



# A sensitive electrochemical molecularly imprinted sensor based on catalytic amplification by silver nanoparticles for 3-indoleacetic acid determination



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## ABSTRACT

A novel strategy for improving the sensitivity of a molecularly imprinted sensor was proposed based on the amplification effect derived from the electrochemical stripping of copper produced by catalytic deposition by silver nanoparticles (AgNPs). Polypyrrole was electrochemically polymerized to prepare a molecularly imprinted polymer film using 3-indoleacetic acid (IAA) as a template. After the competitive reaction between IAA and thiolation-3-indoleacetic acid (IAA-S), IAA-S was labeled with AgNPs, and then copper was catalytically reduced and deposited onto the AgNP surface. The deposited copper was electrochemically dissolved, and the anodic stripping current was recorded using linear sweep voltammetry. The change in signal decreased when IAA-S was replaced by IAA in the samples. The peak current was proportional to the logarithm of the concentration of IAA in the range of  $9 \times 10^{-10}$ – $6 \times 10^{-7}$  mol/L, with a detection limit of  $2.31 \times 10^{-10}$  mol/L determined by the  $3\sigma$  rule. Samples were assayed, and the recoveries of the approach ranged within 99.7–104.2%.

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## 1. Introduction

Molecular imprinting technology is developed to introduce recognition properties into synthetic polymers by synthesizing molecularly imprinted polymers (MIPs) with specific molecular recognition capacity [1]. Three-dimensional cavities are created within a polymeric matrix that is complementary to the size, shape, and functional group orientation of the target molecules [2]. The functional group orientation within the cavity will preferentially bind in specific locations to only the target molecule. Molecularly imprinted sensors, with the strong points of MIPs in selectivity [3,4], show tremendous advantages in organic and biological analyses [5–12]. However, the detection limit of MIP sensors is dissatisfactory in the determination of analytes in trace concentrations. Recently, some efforts have been made to improve the sensitivity of molecularly imprinted sensors on the basis of the combination of molecular imprinting technique and enzyme amplifiers [13,14] and the catalytic effect of molecularly imprinted film [15,16]. Enzyme was expensive, its activities would be affected by the harsh temperature and pH value of the experiment.

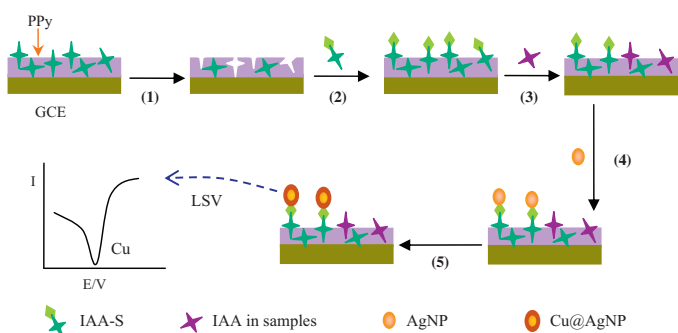
Nevertheless, these techniques have some deficiencies such as costly reagents, tedious procedure, and limited applicability.

Considerable discussion is centered on the asserted assumption that nanoparticles (NPs) are something fundamentally “new” and, thus, cannot be compared to conventional chemicals or bulk materials [17–20]. Owing to their unique physical and chemical properties, NPs have been extensively applied to different kinds of sensors to achieve increased signal response [21–25].

In this work, we established a neoteric and sensitive design of a molecularly imprinted electrochemical sensor for the detection of 3-indoleacetic acid (IAA) based on coupling the crystal nucleus catalysis of silver nanoparticles (AgNPs) with sensitive stripping voltammetric method.

IAA, a kind of trace ubiquitous phytohormone essential in plant tissues, regulates many important physiological activities and determines most properties of the plant at their low concentrations, such as growth, gravitropism, and apical dominance. To control the growth of plants artificially and obtain high yield in agriculture, the widely used IAA is applied exogenously to plants. Monitoring IAA in crops is significant to agriculture and horticulture. Various analytical techniques have been developed for the determination of IAA, such as high-performance liquid chromatography [26], immunoassay [27], liquid chromatography–tandem mass spectrometry [28,29], and colorimetry detection [30]. Some of these techniques require sophisticated instrumentation or radioactive chemicals,

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**Fig. 1.** Schematic diagram of the preparation principle of the pyrrole-based on IAA molecularly imprinted electrochemical sensor. (1) Elution; (2) incubation; (3) competition; (4) labeling; and (5) catalytic copper deposition.

while some are time-consuming. Consequently, the development of a simple, rapid, inexpensive, and sensitive analytical method for routine IAA screening is of particular significance and necessity.

In the first demonstration of this approach, molecularly imprinted polypyrrole (PPy) membrane was prepared on electrode surface by electropolymerization of pyrrole in the presence of a template IAA molecule. Then, IAA was eluted from the MIP film to produce specific recognition cavities. According to the similar principle we previously used [13], the steps of the experiment including elution, incubation, competition, and labeling were adopted (shown in Fig. 1). After incubation, all cavities were occupied by thiolation-3-indoleacetic acid (IAA-S). Then, AgNPs were labeled on IAA-S for copper deposition. After copper deposition onto the labeled AgNPs, the stripping current of copper was recorded and IAA was determined indirectly by the competition reaction. With the aid of stripping voltammetric method, sensitivity was improved significantly and a lower detect limit was obtained than the methods reported [26–30].

## 2. Experimental

### 2.1. Apparatus and reagents

Electrochemical measurements, including cyclic voltammetry (CV) and linear sweep voltammetry (LSV), were performed using an electrochemical workstation (CHI 660B, Shanghai Chenhua Instrument Co. Ltd., Shanghai, China) connected to a personal computer. The classical three-electrode system consisted of an MIP-modified glassy carbon electrode (GCE) (1 mm diameter) as the working electrode, a KCl-saturated Ag/AgCl electrode as the reference electrode, and a Pt wire electrode as the auxiliary electrode. A Cray 50 Ultraviolet (UV) Spectrophotometer (Varian Company, Palo Alto, CA, USA) was used to determine the size distribution of AgNPs. An S-4800 Field Emission Scanning Electron Microscope (Oxford Instruments plc, Abingdon, England) was used to determine the features of NPs on the electrode surface.

The solution for copper catalytic deposition was prepared by mixing of 0.1 mol/L ascorbic acid and 0.1 mol/L  $\text{CuSO}_4$  solutions in the ratio of 1:1 before use.

IAA (chemically pure, >97%) and IAA-S were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Pyrrole was obtained from Aladdin Reagent Database Inc. (Shanghai, China). Phosphate-buffered saline (PBS, pH 7.4) was prepared using  $\text{Na}_2\text{HPO}_4$  and  $\text{NaH}_2\text{PO}_4$ . All other reagents were analytical grade and were used without purification. Ultrapure water obtained from a water purification system ( $\geq 18 \text{ M}\Omega$ ; Youpu Super Water Co., Ltd., Chengdu, China) was used to prepare the solution.

### 2.2. Preparation of MIP-modified and non-imprinted polymer (NIP)-modified electrodes

Both MIP and NIP were synthesized via electropolymerization of pyrrole on the surface of the GCE. Before the polymerization experiment, the GCE was polished on a chamois leather with alumina powder of 1.0, 0.3, and 0.05  $\mu\text{m}$  grain sizes, followed by successive washing with ultrapure water, alcohol, and  $\text{HNO}_3$  (50% in volume). Electropolymerization was performed in 0.2 mol/L PBS containing 0.1 mol/L KCl, 0.01 mol/L IAA, and 0.01 mol/L pyrrole via 10 cycles of CV in the potential range of  $-1.0 \text{ V}$  to  $1.0 \text{ V}$  at  $50 \text{ mV/s}$ . The NIP-modified electrode was prepared at the same experimental conditions in the absence of IAA. The MIP-modified and NIP-modified electrodes were washed with 0.1 mol/L NaOH for 35 min to elute IAA and remove of other adsorbates on the surface of the membranes. Then, the electrodes were washed with deionized water and dried at room temperature.

### 2.3. The preparation of AgNPs

The well-dispersed AgNPs were synthesized with a one-pot synthesis procedure previously reported in literature [31,32], using sodium borohydride as reducer and polyvinylpyrrolidone (PVP) as a protector. Briefly, both 10 mL  $\text{AgNO}_3$  aqueous solution (0.02 mol/L) and PVP aqueous solution (3%) were added into the round-bottomed flask with magnetic stirring for 2 h to obtain uniformly dispersed nucleation sites. Then, 10 mL sodium borohydride aqueous solution (0.01%) was dropped into the solution with stirring. The formation of AgNPs was confirmed when the color of the solution changed to luminous yellow after mixing with sodium borohydride aqueous solution. The size of the AgNPs was measured by UV spectrophotometry and scanning electron microscopy (SEM).

### 2.4. Incubation, competition, and labeling

The modified electrode was immersed into a solution of  $2 \text{ mL}$   $1 \times 10^{-4} \text{ mol/L}$  IAA-S to fill the MIP cavities with IAA-S and then incubated. The sensor was subsequently immersed in sample solutions with different IAA concentrations under stirring for 5 min to allow IAA-S in specific sites of MIP be replaced competitively by the analyte IAA. Then,  $25 \mu\text{L}$  AgNPs aqueous dispersion was dripped onto the electrode surface for 15 min to obtain AgNP-labeled IAA-S. Finally, the electrode was placed into 10 mL of copper deposition solution for 25 min. All the experimental operations were operated at room temperature ( $25^\circ\text{C}$ ).

### 2.5. The electrochemical measurements

Electrochemical measurements for characterization of the formation of MIP and NIP films were carried out in  $3 \times 10^{-4} \text{ mol/L}$   $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$  solution containing 0.5 mol/L KCl. The CV curves were recorded from  $-0.2 \text{ V}$  to  $0.6 \text{ V}$  at a scan rate of  $50 \text{ mV/s}$ .

During the quantitative analysis, the LSV was performed from  $-0.05 \text{ V}$  to  $0.35 \text{ V}$  at a scan rate of  $100 \text{ mV/s}$ , and the oxidative currents of copper were measured in 0.4 mol/L HCl.

## 3. Results and discussion

### 3.1. UV and SEM characterization

The prepared AgNPs were characterized by Cray 50 Ultraviolet Spectrophotometer. Fig. 2 shows the UV–vis spectra of AgNPs solution diluted by ultrapure water to 100-fold. An evident absorbance peak was observed at 395.1 nm, indicating the size distribution at 10–20 nm [33,34].

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