

# Simultaneous determination of guanine and adenine on nano-poly(4-aminothiophenol) patterns modified ITO electrode

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## ABSTRACT

Here, we demonstrated a fabrication method of nano-poly(4-aminothiophenol) patterns modified ITO electrode. The electrochemical behavior of adenine (A) and guanine (G) at the modified electrode was investigated based on differential pulse voltammetry. The results indicated that the modified electrode exhibited an excellent electrocatalytic activity towards the oxidation of A and G. Moreover, the modified electrode was applied to determine A and G in human serum sample. Therefore, this electrode could be used to high sensitivity simultaneous determination of A and G in the related physiology process.

**Keywords:** Deoxyribonucleic acid, Nano-polymer, Differential pulse voltammetry, Human serum.

## 1. INTRODUCTION

The two purine bases, Adenine (A) and guanine (G) are the essential building blocks of nucleic acids. These bases are the fundamental compounds in biological systems that contribute in several

processes such as energy transduction, metabolic cofactors and cell signaling. The changes of the A and G concentration in DNA could be considered as an indication of some diseases. Therefore, the detection of these bases has a great demand.

Recently, the detection of A and G based on electrochemical techniques have attracted attentions due to the advantage of fast response speed, cheap instrument, high sensitivity, excellent selectivity and real time detection [1]. However, the direct oxidation of A and G at bare electrodes shown higher overpotential of their oxidation that leading to a low selectivity and sensitivity [2]. Therefore, several chemically modified electrodes [3] were developed to widen the potential range in which the oxidation of A and G occurs. Although these modified materials showed good improving oxidation signals, however most of them shown complicated electrode preparation process, high background current and leakage of modified material. Therefore, it is still a challenge to investigate stable electrode modified material with high sensitivity and selectivity.

4-Aminothiophenol (ATP) has attracted significant attention in making assembly

layer onto nanoparticles *via* covalent or electrostatic interactions [4]. Self-assembly of ATP on Au electrode has been used for selective determination of dopamine and ascorbic acid [5].

In the present work, a new kind of modified electrode was fabricated based on self-assembly a monolayer of ATP onto Au nanodots/ITO electrode and followed by electro-polymerization of ATP film into poly(4-aminothiophenol) (PATP). The fabricated electrode showed a good selectivity for the electrochemical determination of mixture of A and G.

## 2. EXPERIMENTAL

### 2.1. Materials

ATP, A, G, human serum and phosphate-buffered saline (PBS) were purchased from Sigma (St. Louis, MO, USA).

### 2.2. Electrochemical measurements

All electrochemical experiments were performed using a potentiostat (CHI-660, CH Instruments, USA) controlled by general-purpose electrochemical system software. A homemade three-electrode system consisted of a PATP/Au nanodots/ITO substrate as a working electrode, a platinum wire as the auxiliary electrode and Ag/AgCl as the reference electrode.

### 2.3. Fabrication of PATP/Au nanodot/ITO

Au nanodots/ITO was fabricate based on the deposition of Au layer onto ITO

substrate through polystyrene (PS) mask that was prepared by follow the reported method [6]. An Au layer (50 nm) was thermal evaporated on the top of the deposited PS nanospheres mask. After dissolution of the PS mask in chloroform, an array of ordered triangle Au nanostructures was left on ITO substrate.

## 3. RESULTS AND DISCUSSION

### 3.1. Characterization of PATP/Au nanodot/ITO electrode

The morphologies of Au nanodots/ITO and PATP/Au nanodots/ITO electrodes were characterized by SEM images. Figs. 1a and 1b. demonstrate that the Au nanostructures exhibit triangle shapes of lateral dimensions of about 80 nm.

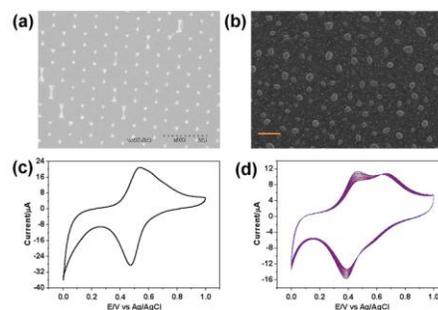


Figure 1. (a) SEM of Au nanodots/ITO substrate. (b) SEM of PATP/Au nanodot /ITO substrate, scale bar 500 nm. (c) The first scan cycle of CV of ATP coated Au nanodots/ITO electrode in 0.5M HClO<sub>4</sub>. (d) Electro-polymerization of ATP coated Au nanodots/ITO electrode in 0.5M HClO<sub>4</sub>, scan rate 50mVs<sup>-1</sup>.

Moreover, this triangle nature was changed after modified with PATP. In addition,

Fig. 1c shows the CV behavior of ATP/Au nanodots/ITO electrode in 0.5M HClO<sub>4</sub> solution that demonstrated an anodic current peak at *ca.* 0.47V and a cathodic current peak at *ca.* 0.53V in the first cycle scan. Interestingly, the anodic peak was noted to decrease after the first cycle scan; in the meantime, another anodic current peak at 0.67 V was appeared and increased gradually with the number of potential cycles (Fig. 1d). The changes of these two anodic current peaks signify the formation of the electroactive monolayer PATP film.

### 3.2. Electrochemical behavior of PATP/Au nanodots/ITO

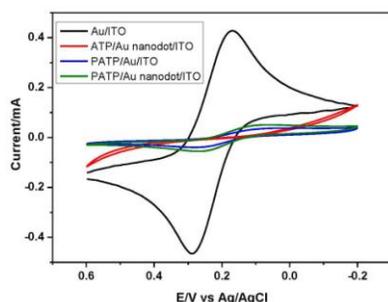


Figure 2 CV of 5mM Fe(CN)<sub>6</sub><sup>3-/4-</sup> at Au nanodot/ITO, ATP/Au nanodot/ITO, PATP/Au/ITO and PATP/Au nanodot/ITO electrodes.

The CV of Au nanodots/ITO, ATP/Au nanodots/ITO, PATP/bare Au/ITO and PATP/Au nanodots/ITO electrodes in 5mM Fe(CN)<sub>6</sub><sup>3-/4-</sup> were shown in Fig. 2. Au nanodots/ITO electrode shows a couple of well-defined redox peaks at 0.28 and 0.17V. While, at ATP/Au nanodots/ITO electrode, the redox peaks disappeared completely, which could be attributed to the negatively charged ATP, blocking the

diffusion of Fe(CN)<sub>6</sub><sup>3-/4-</sup> from solution to the electrode surface [7]. Nevertheless, after electro-polymerization of ATP, the redox peak current increased significantly compared with ATP/Au nanodots/ITO, indicating that PATP can effectively increase the electron transfer rate of Fe(CN)<sub>6</sub><sup>3-/4-</sup>. Moreover, the results demonstrate that PATP/Au nanodots/ITO electrode shown significantly higher redox peak current compared with PATP coated bare Au/ITO, which indicated that the distribution of PATP layer over Au nanodots could provide high surface area.

### 3.3. Electrochemical oxidation behavior of adenine and guanine

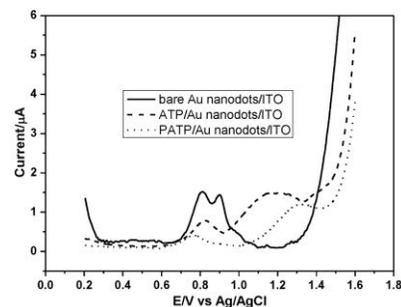


Figure 3 DPVs of 150µM A and 0.1µM G at different electrodes in PBS (pH 4.5).

Fig. 3 shows the DPV of 100µM A and 100µM G in PBS at Au nanodots/ITO that gave two small oxidation peaks at 810 and 900mV for G and A, respectively. While, the DPV response of the bases mixture at ATP/Au nanodots/ITO electrode shows that the oxidation peaks potential was shifted negatively (20mV for G and 260mV for A). On the other hand, the results indicated that the peak-to-peak separation of A and G at PATP/Au

nanodots/ITO was 660mV, which is larger than that at ATP/Au nanodots/ITO (330mV). The large  $\Delta E_p$  can effectively increase the selectivity of the simultaneous determination of A and G.

### 3.4. Simultaneous determinations of guanine and adenine

Fig. 5 shows the DPV curves of different concentration of A in PBS containing 50 $\mu$ M G. The insert of Fig. 5, demonstrate that the  $I_{pa}$  was proportional to the concentration of A in the range of 10–150 $\mu$ M. Therefore, the modified electrode can apply to simultaneous determination A and G.

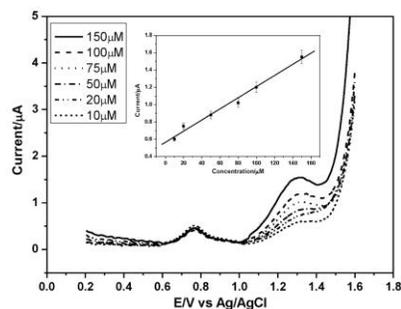


Figure 4. DPVs for the simultaneous determination of different A concentration in presence of G (50 $\mu$ M). Insert Figure 4: calibration plot of the oxidation peak current versus different concentration of A.

### 4. Conclusions

PATP/Au nanodots/ITO electrode was fabricated to monitor the electrochemical oxidation behavior of A and G. The results demonstrated that the peak-to-peak

separation of A and G obtained at the fabricated electrode was a little larger than ATP/Au nanodots/ITO electrode. The modified electrode was successfully used to simultaneous determine A and G.

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