



# Trace dissolved ammonia sensor based on porous polyelectrolyte membrane-coated thin-core fiber modal interferometer

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## ABSTRACT

A fiber-optic ammonia sensor based on a thin-core fiber modal interferometer (TCFMI) is fabricated and evaluated. The fast response to ammonia is achieved via the construction of poly(acrylic acid) (PAA) and poly(allyamine hydrochloride) (PAH) nanoporous films on the side surface of the TCFMI using the layer-by-layer (LbL) assembly technique. The fabricated sensing nanocoating is characterized by FT-IR spectrometer, UV–vis absorption spectroscopy, surface profiler, and scanning electron microscopy (SEM). Porous structure is beneficial to the diffusion of ammonia molecules through the multilayers. The TCFMI with a 10-cycle PAH/PAA nanoporous film sensor presented an excellent reproducibility with a fast response time to ammonia. The optimal detection range of this sensor is around 1–260 ppm with a low limit of detection (LOD).

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## 1. Introduction

With the unhealthy development of the industry and agriculture, the pollutant emissions were increased dramatically, which has caused serious pollution to the aquatic environment. The shortage of water resource has become an important factor which restricting the economy development [1]. The regular indicators for the assessment of water quality including ammonia nitrogen, conductivity and turbidity, heavy metals [2], total phosphorus [3], biochemical oxygen demand (BOD) [4], as well as oxygen demand (COD). The main pollutants of urban surface water are ammonia nitrogen [5], phenol [6], mercury [7] and cyanide [8], etc. Among them ammonia nitrogen pollution in aquatic environment comes mainly from domestic sewage, food industry, meat processing, feed production, steelmaking, oil refining, fertilizer production, inorganic chemistry, glass manufacturing, and pharmaceutical industry, etc. Ammonia nitrogen may increase eutrophication in lakes, rivers, coastal waters, and other important aquatic environment [9], which is the main factor for the degradation of these aquatic ecosystems. Moreover, a proportion of methemoglobinemia can be attributed to nitrate contamination of drinking water which results from oxidized ammonia by nitrobacteria. Ammonia nitrogen is an important indicator among water

environmental monitoring parameters. Thus, a simple and portable sensor is desirable to achieve sensitive detection of ammonia nitrogen.

Soluble ammonia (NH<sub>3</sub>) could react with some certain reagents to generate the color changes. One of the most famous chromogenic reaction is Nessler reaction. But the toxicity and instability of Nessler reagent severely limits its application [10]. Berthelot reaction [11] can also be used to detect NH<sub>3</sub>, but it is time-consuming. NH<sub>3</sub> can also be detected by the spectral characteristic absorption of NH<sub>3</sub> [12] with high sensitivity and good selectivity, but it is cumbersome, expensive and cannot realize remote monitoring. Recently, the optical fiber devices have developed dramatically in the field of sensing [13,14]. It could realize the long-distance data transmission (remote operation) through thousands of meters of optical fiber with low loss. The portable fiber-optic chemical sensor has a fast response. Moreover, it is easy to be fabricated and not susceptible to electromagnetic environment, which can be a potential method for environmental [15] and health monitoring [16].

Thin-core fiber modal interferometer (TCFMI) is fabricated by inserting a short segment of thin-core fiber (TCF) into a standard single-mode fiber (SMF) [17,18]. The working principle of TCFMI is based on the sensitivity of transmission spectrum along with the change of external refractive index. It has similar spectral characteristics comparing with long period fiber grating (LPG), but attracts tremendous attention due to its low cost, simple fabrication method, low temperature interference and high refractive index sensitivity.

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G. Decher [19] and his coworkers have used the polyelectrolyte electrostatic with opposite charge for layer-by-layer (LbL) electrostatic self-assembly to prepare polyelectrolyte multilayer membrane (PEM). LbL electrostatic self-assembly has become a universal and convenient method to prepare ultrathin membrane, which was prepared via immersing the functional substrate into polycation and polyanion solution successively [20]. Desired thickness could be achieved by repeating the cycle. LbL electrostatic self-assembly has been used in the preparation of multilayered films in various areas, such as functional films [21], sensors [22], nanomaterial [23], etc. Up to now, there are several methods for the fabrication of microporous or nanoporous multilayered films. The formation of the pore could be controlled by changing pH value [24], temperature [25], ionic strength of the environment [26] and so on. The formation of porous films based on breakage of the ionic bonds and polyelectrolytes rearranging was caused by disposing the constructed nanoporous polyelectrolyte multilayers (PEM) at different pH value, temperature or ionic strength. Thus formed pores were unstable when changing the external factors. In order to enhance the stability of pores, it was necessary to crosslink the film to lock the structure [27]. It had also been reported another strategy to fabricated porous films by removing a template from three-component multilayer films. The nanoporous films were prepared through immersing the crosslinked multilayer films in basic solution [28]. Therefore, the specific sensing to  $\text{NH}_3$  could be achieved through the LbL films assembled on the side surface of TCFMI.

In this work, we demonstrated a thin-core fiber interferometer coated with LbL electrostatic self-assembly porous polyelectrolyte film on the side surface for ammonia sensing. Poly(acrylic acid) (PAA) could bind amine compounds selectively due to the presence of free carboxy groups [29]. Poly(4-vinylpyridiniummethanecarboxylate) (PVP/PMC) as the cleavable template would disintegrated in the NaCl solution to achieve porous structure. It has developed a simple, efficient method for the fabrication of porous films because it was not necessary to crosslink the films before or after the removal of PVP/PMC. The refractive index of the porous membrane was changed by the variations of the concentration of analyte ammonia solution, resulting in a wavelength shift of the transmission spectrum, which provides the sensor signal. The response of prepared TCFMI ammonia sensor was exhibited a good linearity and reversibility with a fast response time.

## 2. Principle of operation

The schematic diagram of the thin-core fiber interferometer (TCFMI) is shown in Fig. 1. A 20 mm thin-core optical fiber (Nufern 460-HP) with a core diameter of  $\sim 3.0 \mu\text{m}$  and a cutoff wavelength of  $\sim 450 \text{ nm}$  was inserted into a standard single-mode fiber (SMF) to form TCFMI in which high-order cladding modes are excited and interfered with the core mode. The side surface of the TCFMI was then deposited with a polymer (PVP/PMC + PAH)/PAA multiple nanocoatings in this work by electrostatic self-assembly technique. The effective refractive index of high-order mode was changed as the external refractive index modulation. The positively or

negatively interference between the excited cladding modes and the core mode would result in some local maxima or minima, respectively. For a local minimum at the ending point, which results in a transmission nadir of the spectrum, the relative phase displacement  $\phi$  of the interfering two modes can be expressed as:

$$\phi = \frac{2\pi}{\lambda_{\text{TCFMI}}} [n_{\text{core}}^{\text{eff}}(\lambda) - n_{\text{cladding}}^{\text{eff}(v)}(\lambda, n_{\text{sur}})]L = \pi(2i + 1) \quad (1)$$

where  $n_{\text{core}}^{\text{eff}}$  is an effective refractive index of fundamental mode,  $n_{\text{cladding}}^{\text{eff}(v)}$  is an effective refractive index of the  $v$ th order cladding mode,  $n_{\text{sur}}$  is the effective refractive index of external medium,  $L$  is the length of the thin-core fiber,  $\lambda_{\text{TCFMI}}$  is the wavelength of the transmission nadir, and  $i$  is an integer. A change of the refractive index of the polymer coating results in a change of the effective refractive index of the cladding mode propagating within the TCFMI that can be observed by a wavelength shift of the transmission spectrum (see Fig. 1).

## 3. Experimental

### 3.1. Materials

Poly(allylamine hydrochloride) (PAH  $M_w = 65,000$ , 20 wt% aqueous solution), poly(acrylic acid) (PAA  $M_w = 100,000$ , 35 wt% aqueous solution) and poly-(4-vinylpyridine) (P4VP,  $M_w = 60,000$ ) were purchased from Aldrich. Methyl bromoacetate, Ammonia (ca. 30 wt% in  $\text{H}_2\text{O}$ ), diethylamine (DEA), pyridine, and ethanol were obtained from Aladdin. All of these chemicals were reagents of analytical grade, and can be used without further purification. Deionized water with a resistance of  $\sim 18 \text{ M}\Omega$  was used in all experiments.

### 3.2. Synthesis of poly(4-vinylpyridiniummethanecarboxylate) (PVP/PMC)

According to the reported method [30], poly(4-vinylpyridiniummethanecarboxylate) (PVP/PMC) was synthesized as follows. 3 g P4VP was added into three-necked bottle with 30 ml methanol at  $60^\circ\text{C}$ . After complete dissolution, the solution was stirred with a 10-fold excess of methyl bromoacetate for 72 h. Saponification of the ester was performed by adding 1 M NaOH dropwise to the mixed solution at  $60^\circ\text{C}$  for 3 h. The pH value of the solution was always maintained at 10–11. The hydrolysis solution was dialyzed against deionized water for 3 days to remove methanol and ethanol. Deionized water was replaced every 2 h. Finally, the solution was lyophilized to obtain PVP/PMC. The FT-IR spectra of PVP/PMC are determined by infrared spectrometer (MagnaIR550II, Nicolet, USA).

### 3.3. Fabrication of layer-by-layer assembled porous polyelectrolyte on quartz substrates

The chemical structures of the three polyelectrolytes used in this work and the process of LbL electrostatic self-assembly are shown in Fig. 2. The quartz substrates were cut into  $1.5 \text{ cm} \times 2 \text{ cm}$  pieces and cleaned with acetone and ethanol for 20 min, respectively. Then it was immersed in fresh piranha solution (3:7 v/v mixture of 30%  $\text{H}_2\text{O}_2$  and concentrated  $\text{H}_2\text{SO}_4$ ) at  $90^\circ\text{C}$  for 120 min following by thoroughly rinsing with large amount of deionized water, and then dried with nitrogen flow. The quartz substrates surface was negatively charged. PVP/PMC and PAH were dissolved in deionized water to give a total concentration of 2 mg/mL. The polycation composition in the blended solution was PVP/PMC/PAH = 1:1 wt/wt. PAA was diluted to 2 mg/mL by deionized water. Then the activated quartz substrates were immersed into the blended polycation solutions

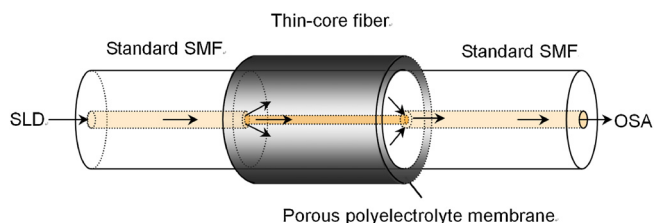


Fig. 1. Schematic configuration of the ammonia sensor based on a polymer-coated TCFMI.

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