# Surface plasmon resonance sensor for detecting of arsenic in aqueous solution using polypyrrole-chitosan-cobalt ferrite nanoparticles composite layer

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## ARTICLE INFO

## ABSTRACT

The detection and measurement of low concentrations of arsenic (V) are the subjects of intense research interest in chemistry and environmental activity. In this research, a polypyrrole-chitosan/cobalt ferrite nanoparticles composite layer was prepared using an electrodeposition method on a gold-coated glass slide. The composite layer was characterized using field emission scanning electron microscopy, energy-dispersed spectroscopy, atomic force microscopy, and a high surface stylus profilometer. The composite layer was used to detect the arsenic in water, and the sensor limitation was about 0.001 ppm. The composite layer was tested using atomic-force microscopy before and after the detection of arsenic. As a result, the roughness was disoriented, as the arsenic was bound on the surface of the composite layer.

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## 1. Introduction

Arsenic is a toxic element with atomic number 33 in group 5 of the periodic table of chemical elements. Contamination of arsenic is considered in drinking water, food, and agriculture products. Arsenic components can be found in arsenic gas, in organic and inorganic forms, and they can dissolve in water. The toxicity of arsenic depends on valance state, solubility, and organic and inorganic forms. For example, inorganic trivalent components and element arsenic have the highest and lowest contamination in the environment, respectively [1]. Ingestion and exposure of a large amount of arsenic can cause lung [2,3], bladder [4], kidney [5], and skin [6] cancer. The measurement of arsenic concentration is an interesting activity in an environmental and chemical laboratory. Numerous methods are used to detect and measure low concentrations of arsenic such as inductively coupled plasma mass spectroscopy [7], atomic absorption spectroscopy [8], neutron activation analysis [9], hydride generation atomic fluorescence [10], graphite furnace atomic absorption [11], high-performance liquid chromatography [12], voltammetry and stripping analysis [13–15], bacteria-based bioassays [16], ion chromatography [17], laser-induced breakdown spectroscopy [18], and surface-enhanced Raman spectroscopy [19,20]. The mentioned methods require expensive instruments and calibration curves. These methods are well established and accurate, but they require a chemical knowledge base and the necessary samples to be transported to a laboratory center for measurement.

A sensor based on the surface plasmon resonance (SPR) [21] is a versatile and portable method for detecting toxic chemicals. The SPR sensor was used to detect arsenic in groundwater using thiol-containing organic compounds, and the limitation sensor was 0.01 ppm.

The detection of arsenic and arsenic compounds were considered using nanomaterials. For example, gold nanoparticles were used to detect arsenic and arsenic components [22–25], and a silver nanoplate was utilized using the colorimetric method to detect arsenic [26]. Arsenic can enhance luminescence properties; hence, $YPO_4:Eu^{3+}$ nanoparticles were used to measure the concentration of arsenic with a limitation of about 1 ppm [27].

Nowadays, magnetic nanoparticles are intensively studied in sensor and biosensor applications, as they have been applied to enhance the sensitivity and selectivity of sensors for detection of toxic chemicals [28]. Arsenic was detected using a superparamagnetic iron oxide ($Fe_3O_4$) nanoparticle with a surface functionalization of dimercaptosuccinic acid in the presence of a 1.2 T magnetic field in seawater, groundwater, and human blood and plasma [29]. Magnetite nanoparticles functionalized with a carboxyl (succinic acid), amine, and thiol group were used for

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detection and of heavy metal and arsenic [30]. The combination of multi-walled-born nitride nanotubes and $Fe_3O_4$ nanoparticles was reported to remove the arsenic from water [31]. The sensitivity was about 1 mg/L, and the adsorption mechanism of arsenic reported a combination of chemical complexation and physical electrostatic attraction. Chowdhury and Yanful focused on the mixture of magnetite and magnetite nanoparticles for adsorption of arsenic [32]. The authors reported that the maximum arsenic adsorbed was about 3 mg/L. In accordance with the literature [28–32], the sensitivity and selectivity of $Fe_3O_4$-NPs for detection and adsorption of heavy metals are higher than in arsenic. Consequently, $Fe_3O_4$-NPs have the potential to remove and adsorb the heavy metal and arsenic very well, and magnetic nanomaterials are subjects of intense interest in sensors and biosensors. In order to overcome the difficulty of experiment, limitation in sensitivity, and high cost of instruments, the composite of polypyrrole and chitosan with magnetic nanoparticles has been suggested to detect arsenic based on the SPR sensor. In this study, the polypyrrole-chitosan/$CoFe_2O_4$-NPs (PPy-Chi/$CoFe_2O_4$-NPs) composite layer was prepared to detect arsenic and measure the low concentration of arsenic in water. The PPy-Chi/$CoFe_2O_4$-NPs was prepared using the electro-deposition method, and the prepared sample was characterized using field emission scanning electron microscopy (FE-SEM), energy-dispersed spectroscopy (EDX), and Raman spectroscopy. The binding effect of arsenic and the sensing layer was demonstrated using atomic-force microscopy (AFM) and inductively coupled plasma mass spectroscopy (ICP-MS).

## 2. Experimental methods

### 2.1. Preparation of cobalt ferrite nanoparticle

The procedure of preparation of cobalt ferrite nanoparticles was reported in Ref. [33], and Naseri et. al obtained the best calcination of cobalt ferrite nanoparticles. Briefly, the preparation of cobalt ferrite nanoparticles is as follows:

Metal nitrate reagents, poly(vinyl pyrrolidone) (PVP) and deionized water were used as precursors and a capping agent to reduce the agglomeration of the particles, the solvent, respectively. Iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) and cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$), were purchased from Acros Organics with purities exceeding 99%, respectively. PVP (MW=29,000) was purchased from Sigma Aldrich, and it was used without further purification. An aqueous solution of PVP was prepared by dissolving 3 g of PVP in 100 ml of deionized water at 343 K, prior to mix 0.2 mmol of iron nitrate and 0.1 mmol of cobalt nitrate (Fe:Co=2:1) into PVP solution. The mixture constantly was stirred for 2 h using a magnetic stirrer until a colorless and transparent solution was obtained. The solution had a pH from 1 to 2 measured by means of a glass electrode. No precipitation of materials occurred before the heat treatment. The mixed solution was poured into a glass Petri dish and was heated at 353 K in an oven for 24 h to evaporate the water. The resulting orange solid was crushed for 15 min in a mortar to form powder. The calcinations of the powder were conducted at 673, 723, 823, and 923 K for 3 h for the decomposition of the organic compounds and the crystallization of the nanoparticles [33]. Naseri et al. characterized the final products and they found the best calcination was occurred in 932 K, and they investigated the magnetic properties using.

A vibrating sample magnetometer (VSM) (Lake Shore 4700) at room temperature with a maximum magnetic field of 15 kOe; hence, in this research, the magnetized prepared powder in 932 K was used to investigate the absorption of arsenic.

### 2.2. Electrodeposition of polypyrrole-chitosan/cobalt ferrite

nanoparticles

Prior to do experiment, the gold-coated glass slide was prepared with a sputtering coating at a thickness of 46.3 nm. The PPy-Chi/$CoFe_2O_4$-NPs composite layers were synthesized using electrochemical polymerization of distillated pyrrole in the presence of the $CoFe_2O_4$ nanoparticles. At first, the sodium dodecylbenzenesulfonate (SDBS) was dissolved in distilled water and the ratio of the SDBS to $CoFe_2O_4$ -NPs to SDBS was 9:1. The $CoFe_2O_4$ nanoparticles which had a 0.04% weight ratio to pyrrole monomer, were dissolved in the SDBS solution that was sonicated for 7 h to enhance the disaggregation of any nanoparticles bundles.

0.7% w/v of chitosan was dissolved in acetic acid at room temperature prior to the electro-deposition of layers. Then, the mixture of $CoFe_2O_4$-NPs and SDBS solution was dispersed into the chitosan solution during mechanical stirring. Afterward, the pyrrole was added to the mixture. The premixed solution of PPy-Chi/$CoFe_2O_4$-NPs was electro-polymerized at +1.2 V in a three-electrode electrochemical cell. A gold-coated glass slide electrode, a graphite rod and a saturated calomel electrode were used as the working, the counter and the reference electrode, respectively. The electro-deposition of layers was carried out at room temperature using an electrochemical instrument (Versa stat 3, Ametek, Princton Supplied Research), and the deposition time was 80 min. The final PPy-Chi/$CoFe_2O_4$-NPs thin layer was washed with water and methanol to remove the electrolyte solution and dried under vacuum at 23 °C for 24 h [34]. The layer of PPy-Chi/$CoFe_2O_4$-NPs was characterized using field emission scanning electron microscopy (FE-SEM, Hitachi, SU8000 Series), Energy dispersive spectroscopy (EDX, Oxford Instrument, X-Max) and atomic force microscopy.

### 2.3. Surface plasmon resonance setup

Measurements of low concentration of arsenic (V) were carried out using a home-built surface plasmon resonance setup [35]. The SPR setup (Fig. 1) was based on the Kretschmann configuration using a high index prism ($n$=1.83956, Foctek). A gold-coated glass slide, which was used to prepare the sensing layer, was attached on the prism from on uncoated side. A $p$-polarized He–Ne laser beam (633 nm) was passed through the prism and focused onto the gold metal layer. The prism was placed on the precision rotation stage bench and rotated up to 30° in increments of a 0.01°. The variation of the laser beam intensity was registered when the
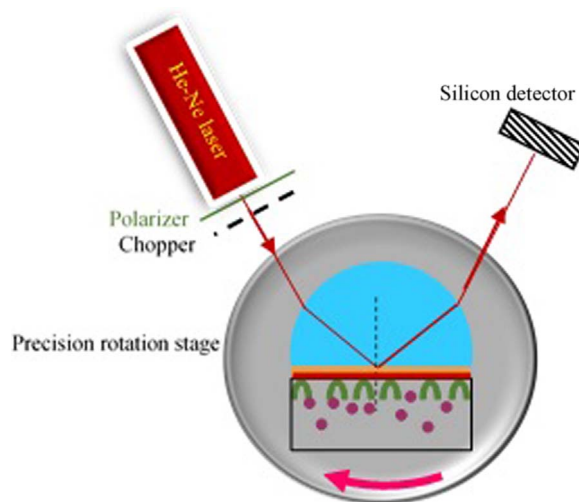


**Fig. 1.** The home-built SPR setup contains a He-Ne laser, polarizer, chopper, prism, precision rotation stage, and silicon detector.