leads to the fluorescence quenching. However, for a weak acid solution with pH range from 4.0 to 6.0, the fluorescence of morin-Al doped in the gel-MPOF is quite stable. Here the response of the probe to analytes of fluoride is studied under pH 4.6.

5. Response of the morin-Al-gel-MPOF probe to fluoride ions

In order to develop F⁻ ion sensor, the fluorescent response of the morin-Al-gel-MPOF probe is investigated in different concentrations of fluoride buffer solutions. The results are shown in Fig. 6. With the increasing F⁻ ion concentration, fluorescence intensity is decreased because F⁻ ion captured the Al³⁺ from morin-Al. Based on Stern-Volmer model for the fluorescent quenching analysis [29], there is a relationship between I_0 and I as below:

$$\frac{I_0}{I} = 1 + K_{SV}[M] \quad (1)$$

where M is the concentration of analyte, F⁻, I_0 and I are fluorescence intensities in the absence and the presence of F⁻, respectively. K_{SV} is

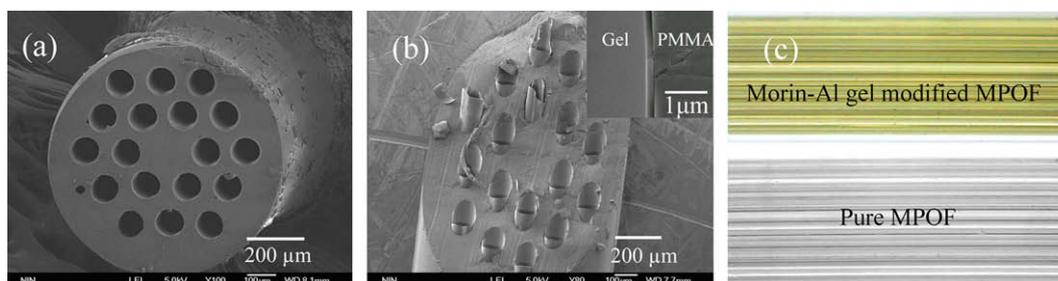


Fig. 1. SEM of MPOFs. (a) MPOF. (b) Gel-MPOF (Insert is a high resolution SEM at the interface of Gel film and PMMA substrate). (c) Comparison of morin-Al-gel film modified and unmodified MPOFs.

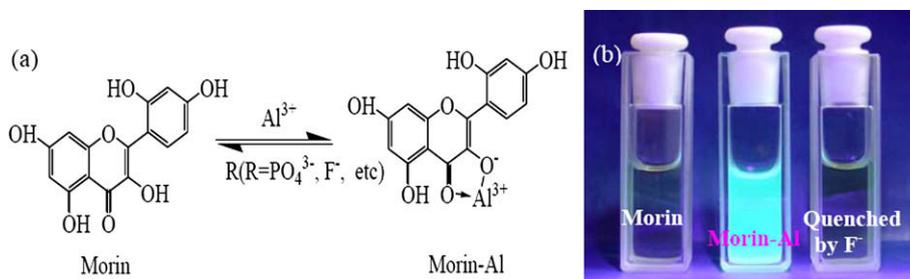


Fig. 2. Structure of morin and morin-Al and mechanism of fluorescence quenching.

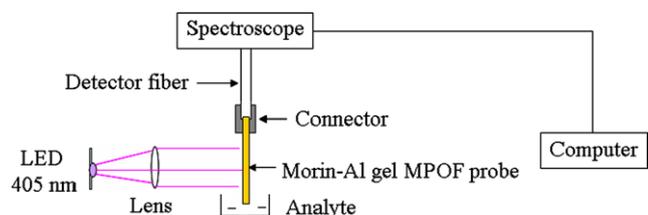


Fig. 3. Sketch of experimental setup for fluoride sensor probe characterization.

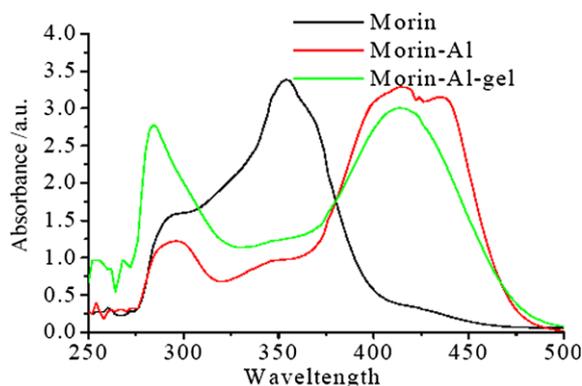


Fig. 4. UV-vis absorption spectra of morin, morin-Al, morin-Al-gel.

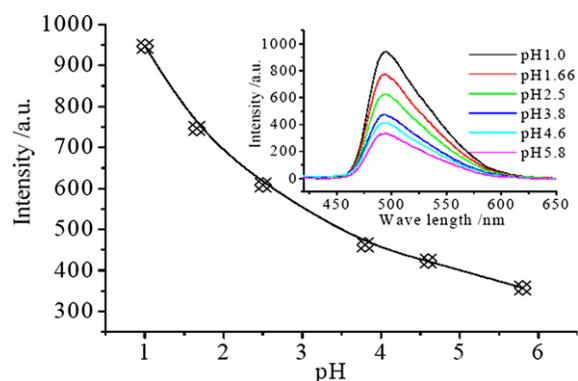


Fig. 5. Influence of pH on the fluorescence intensity of the morin-Al-gel-MPOF probe.

the Stern-Volmer quenching constant which showed the sensitivity. For this ideal case, there is a linear relationship between fluorescence quenching ratio I_0/I and the concentration of quencher, F^- . As a result, the calibration graph can be obtained within the range of 5–50 mmol/L. Its linear equation is evaluated as:

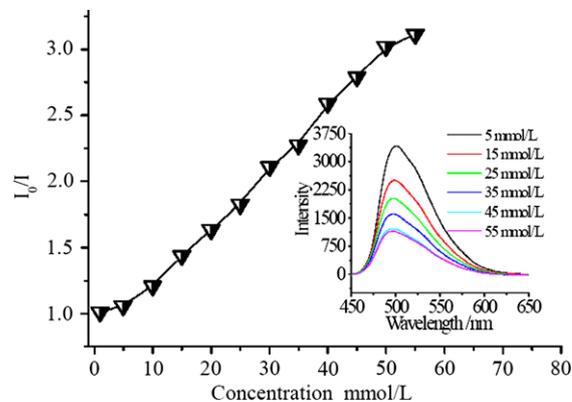


Fig. 6. Response curve of morin-Al-gel-MPOF probe to F^- .

$$y = 0.042x + 0.8440, \quad \text{with correlation coefficient } R^2 = 0.9965 \quad (2)$$

The effects of coexisting ions on response of the F^- probe are also studied. For the common cations such as Cu^{2+} , Zn^{2+} , Mg^{2+} , Ca^{2+} , PO_4^{3-} and CO_3^{2-} , and some oxidizing ions such as Fe^{3+} and $Cr_2O_7^{2-}$, there is no obvious quenching effect on the Al-morin-Gel-MPOF probe, which is because that their free-volume in aqueous solution is too big to enter the morin-Al-gel network. Therefore, selectivity of the Al-morin-gel-MPOF probe for fluoride sensing is quite high with the help of the compact silica gel network.

6. Conclusions

In this paper, a novel fluorescence fluoride sensitive MPOF probe based on sol-gel modification is fabricated. The fluorescence of morin-Al-gel-MPOF probe is strongly quenched by fluoride ion in the aqueous solution, enabling the detection of fluoride concentrations in the concentration range about 5–50 mmol/L, in a given pH value of 4.6. The present work proves that the sol-gel method is a favorable route for functionalizing MOF with uniform optical sensing film. It also demonstrates new potentials of MPOF in more broad fields of high sensitive and high selective microanalysis or in vivo biosensing. To improve the sensing properties, we aim to use hollow-core MPOF with PBG structure as sensing carrier and signal propagation medium. New results based on this geometry will be reported in the future.

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