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INVESTIGATION OF ELECTROCHEMICAL PROPERTIES OF HOMEMADE NANO GOLD ELECTRODES AND APPLICATION IN DETERMINATION OF Hg(II) AT THE TRACE LEVELS

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Abstract

The electrochemical properties of two nanoscale electrodes: Au nanodendrite and nanopartiles fabricated on Pt substrate disk have been studied. The initial results showed that the electrodes have a good electrochemical behavious. Using DPASV techniques with pulse height 50 mV, pulse width 40 ms, it is possible to determine amount of Hg(II) in water until ppb levels. Due to larger active area with porous structure, Au-ND/Pt can be used to detect a smaller amount of Hg(II) in water compared to Au-NPs/Pt. Detection limits found in these two cases is 0.081 ppb and 0.037 ppb for Au-NPs/Pt and Au-ND/Pt respectively and these electrodes are applicable to directly detect Hg(II) in water environment.

Keywords. Gold nanodendrite, gold nanopartilces, mercury detection, trace level.

1. INTRODUCTION

Mercury is a metal that has been extensively studied, being the high toxicity one of its most important characteristic. Therefore, the level of mercury has to be analysed in different samples using analytical methods [1]. The most used analytical methods for the determination of mercury are cold vapor atomic absorption spectroscopy (CVAAS) [2] cold vapor atomic fluorescence spectroscopy (CVAFS) [3] and also inductively coupled plasma mass spectrometry (ICPMS) [3]. These methods are well established however have several significant drawbacks such as the long time consumed for the analysis and the high cost of the equipment. Moreover, it is also necessary to perform several complex steps which requires specialist personal. For these reasons, researchers are still searching for a method that can overcome these issues and be sensitive enough to replace the more established methods in routine analysis. Electrochemical techniques to analysis of mercury are considered as a good solution to overcome these difficulties. For this purpose, gold electrodes have become more used in practice. In the stripping analysis of mercury, gold electrodes produce well-defined peaks so that low detection limits can be achieved [4-7]. Golimowski *et al.* [8] employed gold disk electrodes for determining mercury in residual waters by a voltammetric method. Commercially available gold electrodes are quite expensive and require several steps of mechanical and/or electrochemical cleaning prior to analysis [4]. The main disadvantage of solid gold electrodes is the wellknown phenomenon of structural changes of the gold surface, caused by amalgam formation, and the time-consuming and complex electrochemical pretreatments that are needed to achieve reproducibility. The gold electrodes for analytical applications can be manufactured by electrolysis deposition of gold on a glassy carbon electrode [9] or by other deposition procedures on different supports [10-11]. The synthesis of nano-structures on electrode surface has been recently studied to improve sensitivity of electrochemical measurement by increasing surface area for analysis [12]. Among them, gold (Au) nanodendrites have drawn a great attention due to availability of large surface area within a structure. There are may ways to prepare gold (Au) nanodendrites for electrochemical sensors [13]. However, electrochemical synthesis of Au dendrite is much faster and simpler without extensive use of reagents [14]. In this article, we present a simple and fast electrochemical synthesis and its application to detect mercury in water environment. The basic methodology for synthesis of the structure was the combination of two simultaneously occurring electrochemical reactions: electrodeposition of Au onto a platinum surface in presence of iodide as a co-reagent to drive continual eneration of nanodendrites and the simultaneous release of a hydrogen bubble at the surface to create pores (~5–10 µm) within the network structure. To compare the sensitivity of measurement, Au nanoparticle on Pt disk electrode were also prepared and used for the same measurement.

2. EXPERIMENTAL

2.1. Materials and Reagents

All reagents were of analytical grade and were used without of further purification. Solutions were prepared by dissolving the reagents in distilled water. Solutions 1 mM $HAuCl_4$ (Merck) in 0.5 M H_2SO_4 were used to fabricate gold nanoparticle on Pt surface and a mixture of solution 20 mM $HAuCl_4$, 1 mM KI and 5 M NH_4Cl in 0.5 M H_2SO_4 were used to prepare gold nanodendrite on Pt surface.

Solutions 5 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ and 0.1 M phosphate buffer solution (PBS) K_2HPO_4 + KH_2PO_4 at pH 7 were used to investigate the electrochemical behavious of gold electrodes and 0.1 M KCl + HCl pH3 used for detection of mercury using differential pulse anodic stripping voltametry (DPASV) technique. Standard mercury solution of 1000 ppm was obtained from $Hg(NO_3)_2$ in 2 M HNO_3 (Merck). An intermediary standard of a 10 ppm Hg(II) concentration was prepared from the above solution by dilution with 0.01 M HNO_3 solution. This solution was prepared on a weekly basis.

2.2. Preparation of the electrodes

In this research, two different configulation of gold layers are created on platinum disk electrodes (d = 1 mm):

- Gold nanopartical electrode on Pt substrate (Au-NPs/Pt).
- Gold nanodendrite porous electrode on Pt substrate (Au-ND/Pt).

2.2.1. Preparation of Au-NPs/Pt

The gold particles were deposited on the surface of a platinum electrode with a surface area of 0.79 mm^2 (d = 1 mm). Before deposition, Pt surface was polished with Al_2O_3 on a piece of velvet and rinsed with water. Following sonication in water for 5 min., Pt electrode was electrochemically cleaned by appllying a potential of -1.0 V in 0.5 M H_2SO_4 for 90 s, until small gas bubble evaporated from solution. The Au-NPs/Pt were prepared in *ex-situ* manner by depositing the gold from Au(III) ions using 1 mM $HAuCl_4$ solution by 3 successive electrolysis steps at +0.5 V for 120 s. A stirring rate of 60 rpm was used in the deposition period.

2.2.1. Preparation of Au-ND/Pt

Pt disk was mechanical polished and electrochemical cleanes as described above. Galvanostatic techniques was used to fabricate gold nanodendrite structure. Pt disk electrode was immersed in a mixture of 20 mM $HAuCl_4$, 1.0 mM KI, 5 M NH_4Cl and 0.5 M H_2SO_4. Constant current of 70 mA was applied for about 60 s. Produced electrode was then rinsed by distilled water and kept in decicator for later usage. Cleaning and reactivation between individual measurements are necessary for attaining reproducible results**.** However, the electrode allows a series of measurements without any treatment as long as it does not come into contact with the air.

2.3. Electrochemical Measurement

The electrochemical behavior of Au-NPs/Pt and Au-ND/Pt was investigated by cyclic voltammetry (CV) in 5 mM $K_3Fe(CN)_6$ / $K_4Fe(CN)_6$ in 0.1 M PBS solution to check the behaviors of prepared electrodes from E_1 = - 0.2 V; E_2 = 0.9 V. Scan rate was from 10 mV/s to 400 mV/s. The detection of Hg(II) was carried out by DPASV method in the following steps: the first step to concentrate amount of Hg(II) onto gold electrode surface by applying a potential at 0 V (vs Ag/AgCl) for 180 s in the stirring 0.1 M KCl + HCl pH 3 solution; the second step was used to record the stripping voltammograms by scanning from 0 V to +0.9 V after 10 s quiescence.

All electrochemical measurements in this study were performed at room temperature using a three-electrode system, in which Ag/AgCl and Pt wire were used as a reference and counter electrode, respectively. Working electrodes used in this study were Au-ND/Pt and Au-NPs/Pt for comparison

The potential measurement was performed relative to a Ag/AgCl reference electrode. The three electrode system was connected to a custom-made multi-function potentiogalvanostat manufactured at Vietnam Academy of Science and Technology, Hanoi, Vietnam. It was equipped with 12 byte analog–digital/digital analog converter (ADC/DAC) and the signal was amplified by two operational amplifiers with an active filter. Noise was reduced this active filter and a custom-written noise reduction algorithm. Overall, it provided current resolution down to 0.008 nA, valuable for sensitive measurements. The data acquisition was performed using custom-written software [15].

3. RESULTS AND DISCUSSION

3.1. Formation of gold thin layer on electrodes

Formation of gold thin layer on electrodes was investigated using cyclic voltametry technique by applying a potential from 0.4 V to 1.8 V in 0.5 M H_2SO_4 as described in [16].

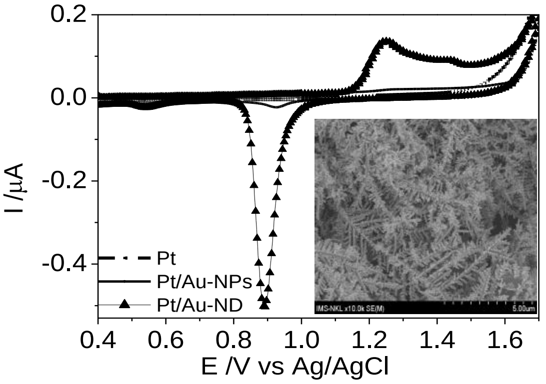

Figure 1: Oxidation-reduction reaction of gold initiated on Pt electrode in 0.5 M H_2SO_4, $\nu = 0.1$ V/s and SEM of Au-ND/Pt (Inset)

It is seen in Fig. 1 that on bare Pt electrode, no electrochemical signals were found in scanned potential range. It means no oxidation- reduction of Pt electrode in studied environment. With Au-NPs covered on Pt electrode, two peaks were found at 1.1 V (vs Ag/AgCl) for forward scan and at 0.9 V for backward scan. They are signals of pure Au in acidic environment when potentials are scanned. For Au-ND, voltametric signals is much higher than what obtained from Au-NPs/Pt (~3 times). It can be explaind by active electrochemical areas obtained from Au-ND/Pt is much higher than Au-NPs/Pt electrode. This observation is in agreement with phormological images of both electrodes (SEM image of Au-ND/Pt inset). This increasing of electrode area was explained that in the process of electrolysis to create Au-ND/Pt, iodide plays an important role in the prevention of continual growth of Au particles as well as inhibiting particle aggregation. At early stage of electrodeposition, iodide ions were instantaneously adsorbed onto the surfaces of newly generated Au crystals, producing a negative charge on their surface. The repulsion among the negatively charged particles increased the rate of nucleation greater than that of particle growth, so formation of the nanodendrite structure was preferable to larger particle growth or aggregation. Further, in the presence of iodide, the negatively charged nanodendrites continued to network themselves in both lateral and axial directions, without coalescence of neighboring nanodendrites. Also, the use of NH_4Cl as a co-reagent increased the rate of hydrogen bubble generation [17], leading to a uniform porous structure and fostering the continual growth of the network structure by hindering of dendrite aggregation [14].

For these reasons, porous Au-ND/Pt has active electrode areas much higher than that of Au-NPs/Pt– with Au spherical nanoparticles.

3.2. Electrochemical behavior of prepared electrodes

$K_3[FeCN]_6/K_4[FeCN]_6$ was selected as a probe to evaluate the performance of the prepared electrodes to evaluate the differences of signals received on the electrode modified with different ratios. Results are shown in figure 2. Two clear reversible peaks are visible at a two curves response to $[Fe(CN)_6]^{3-/4-}$ redox couple according to the reaction: $[Fe(CN)_6]^{3-} + e \Leftrightarrow [Fe(CN)_6]^{4-}$.

It can be seen from Fig. 2 that, for example with the same scan rate of 100 mV/s in a survey buffer solution, the curent signal received on the Au-ND/Pt is much higher than that on Au-NPs. Current obtained values are nearly two times compared with the values obtained at the Au-NPs/Pt electrode. It is explained by the increasing of acting areas created on Au-ND/Pt electrode. It also shows that for both produced electrode, electrochemical oxidation-reduction signals of Fe^{3+}/Fe^{2+} couple are clearly observed and the peak currents are proportional to the square root of the scan rate, follow correctly Randles – Sevcik equation (at 25 °C) [18].

$$i_p = (2,69.10^5).n^{3/2}.A.D^{1/2}.C.v^{1/2} \qquad (1)$$

Here, i_p is the peak current corresponding to reduction of redox species (Fe^{3+}/Fe^{2+}) (A), n is the number of electron transfer, D is the diffusion coefficient of an analyte *(cm^2/s)*, A is the diffusional electrode area *(cm^2)*, C is the molar concentration of an analyte and is the scan rate (*V/s*).

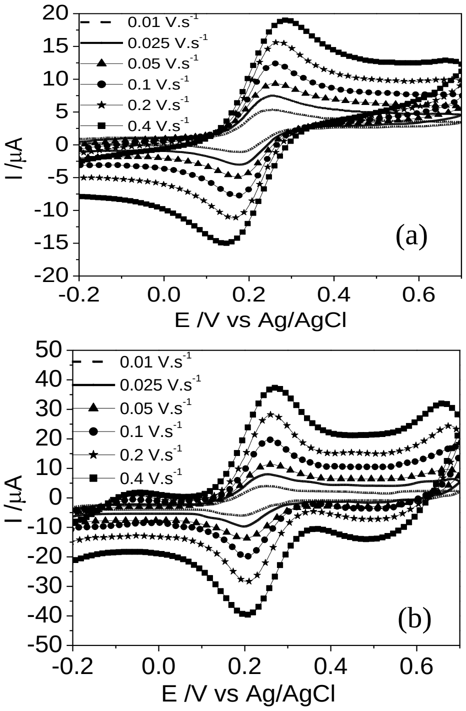

Figure 2: Cyclic voltammograms of Au-NPs/Pt (a) and Au-ND/Pt (b) in 5 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ + 0.1 M PBS pH 7 at different scan rate.

It is indicated that two study electrode in ferro/ferri system are electrochemical reversibility. Based on equation (1) and from obtained data, the calculated active electrochemical areas for these cases are 5.5×10^{-3} cm^2 and 13.7×10^{-3} cm^2 for Au-NPs/Pt and Au-ND/Pt electrode respectively. It means for Au-ND/Pt/Pt surface, active areas are 2.5 times higher than that on Au-NPs.

The voltage separation measured from Fig. 2 between the current peaks is about 60 mV for Au-ND/Pt. Theorically, as mentioned Nerst equation:

$$\Delta E_p = |E_{pa}-E_{pc}| = \frac{0,059}{n} \quad \text{(at T = 25 °C)} \qquad (2)$$

Number of electrone transfer here is equal to 1. It is in agreement with theory data of this system.

3.3. Electrochemical signals of Hg(II) on two produced electrodes

Fig. 3 show signals of Hg(II) on two produced electrodes as well as on bare Pt electrode. It can be seen that, compare with background (for bare Pt case), adding Hg(II) at 20 ppb level, a peak at 0.55 V clearly appreared on both Au-NPs/Pt and Au-ND/Pt electrodes. This peaks corresponds to oxidation reaction of Hg(II) accumulated on electrode surface when electrochemical deposition at 0V for 180 s. This data is in agreement with previous publication of other group [19]. Height of obtained currenet peak (i_p) is propotional with Hg(II) concentration in study environment. With the same Hg(II) concentration, i_p obtained Au-ND/Pt is 2.45 time higher than i_p measured on Au-NPs. This is consistent with the results calculated in the study on section 3.2 about the active surface area of the two electrodes. Moreover, dendrite porous structure on the Au-ND lead to appearance of more electrochemical hot spots, facilitating the Hg(II) ions to exchange easily electrons, thereby the measured current signal increased.

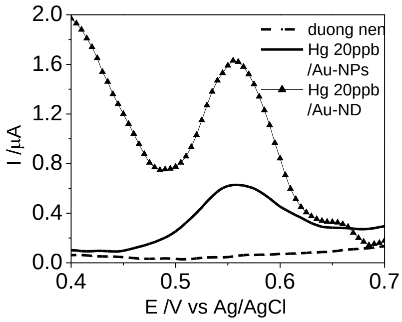

Figure 3: DPASV voltammograms of Hg(II) 20 ppb on Au-NPs/Pt (□) and Au-ND/Pt (-▲-) and background (- -) in solution of 0.1 M KCl + HCl pH 3, pulse height 70 mV and pulse width 40 ms

3.4. Calibration curve of Hg(II)

In order to investigate influence of environment on Hg(II) reduction peak, in the study, the initial studies were carried out in 0.1 M acetate buffer pH 3; 0.1 M $NaNO_3$ in HNO_3 acid pH 3 and 0.1 M KCl in HCl pH 3.

Results obtained show that at the same concentration of Hg(II), current peak of Hg(II) in 0.1 M KCl/HCl pH 3 was highest for both Au-NPs/Pt and Au-ND/Pt. The DPASV voltammograms registered for each analysed mercury concentration are shown in figure 4a for Au-NPs/Pt and (4b) for Au-ND/Pt. Calibration lines drawn within 1-100 ppb of Hg(II) range is given in inset of this figure. After each measurement, the gold electrode surface was cleaned *in-situ* for 60 s at a potential of 0.9 V. The straight - line equation was y = 0.01845x + 0.05523, R^2 = 0.9968 and y = 0.05343x + 0.08397 R^2 = 0.9988 for Au-NPs/Pt and for Au-ND/Pt respectively. Standard relative error calculated for a concentration of Hg(II) 20 ppb was 1.92 % (n = 6). At a deposition time at 180s, the detection limit was 0.081 ppb for Au-NPs/Pt and 0.037 ppb for Au-ND/Pt (based on three times the standard deviation corresponding to a blank sample). These values are much lower than allowable Hg(II) concentration in water as mentioned in QCVN08:2008 for surface water.

4. CONCLUSION

The electrochemical properties of two nanoscale electrodes: Au nanodendrite and nanopartiles fabricated on Pt substrate disk have been studied. The initial results showed that the electrodes have a good electrochemical behavious. Using DPASV techniques with pulse height 50 mV, pulse width 40 ms, it is possible to determine amount of Hg(II) in water until ppb levels. Due to larger active area with porous structure, Au-ND/Pt can be used to detect a smaller amount of Hg(II) in water compared to Au-NPs/Pt. Detection limits found in these two cases is 0.081 ppb and 0.037 ppb for Au-NPs/Pt and Au-ND/Pt respectively and these electrodes are applicable to directly detect Hg(II) in water environment.

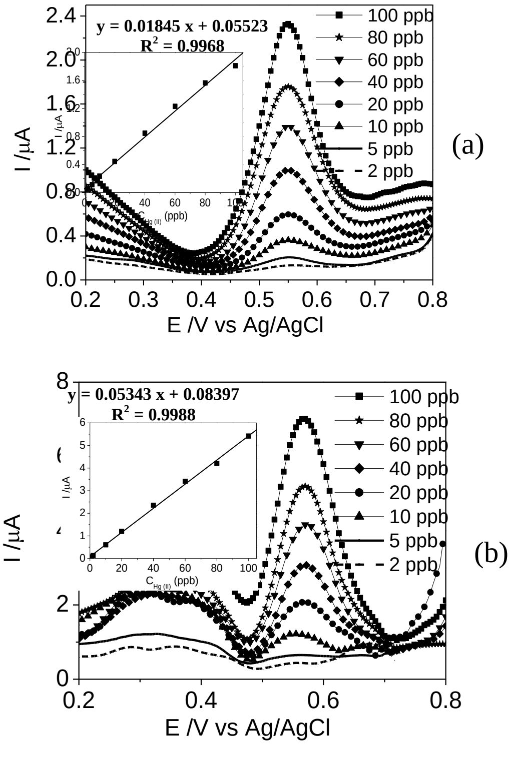

Figure 4: DPASV voltammograms of Hg(II) at Au-NPs/Pt (a) and Au-ND/Pt (b) in 0.1 M KCl/HCl pH 3 with different concentrations of Hg(II) with initial potential of 0.2 V, final potential 0.8 V, pulse height 50 mV, pulse width 40 ms and dependence of reduction peak current density on concentrations of Hg(II) (Inset)

It has been stated that, a gold electrode with nanopartical or/and porous nanodendrite structure can be used to determination of Hg(II) in environment at very low level and it is applicable for real sample to detect Hg(II).

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