

Determination of trace chromium (VI) using a hollow-core metal-cladding optical waveguide sensor

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Abstract: A biosensor capable of highly sensitive detection of trace chromium (VI) with a simple hollow-core metal-cladding waveguide (HCMW) structure is theoretically modeled and experimentally demonstrated. Owing to the high sensitivity of the excited ultrahigh-order modes in the waveguide, a tiny variation of the extinction coefficients in the waveguide guiding layer where the chromate ions reacts with the diphenylcarbazide (DPC) can lead to a significant change of light intensity in the reflection spectrum. The experimental results indicate that using the proposed method, the chromium (VI) sensitivity detection limit can be as low as 1.2 nM, which represents a 16-fold improvement compared to the surface plasmon field-enhanced resonance light scattering (SP-RLS) method, and a 4-fold improvement compared to the flame atomic absorption spectrometry and fluorimetry spectroscopy, respectively.

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1. Introduction

In addition to the weathering of rocks and the erosion of soils, trace chromium (Cr) is usually found in environment as a result of the discharge of many industrial manufacturing activities, such as stainless-steel production, leather tanning, electroplating and pigment fabrication and in tap water supply systems. Chromium is generally in two most stable states of Cr (III) and Cr (VI). The physiological effect of these two states on the biological systems are totally opposite: Cr (III) is essential to human health at trace level; Whereas Cr (VI) is readily absorbed by the lungs, digestive tracts, mucous membranes and skins and is toxic and carcinogenic, and is considered as a serious pollutant in environment. The determination of Cr (VI) in environmental and at industrial sites is consequently important.

Nowadays, a lot of approaches have been developed to determine the Cr (VI). The most widely used methods are spectroscopy techniques [1], such as electrothermal atomization atomic absorption spectrometry (ET-AAS) [2,3], flame atomic absorption spectrometry (FAAS) [4–6], fluorimetry [6–8] and so on. Mass spectrometry techniques are also used to

determinate Cr(VI) such as inductively coupled plasma-mass spectrometry (ICP-MS) [9,10], isotope dilution mass spectrometry (ID-MS) [11,12]. These methods are sensitive and accurate, but suffer from system complexity, long testing time and high cost. Ultraviolet visible light absorption spectrometry (UV/VIS) based on the reaction of chromate ions with diphenylcarbazide (DPC) is a matured technique in analytical chemistry. One limitation with this method for monitoring Cr (VI) is that the detection sensitivity is limited to be about 20 ppb [13]. With the current strict drinking water regulations that require high detection sensitivity (<1 ppb) and short testing time, the applications of these methods are found limited. It is necessary to develop some new techniques to overcome these disadvantages. Recently, there is a growing interest in evanescent field detection methods based on optical resonant modes due to their relatively high sensitivity, fast response, small dimensions, and high mechanical stability. The methods reported include surface plasmon resonance (SPR) [14], long-range surface plasmon resonance (LRSPR) [15], resonant mirror (RM) [16], reverse symmetrical waveguide (RSM) [17] and metal-clad leaky waveguide (MCLW) [18]. For example the SPR technique applied to the determination of Cr (VI) has achieved a detection limit of 20nM [19]. The common feature of these techniques is that the sample to be detected is located in the region where the evanescent wave propagates. However, recent research results based on sensitivity analysis [20,21] suggest most of these optical evanescent wave sensors still suffer from low sensitivity due to various reasons. These reasons include (1) the limited power portion existing in the sensing region; (2) refractive index of the analyte must always be less than the effective index of the resonant modes; and (3) the short penetration depth of the evanescent field makes the large analytes, such as bacteria, outside the sensing region, resulting in further insufficient sensitivity of the system.

In this paper, a new method is proposed by using a hollow-core metal-cladding waveguide (HCMW) for highly sensitive detection of chromium (VI). In HCMW the sample solution is not placed in a region where evanescent field exists, but in the guiding layer where the oscillation field propagates. The millimeter scale thickness of the guiding layer not only increases the detecting depth and test sample volume, but also makes it possible to accommodate the ultrahigh order modes with high sensitivity. By using DPC as the chromogenic reagent to amplify the change of extinction coefficient, trace chromium (VI) is detected in a relatively simple optical configuration.

2. Material and methods

2.1 HCMW sensor chip

As shown in Fig. 1(a), the HCMW's structure in the experiment is composed of three parts: (i) a polished glass substrate of 0.5mm thickness has a thin silver film coated on the top side to act as a coupling layer, (ii) two parallel glass strips of 0.5mm thickness are placed at a distance of 4mm to form the sample confinement walls, (iii) another polished glass substrate of 0.5mm thickness has a relatively thick silver film deposited on the base side to prevent light leakage. The sample cell is formed by above three parts in a sandwiched configuration. The top and base silver films are deposited in vacuum by a sputtering system (SPF-210B, Anelva Corporation, Tokyo, Japan). The top silver film of 35nm thickness works as a coupling layer, which makes it possible to allow the light going into the guiding layer, and the base silver film has thickness greater than 200nm to minimize the light leakage. The sample cell together with the up and base substrates, constitute the guiding layer of the HCMW. All the glass substrates and strips (BK7, $n = 1.519$ [22]) are optically contacted to ensure the parallelism in the HCMW sensor chip (provided by Shanghai Optics Engine Inc. Shanghai, China). The metal layers were not placed at the inside surface of glass layers to construct a more simple three-layer (metal-solution-metal) waveguide. That was on the purpose to prevent the complex material produced by Cr(VI) solution and color-forming reagent attaching on the surface of metal. The attachment would create residue problem.

Besides, it is convenient to re-sputter the top metal layer, when the thickness of top layer does not reach the setting value.

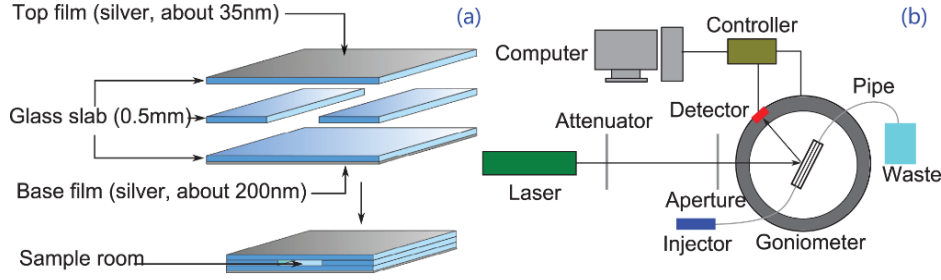


Fig. 1. (a). HCMW Sensor Chip, thicknesses of each layer from above are 35nm, 0.5mm, 0.5mm, 0.5mm, 200nm. The volume of middle sample room is about $4\text{mm} \times 10\text{mm} \times 0.5\text{mm}$. (b). Experiment configuration of the oscillation field sensor system.

2.2 Experiment configuration

The schematic diagram of the experimental setup is shown in Fig. 1(b). To excite the ultrahigh order modes of the HCMW, a TE polarized laser beam from a solid-state laser (532nm, MW-SL-532/30mW, Shanghai Optics Engine Inc. Shanghai, China) is incident on the upper silver film at certain optical angles. The fluctuation of the laser intensity reaches 0.02% through the special current and temperature control and the noise of the intensity measurement system is below 0.01%. During the experiment, in order to keep the temperature of the analyte stable in room temperature, an attenuator was added in front of laser to reduce the thermal effects in cell room. An aperture with a diameter of 1 mm was inserted into the beam path to further confine the divergence angle to about 0.4 mrad. The sample solution was pumped into and out the cell room by a syringe through inlet and outlet pipes with 0.5mm inner diameter. A computer-controlled $\theta/2\theta$ goniometer was used to carry out the angular scans. The intensity of the reflected beam was detected by a photodiode and then an attenuated total reflection (ATR) dip was recorded as a function of the beam incident angle to reveal the ultrahigh-order guided modes in the HCMW structure.

2.3 Sensitivity analysis

The sensor chip in the experiment is essentially a five-layered optical waveguide. The sample cell and the two glass slabs make up the guiding layer of the HCMW. As the thickness of guiding layer is at millimeter level, the waveguide can support thousands of guide modes. According to the properties of the ultrahigh-order modes [23], there exists an extended range of the effective refractive index, i.e., $0 < N < 1$, which makes it possible to couple light energy from free space into the HCMW [24]. Attributing to these advantages, the measuring system can be free from the coupling elements, such as prism and grating.

For a five-layered optical waveguide, by applying the derivation method described in references [25,26], the minimum reflectivity can cast in the form:

$$R_{\min} \propto 1 - \frac{4 \text{Im}(\beta^0) \text{Im}(\Delta\beta^t)}{[\text{Im}(\beta^0) + \text{Im}(\Delta\beta^t)]^2} \quad (1)$$

where $\text{Im}(\beta^0)$ and $\text{Im}(\Delta\beta^t)$ represent the intrinsic damping and the radiative damping respectively. $\beta^0 = k_0 N = k_0 n_0 \sin \theta$ is the transverse propagation constant with the effective index N of the guided mode. $k_0 = 2\pi/\lambda$ is the wavenumber with light wavelength λ in free space, and θ is incident angle. Reference [25] and [26] give the detailed description of the procedure. The intrinsic damping indicates the transmission loss of guided wave, which is closely related to the extinction coefficient of guiding layer and the absorptions from the

metallic claddings. The radiative loss represents leakage loss of the guided wave back into air, which is strongly dependent on the thickness of the top silver film. It is shown from Eq. (1) that the minimal reflectivity of the system becomes zero when the intrinsic damping is equal to the radiative damping, that is to say

$$\text{Im}(\beta^0) = \text{Im}(\Delta\beta^L) \quad (2)$$

As the concentration of Cr (VI) in aqueous solution changes, the extinction coefficient of the solution and the intrinsic damping of HCMW change too. Consequently, Eq. (2) becomes invalid, that means an increase of $R_{\min}$. When the change of the extinction coefficient is small enough, the relationship between $R_{\min}$ and the extinction coefficient is approximately linear, which was shown in Fig. 3 experimentally.

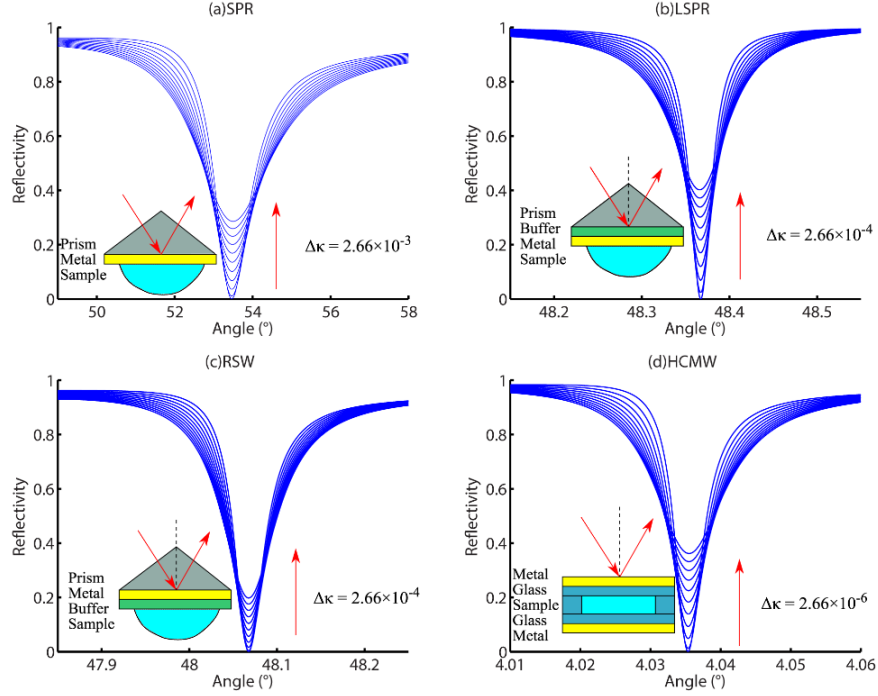


Fig. 2. Simulation results of the change of $R_{\min}$ with the increasing of the distinction coefficient of the analyte in four different resonant configurations ($\Delta\kappa \neq 0$). (a) SPR, (b) LRSPR, (c) RSW, (d) HCMW.

In fact, the relationship between the concentration of solution and the imaginary part of dielectric constant can be derived from the Beer-Lambert law as below [27]

$$\text{Im}(\varepsilon) = \frac{nK_m}{\ln 10 \cdot k_0} C \quad (3)$$

where C is the concentration of solution, K_m is the molar absorptivity, n is the real part of refractive index of the solution. Combining Eq. (1) and Eq. (3) we can get the relationship between reflectivity and the concentration of solution.

Table 1. Parameters for the four sensor type being simulated.^a

Construction parameters	Sensors			
	SPR	LRSPR	RSW	HCMW
Prism(ϵ_0)	3.24	3.24	3.24	-
Buffer($\epsilon_1, d_1(\text{nm})$)	-	1.78, 1060	-	-
Top Metal($\epsilon_2, d_2(\text{nm})$)	$-12 + i0.5$, 50	$-12 + i0.5$, 15	$-12 + i0.5$, 50	$-12 + i0.5$, 39
Upper Glass($\epsilon_3, d_3(\text{mm})$)	-	-	2.25, 0.0015	2.25, 0.5
Guiding($\epsilon_4, d_4(\text{mm})$)	-	-	-	1.78, 0.5
Base Glass($\epsilon_5, d_5(\text{mm})$)	-	-	-	2.25, 0.5
Bottom Metal($\epsilon_6, d_6(\text{nm})$)	-	-	-	$-12 + i0.5$, 200
Substrate(ϵ_7)	1.78	1.78	1.78	-
$\Delta\kappa$	0.00266	0.000266	0.000266	0.00000266

^aThe wavelength of the incident light are all 532nm, and $\Delta\kappa$ represents the change step of the extinction coefficient of sample solution.

Sensitivity comparison for four different configurations is demonstrated in Fig. 2 by conducting a simulated calculation. The optimized parameters for simulation are presented in Table 1. The dielectric constant of silver is from reference [28]. The selection criteria of the parameters is that the minimal reflectivity equals to zero, when the extinction coefficients of the analytes are zero. As is shown, $R_{\min}$ increases with the increasing of the extinction coefficient κ of the analyte for all sensors. It is clear that the sensitivity of HCMW sensor is at least two orders of magnitude higher than that of the other three types of sensors.

The sensitivity of biosensors mentioned above is closely related to the energy ratio (the light energy in sample region to the total light energy in sensor) and the effective index in waveguide [29]. The bigger the energy ratio is and the smaller the effective index is, the higher the sensitivity reaches. In HCMW, the achievement of the high sensitivity are due to (1) the strong power confinement of the oscillating field, resulting in a sufficient interaction between light and the analyte solution and also a high energy ratio; (2) excitation of the ultrahigh-order modes with ultra-low effective index (close to zero). However, in the three other types of sensors (SPR, LRSPR, RSW) mentioned above, the energy ratio and power confinement is relatively weak due to the characteristics of the evanescent field: in these evanescent field biosensors, the effective index of the resonant mode, which acts as the sensing probe, is always greater than the refractive index of cover medium, resulting in poorer sensitivity.

2.4 Chemicals

Acetone ($\text{C}_3\text{H}_6\text{O}$), sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) and 1,5-Diphenylcarbazide (DPC, $\text{C}_{13}\text{H}_{14}\text{N}_4\text{O}$). All the chemical reagents were analytical reagent grade, bought from Sinopharm Chemical Reagent Co.,Ltd (Shanghai, China).

2.5 Preparation and measurement

Sulfuric acid (1:1) and phosphoric acid (1:1) were prepared by diluting 50ml of acid in 50ml of water. Chromogenic reagent was prepared by dissolving 2g of DPC in 50ml acetone, and then diluting in water with a 100ml measuring flask. Chromogenic reagent was prepared just before use. A 400 $\mu\text{g/l}$ of Cr(VI) stock solution was prepared by dissolving $0.2829 \pm 0.0001\text{g}$ of potassium dichromate in water with a 250ml measuring flask. A 4 $\mu\text{g/l}$ of Cr(VI) standard solution was prepared by diluting 1ml of Cr(VI) stock solution in water with a 100ml measuring flask just before use. The Cr(VI) working standard solutions were prepared by

appropriate dilution by water before use. All the water used in experiment was de-ionized water produced by an ultra-pure water system (Milli-Q Direct-Q8, EMD Millipore Corporation, Billerica, MA, USA).

Color reaction took place by adding 0.25ml of Sulfuric acid (1:1), 0.25ml of phosphoric acid (1:1) and 1ml of chromogenic reagent to 25ml of each Cr (VI) working standard solution. The reaction lasted for 7 minutes. The concentration of Cr (VI) working standard solution selected in this experiment were 0, 0.24, 0.48, 0.72, 0.96, 1.2, 1.44, 1.92, 2.16, 2.64 $\mu\text{g/l}$. After reaction, the mixed solutions were injected into sensor chip. And then ATR spectrum of each solution was measured by rotating the goniometer. Before the injection of each solution, the sensor chip was washed by pumping 20ml of de-ionized water to avoid residue.

3. Results and discussion

3.1 Determination of Cr (VI)

Figure 3(a) shows the ATR spectra of the sample solutions. As the Cr (VI) concentration increases, the reflectivity at coupled angle varies from 0.097 to 0.118. Figure 3(b) shows the relationship between minimum reflectivity and the concentration of Cr (VI). It produces an approximate linear response about Cr (VI) concentrations:

$$R_{\min} = (0.007965 \pm 0.000814) \cdot C(\text{Cr(VI)}) + (0.09763 \pm 0.00117) \quad (4)$$

with the fitting relation coefficient $R^2 = 0.9845$ ($n = 7$, the relative standard error of blank sample is 0.00017), where $C(\text{Cr(VI)})$ is the concentration of Cr(VI) in $\mu\text{g/l}$. The relative standard deviations of solution are presented in Table 2. The limit of detection, defined as three times of the standard deviation of the measurement blank (a concentration of zero), is

$$\frac{3 \times 0.00017}{0.007965} = 0.064 \mu\text{g} \text{ or } 1.2 \text{ nM via the linear response curve. The sample required is about } 20 \mu\text{l},$$

which is the volume of the sensor cell room.

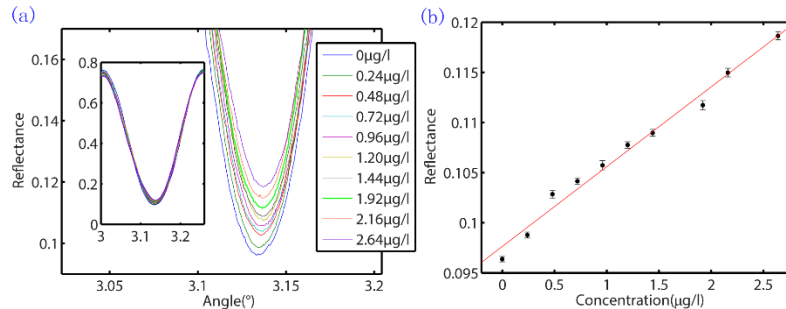


Fig. 3. (a). ATR spectra of different concentration of Cr (VI). Left curves are the whole ATR spectra while the curves in middle part are the enlarged ones around $R_{\min}$; (b). Reflectance at coupled angle of different concentration of Cr (VI) and the concentration response curve (the fitted line).

In Fig. 3(a), we could also found the shift of the resonant dip with the Cr (VI) concentration changes. It indicates the change of the real part of refractive index of solutions. This phenomenon has been already used in many applications [30,31]. The shift is approximately linear, when the change of refractive index is small enough. However, the shift of ATR resonance dip is too small to be identified clearly in the experiment. And it is not the purpose of the experiment.

The experiment was conducted at room temperature. In order to eliminate the effects of the temperature change on the detection results, the HCMW is placed in a thermal shield box made of the polymethyl methacrylate.

Table 2. The relative standard deviations of solutions.

Concentration ($\mu\text{g/l}$)	RSD (10^{-4})	Concentration ($\mu\text{g/l}$)	RSD (10^{-4})
0 (blank)	1.7	1.20	3.2
0.24	2.9	1.44	3.4
0.48	3.7	1.92	4.6
0.72	3.3	2.16	4.3
0.96	4.5	2.64	4.0

Since the HCMW has relatively simple structure and is convenient to detect the extinction coefficient of sample layer, it can be used to determine not only Cr (VI) but also many other materials by using the suitable color-forming reagent and laser excitation wavelengths as explained below.

3.2 Color reaction and interference

Determination of Cr (VI) was based on the color reaction with DPC. The reaction takes place at a pH of 1.0 ± 0.3 , and forms absorbing complex at the wavelength around 540nm. Therefore, a laser of 532 nm was used as the light source in the experiment. Certainly some substances may interfere the detection signal if the chromium concentration is relatively low. These include iron, hexavalent molybdenum and mercury. However, the interference caused by hexavalent molybdenum and mercury in the concentration lower than 200 mg/l and iron in the concentration lower than 1mg/l can be ignored in this specified pH [32]. Incorporating with color reaction, the change of extinction coefficient caused by the change of the Cr(VI) concentration will be amplified, which improves the sensitivity of detection.

4. Conclusions

The HCMW sensor provides a simple and sensitive method to detect Cr (VI). The sensitivity of this HCMW sensor is at least two orders of magnitude higher than the traditional evanescent field sensors (SPR, LRSPR and RSW) theoretically. A determination limit of 1.2 nM was got via the concentration response curve with a low volume of sample solution (20 μl) experimentally. This method is potentially applicable to the determination of other samples based on the extinction coefficient.

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