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Using PEDOT Film Modified Electrode to Monitor Iodide and Its Enhancement of Arsenite Sensing

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Iodide was investigated using poly(3,4-ethylenedioxythiophene)/glassy carbon electrode (PEDOT/GCE) as an monitoring tool. When this electrode was scanned to the positive potential (+0.7 V) in the presence of 6×10^{-3} M, the redox couple was gradually separated into two redox couples involving the iodide/triiodide and triiodide/iodine redox processes due to the iodide doping behavior occurs easily with the sufficient positive potential and the higher iodide concentration. The I_2-PEDOT may be the doping result and it lowers the activation energy of iodide redox processes. The PEDOT/GCE shows linear current response (I_{pa}(mA) = 21.553[KI](M) + 8.2602, R^2 = 0.9995, S/N = 3) to iodide. Through the iodide mediator, PEDOT/GCE can determine As(III) with a sensitivity of 303.3 μA mM^{-1} cm^{-2}. Particularly, it can enhance the current response for As(III) by increasing the iodide molar ratio. The current ratio of $I_{As(III)}/I_{I^-}$ was about 1.66 amplification when molar ratio of $n_{I^-}/n_{As(III)}$ was 0.3.

Keywords: Iodide, PEDOT, arsenite, electrochemical sensor, electrocatalysis

1. INTRODUCTION

Polymer film-coated electrodes can be differentiated from other modification methods because of their adsorption and covalent bonding, in that they usually involve multilayers, as opposed to the monolayers that are frequently encountered with the latter methods. Conductive/electroactive polymers, such as polypyrrole, polyaniline, polythiophene, etc., are prepared through an electropolymerization procedure and used as modifiers for the construction of chemically modified electrodes [1–4].

Conducting polymers have become an important research focus during the past 30 years because of their unique optical, electronic, and mechanical properties with many potential applications [5–9]. Recently, much research has been focused on micro/nanostructured materials because of their promising applications in electrical or optoelectronic nanodevices and chemical sensors [10–15]. Among various conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) is a relatively new and well-known p-conjugated conducting polymer of the polythiophene class. It has received more and more attention because of its high electrical conductivity, moderate band gap, and excellent environmental stability [16–19]. Moreover, thin PEDOT films can vary from light to dark blue. These unique properties mean that PEDOT can be applied in many fields such as chemical and biochemical sensors, antistatic coatings, electrically switchable windows, and polymeric light-emitting diodes [20–22].

As far as we know, PEDOT can act as a very stable and promising electrode material to detect some types of compounds such as iodate ion [23], nitrite ion [24], dopamine, and ascorbic acid [25]. However, the above PEDOT-modified electrodes were mostly prepared through electrochemical polymerization of 3,4-ethylenedioxythiophene (EDOT) at a certain potential on the electrode surface, where the morphology of PEDOT was usually an irregular film. It is necessary to investigate the related topics.

Iodine is an indispensable element to life. More and more research has focused on the oxidation of iodide ion and the reduction of iodine on electrodes to achieve the quantitative determination of iodine. Shiotani et al. have reported cyclic voltammetry of KI at high concentrations using Pt and polyaniline-modified Pt electrodes [26]. Biallozor et al. have studied the behavior of a PEDOT film in I^-/I_2 solution [27]. Li et al. have investigated the detection of iodate ion with an amperometric sensor in the range of 5–500 μM [28] but not for the detection of iodide ion.

Recently, the effects of I^- adlayer at a Au(poly) electrode on the H_2O_2 reduction reaction in alkaline media was reported [29]. Regarding the behavior of iodide ion as a mediator, the electrochemical oxidation of iodide ion in the presence of barbituric acid, phenol, and *o*-cresol was investigated, in which iodide ion is oxidized to iodine, and the iodine then reacts with barbituric acid, phenol, or *o*-cresol in a quasi-catalytic chemical reaction. In addition, the results of this work show that iodide ion can be used as a mediator in the determination of these compounds [30–32]. Moreover, the reaction of iodine, electrogenerated from iodide ion, was used for the detection of As(III) via electrocatalytic reaction in the diffusion layer of a boron-doped diamond electrode [33].

In this work, the PEDOT modified electrode was used to investigate the iodide electrochemical behaviors due to its clear voltammetric window (no redox peaks in the original signal) and selectivity. Based on PEDOT modified electrode, the iodide electrochemical process (I^- oxidized to I_3^-, I_3^- oxidized to I_2, I_2 reduced to I_3^-, I_3^- reduced to I_2) was investigated by cyclic voltammetry with controlling the PEDOT preparation (potential scanning cycles of EDOT monomers, KI concentration, and scanning rate. The morphology of PEDOT/GCE and iodide-doped-PEDOT/GCE was studied by SEM. The iodide spectroelectrochemical behaviors were studied by UV-Vis spectroelectrochemistry with switching PEDOT/GCE potential. This electrode was also used to determine iodide and arsenite. Interference study of PEDOT/GCE (as an iodide amperometric sensor) was examined with other halides (such as bromide and chloride) by amperometry.

2. EXPERIMENTAL

2.1. Reagents

3,4-ethylenedioxythiophene (EDOT) was purchased from Sigma-Aldrich (USA). All other chemicals including halide ions and halate ions were purchased from Wako (Japan). Double distilled deionized water (DDDW) was used to prepare all solutions. All chemicals used were of analytical grade. The condition of pH 1.5 was prepared by 0.1 M sulfuric acid in DDDW. Pure nitrogen was purged through all of the experimental solutions and nitrogen atmosphere was maintained over the solutions during the experiments to prevent the reentry of atmospheric oxygen.

2.2. Apparatus

All of the electrochemical experiments were performed using a CHI-1205a electrochemical workstation (CH Instruments, Austin, TX). A conventional three-electrode system, which consists of Ag/AgCl (saturated KCl) as a reference electrode, GCE (d = 0.3 cm in diameter) as a working electrode, and platinum wire as counter electrode, was used for all of the electrochemical experiments. Prior to the electrochemical deposition process, the GCE was well polished using a BAS polishing kit with aqueous slurries of alumina powder (0.05 μm), rinsed, and ultrasonicated in DDDW.

2.3. Experimental details

A glassy carbon electrode with a diameter of 3 mm, after being polished with 0.05 μm alumina and cleaned in DDDW, was electrodeposited with a film of PEDOT at a potential cycle of 0.2-1.3 V in a solution of 0.01 M EDOT and 0.1 M H_2SO_4 (pH 1.5) with several scanning cycles to prepare PEDOT films with different thickness. The PEDOT film, created by scanning cycles was denoted as n-PEDOT/GCE (for instance, 5-PEDOT/GCE for the case of n = 5 scanning cycles. The electrode was washed by dipping in DDDW and transferred into the test solution. Steady-state CV responses of KI were then recorded at scan rates of 50-350 mV s^{-1} in KI solutions with 0.1 M H_2SO_4 (pH 1.5) as background electrolyte. The experiment was conducted in a typical three-electrode cell with a wire Pt counter electrode and a saturated potassium chloride reference electrode ($Ag/AgCl_{(sat)}$). All the electrochemical experiments were performed at 25 °C under an inert atmosphere, using a CHI-1205a potentiostat (CH Instruments, Austin, TX).

A glassy carbon electrode (0.0707 cm^2) was used to prepare the samples of PEDOT/GCE and I_2-PEDOT/GCE for SEM measurement. Using the PEDOT/GCE electrode in 0.1 M H_2SO_4 solution (pH 1.5) containing 6×10^{-3} M KI, the I_2-PEDOT film was prepared by the repeatedly potential cycling between 0.1 V and 0.9 V at 100 mV s^{-1} with 10 scanning cycles.

The morphological characterization of composite films was examined by means of SEM (S-3000H, Hitachi).

UV–vis absorption spectra were measured with a Hitachi Model U-3300 spectrophotometer. In-situ UV–vis spectroelectrochemistry was performed in 0.1 M H_2SO_4 solution (pH 1.5) at room temperature using an electrochemical quartz cell with a three electrode arrangement (PEDOT/ITO or bare ITO as a transparent working electrode) and a Power Module PWR-3 potentiostat.

2.4. Preparation of PEDOT film

The PEDOT modified glassy carbon electrodes (PEDOT/GCE) were prepared through the EDOT electropolymerization by cyclic voltammetry.

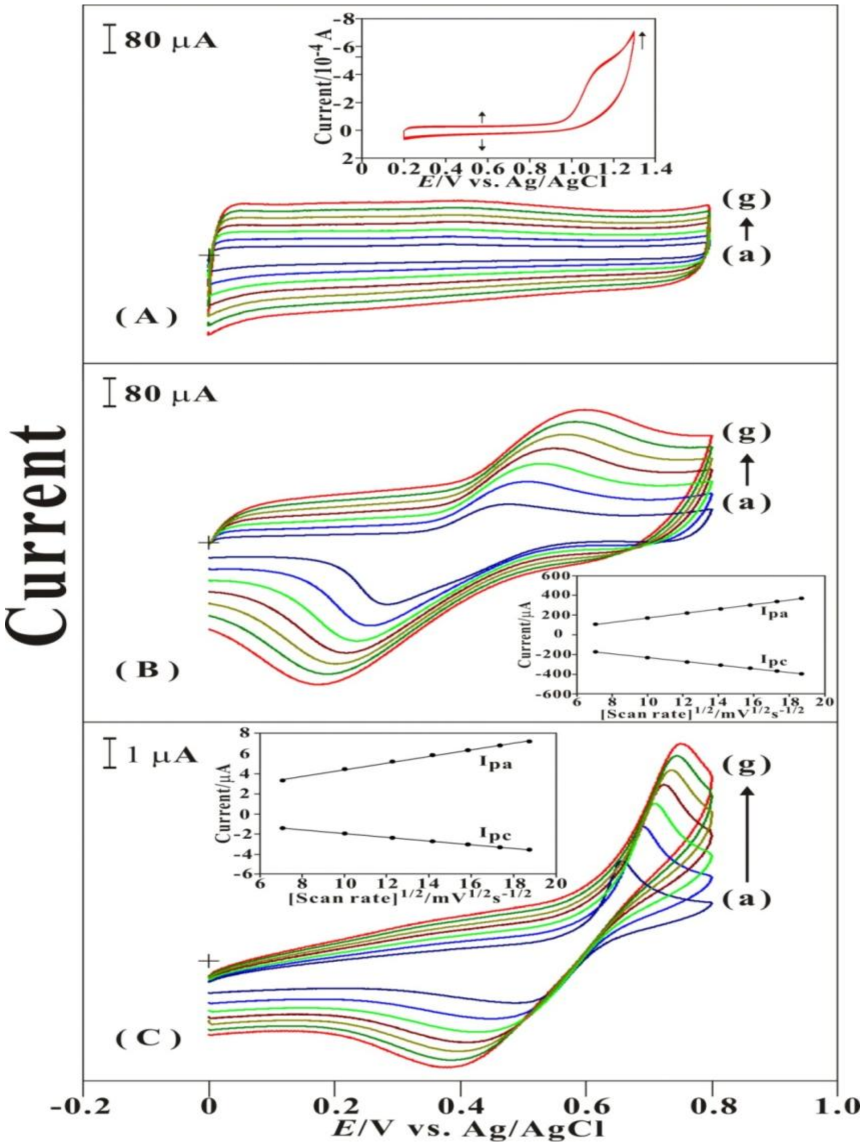


Figure 1. Cyclic voltammograms of PEDOT/GCE and bare GCE electrodes examined in 0.1 M H_2SO_4 solution (pH 1.5) with various scanning rates of (a) 50, (b) 100, (c) 150, (d) 200, (e) 250, (f) 300, and (g) 350 mV s^{-1}, respectively. The PEDOT/GCE was examined in the (A) absence and (B) presence of 5×10^{-3} M KI. (C) The bare GCE examined in the presence of 5×10^{-3} M KI. Inset of (A) was the cyclic voltammogram of EDOT electropolymerization (PEDOT/GCE preparation) using bare GCE in 0.1 M H_2SO_4 solution (pH 1.5) containing 0.01 M EDOT. Insets of (B) & (C) were the plots of the redox peak current (I_{pa} and I_{pc}) versus the square root of the scan rate ($v^{1/2}$).

Due to the PEDOT film formation was known for the EDOT oxidation potential at 1.1 V, the EDOT electropolymerization occurred with scanning electrode in the potential range of 0.2－1.3 V in 0.1 M H_2SO_4 solution (pH 1.5) containing 0.01 M EDOT. Moreover, we prepared different PEDOT modified electrode with different scanning cycles (5, 10, 20 cycles) of EDOT electropolymerization to accomplish the related experiments.

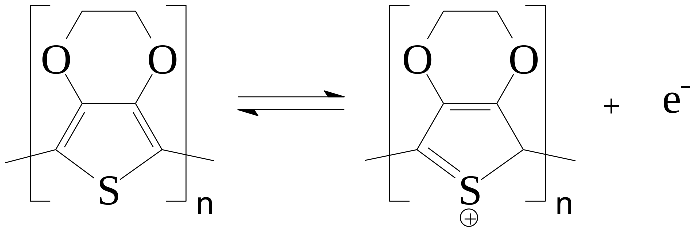
In the various scan rate study, the PEDOT/GCE was prepared with 10 scanning cycles (0.2－1.3 V) and scan rate of 0.1 V s^{-1} (as the cyclic voltammograms of Fig. 1A & B). Without special statement, the PEDOT modified electrode prepared with 5 scanning cycles was used to study in each case.

Fig. 1A shows the cyclic voltammogram of PEDOT/GCE (prepared by 5 scanning cycles of EDOT electropolymerization) in 0.1 M sulfuric acid solution (pH 1.5). It exhibits almost no redox peaks with various scanning rates (50–350 mV s^{-1}). This modified electrode was further examined in the presence of 5×10^{-3} M KI.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammograms of iodide through PEDOT film modified electrodes with various scanning rates

Fig. 1A shows the cyclic voltammogram of PEDOT/GCE (prepared by 5 scanning cycles of EDOT electropolymerization) in 0.1 M H_2SO_4 solution (pH 1.5). It exhibits almost no redox peaks with various scanning rates (50–350 mV s^{-1}). That's involving the PEDOT redox process with one electron transfer (Scheme 1).



Scheme 1. PEDOT redox process.

This modified electrode was further examined in the presence of 5×10^{-3} M KI. It has one obvious redox couple (Fig. 1B) with a broad anodic peak of around 0.4–0.6 V and a broad cationic peak of around 0.25–0.15 V. It is involving oxidation-reduction process of iodide (I^- oxidized to I_3^-, I_3^- oxidized to I_2, I_2 reduced to I_3^-, I_3^- reduced to I_2). The iodide oxidation may be occurred at the electrode as following reactions [24]:

$$2I^- \rightarrow I_2 + 2e^- \quad (1)$$

$$3I^- \rightarrow I_3^- + 2e^- \quad (2)$$

$$2I_3^- \rightarrow 3I_2 + 2e^- \qquad (3)$$

Compared with bare GCE (Fig. 1C), which has a broad anodic peak of around 0.65–0.75 V and a broad cationic peak of around 0.5–0.4 V, PEDOT/GCE shows higher current response and lower potential in the same iodide concentration. By the plots of peak current versus the square root of the scan rate (as insets of Fig. 1B & C), both PEDOT/GCE and bare GCE show a linear correlation between the peak current and the square root of the scan rate as following regressing equations:

At PEDOT/GCE:

$$I_{pa}(\mu A) = 22.5v^{1/2}(mV^{1/2}\ s^{-1/2}) - 54.6\ (R^2 = 0.9997) \qquad (4)$$

$$I_{pc}(\mu A) = -18.9v^{1/2}(mV^{1/2}\ s^{-1/2}) - 40.6\ (R^2 = 0.9996) \qquad (5)$$

At bare GCE:

$$I_{pa}(\mu A) = 0.332v^{1/2}(mV^{1/2}\ s^{-1/2}) + 1.107\ (R^2 = 0.9975) \qquad (6)$$

$$I_{pc}(\mu A) = -0.186v^{1/2}(mV^{1/2}\ s^{-1/2}) - 0.071\ (R^2 = 0.9999) \qquad (7)$$

It means that the process is diffusion control. The slope value of PEDOT/GCE current regressing equation is much higher than that of bare GCE. Based on the nearly 1 of I_{pa}/I_{pc} ratio and the larger slope in I_{pa} and I_{pc} regressing equations, PEDOT/GCE can be concluded that it has potential to be a good iodide sensor.

3.2. Electrochemical analysis for Iodide Sensing through PEDOT film modified electrodes

The PEDOT/GCE current response (I_{pa} and I_{pc}) for iodide was studied by different prepared condition of EDOT electropolymerization. Scanning cycles of EDOT electropolymerization were controlled and compared with their corresponding cyclic voltammograms in the presence of 5×10^{-3} M KI. Fig. 2(A)–(C) showed the cyclic voltammograms of iodide examined with various PEDOT/GCE prepared by 5, 10, and 20 scanning cycles, respectively. It was found that PEDOT/GCE showed a more negative redox couple (much lower over-potential) and higher current response for iodide than that of bare GCE.

In this case, the PEDOT/GCE prepared by 10 scanning cycles of EDOT electropolymerization had the higher current response. This might be due to limit of EDOT electropolymerization on the electrode surface and the specific doping behavior of iodide.

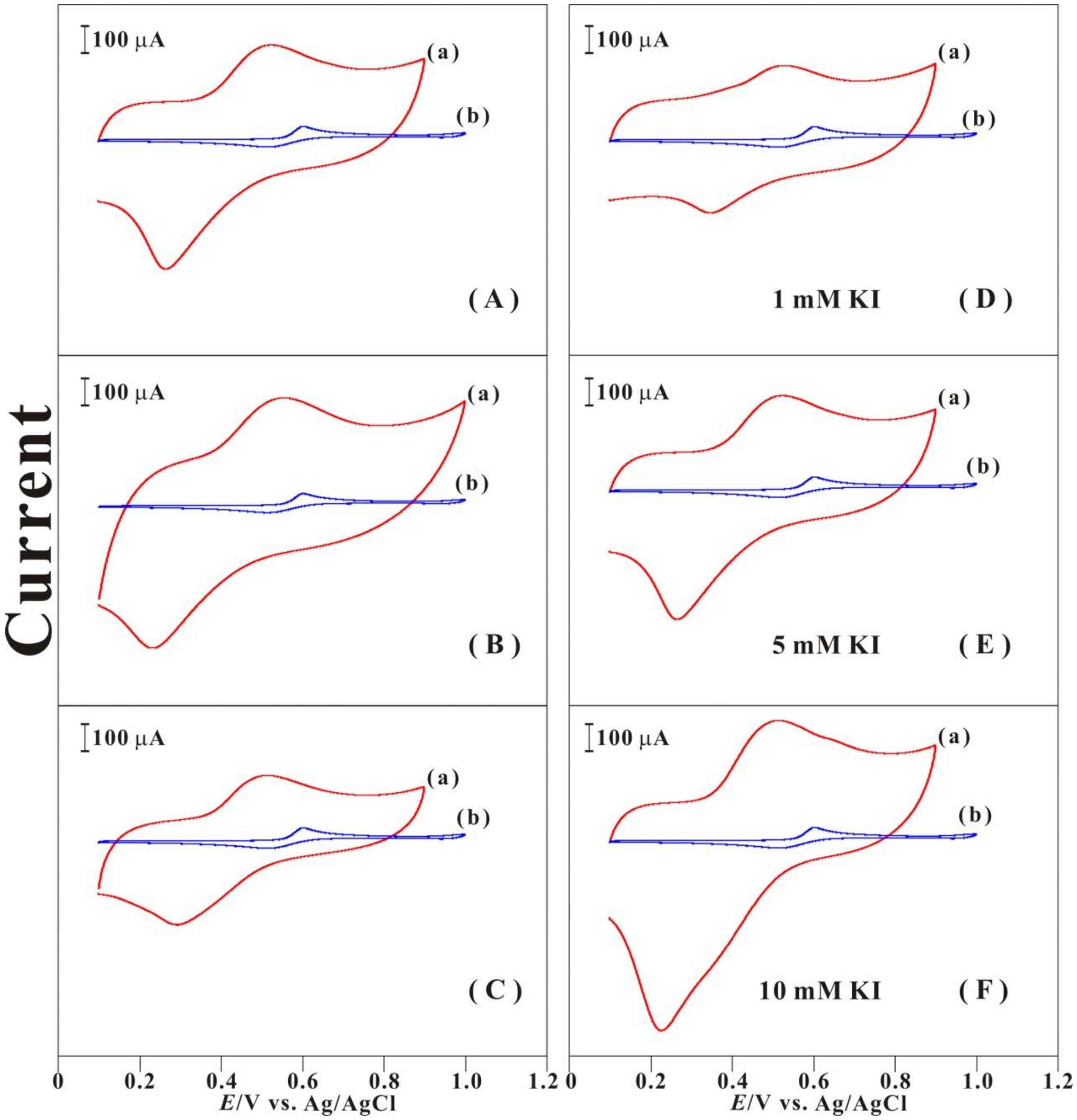


Figure 2. (A)–(C) were the cyclic voltammograms of (a) PEDOT/GCE and (b) bare GCE examined in 0.1 M H_2SO_4 solution (pH 1.5) containing 5×10^{-3} M KI. The PEDOT/GCEs of (A)-(C) were 5-PEDOT/GCE, 10-PEDOT/GCE, and 20-PEDOT/GCE, respectively. (D)–(F) were the cyclic voltammograms of (a) 5-PEDOT/GCE and (b) bare GCE examined in 0.1 M H_2SO_4 solution (pH 1.5) in the presence of (D) 1×10^{-3} M KI, (E) 5×10^{-3} M KI, and (F) 1×10^{-2} M KI, respectively. Scan rate = 100 mV s^{-1}.

Various KI concentrations were studied using the PEDOT/GCE which was prepared by 5 scanning cycles of EDOT electropolymerization. Fig. 2(D)–(F) showed the cyclic voltammograms of PEDOT/GCE examined in the presence of 1×10^{-3} M KI, 5×10^{-3} M KI, and 1×10^{-2} M KI, respectively. Peak current response (I_{pa} & I_{pc}) was found increasing with the increase of KI concentration. From Fig. 2F, the more positive redox peaks were found at E_{pa} = 0.651 V and E_{pc} = 0.374 V differed from the original peaks at E_{pa} = 0.515 V and E_{pc} = 0.230 V. These two new peaks seem the result of I_3^-/I_2 oxidation-reduction processes. The data of the redox peaks of different PEDOT/GCE were recorded with various KI concentrations in Table 1. As well known of several redox states for iodide, it can be concluded that PEDOT/GCE lowers the over-potential of iodide electrochemical process as reaction equations (2) & (3). At higher KI concentration, iodide ion oxidized sequentially to triiodide ion and then to iodine proceeded easily with PEDOT/GCE.

Table 1. Redox peaks for different KI concentrations through various PEDOT/GCE sensing.

KI(M)	n-PEDOT/GCE[a]	Number of Redox couples	E_{pa}[b] (V)	I_{pa}[c] (μA)	E_{pc}[d] (V)	I_{pc}[e] (μA)
5×10^{-3}	5-PEDOT/GCE	1	0.513	348	0.269	482
5×10^{-3}	10-PEDOT/GCE	1	0.543	426	0.239	570
5×10^{-3}	20-PEDOT/GCE	1	0.501	241	0.295	312
1×10^{-3}	5-PEDOT/GCE	1	0.529	273	0.352	272
5×10^{-3}	5-PEDOT/GCE	1	0.513	348	0.269	482
1×10^{-2}	5-PEDOT/GCE	2	0.515	442	0.230	704
			0.651	372	0.374	424

[a] n-PEDOT/GCE: The PEDOT film, created by scanning cycles was denoted as n-PEDOT/GCE (for instance, 5-PEDOT/GCE for the case of n = 5 scanning cycles).
[b] E_{pa}: potential of anodic peak.
[c] I_{pa}: current of anodic peak.
[d] E_{pc}: potential of cathodic peak.
[e] I_{pc}: current of cathodic peak.

In order to study this specific phenomenon, the addition of different KI concentration was taken into the electrochemical system monitored by PEDOT/GCE. In the gradual additions of KI in 0.1 M sulfuric acid solution (pH 1.5) by cyclic voltammetry, Fig. 3A showed the voltammograms of 5-PEDOT/GCE examined in the presence of iodide concentration from 0 to 9×10^{-3} M (a–j). Compared with bare GCE in the (a) absence and (j) presence of 9×10^{-3} M KI (Fig. 3B), the redox couple was separated from one to two in KI concentration of $5\times10^{-3} - 6\times10^{-3}$ M. One redox couple on the relatively negative side had redox peaks at E_{pa1} of 0.47–0.43 V and E_{pc1} of 0.35–0.25 V. The other one had redox peaks at E_{pa2} of 0.47–0.58 V and E_{pc2} of around 0.35 V. These peaks had good linearity between current response and KI concentration as following equations:

$$I_{pa1}(\mu A) = 16.87[KI](mM) + 69.43\ (R^2 = 0.959) \qquad (8)$$

$$I_{pc1}(\mu A) = -32.32[KI](mM) - 77.37\ (R^2 = 0.990) \qquad (9)$$

$$I_{pa2}(\mu A) = 25.6[KI](mM) + 13.7\ (R^2 = 0.9995) \qquad (10)$$

$$I_{pc2}(\mu A) = -38.42[KI](mM) - 68.1\ (R^2 = 0.9997) \qquad (11)$$

Compared with bare GCE, PEDOT/GCE shows much lower potential of redox couples to iodide redox process. This is may be due to the new composite of iodide doping result lowers the activation of iodide redox processes. It also has good linearity between current response and iodide concentration. By the result, we know that the new redox couple appears obviously when the PEDOT/GCE is scanned with sufficient positive potential in the solution of higher KI concentration.

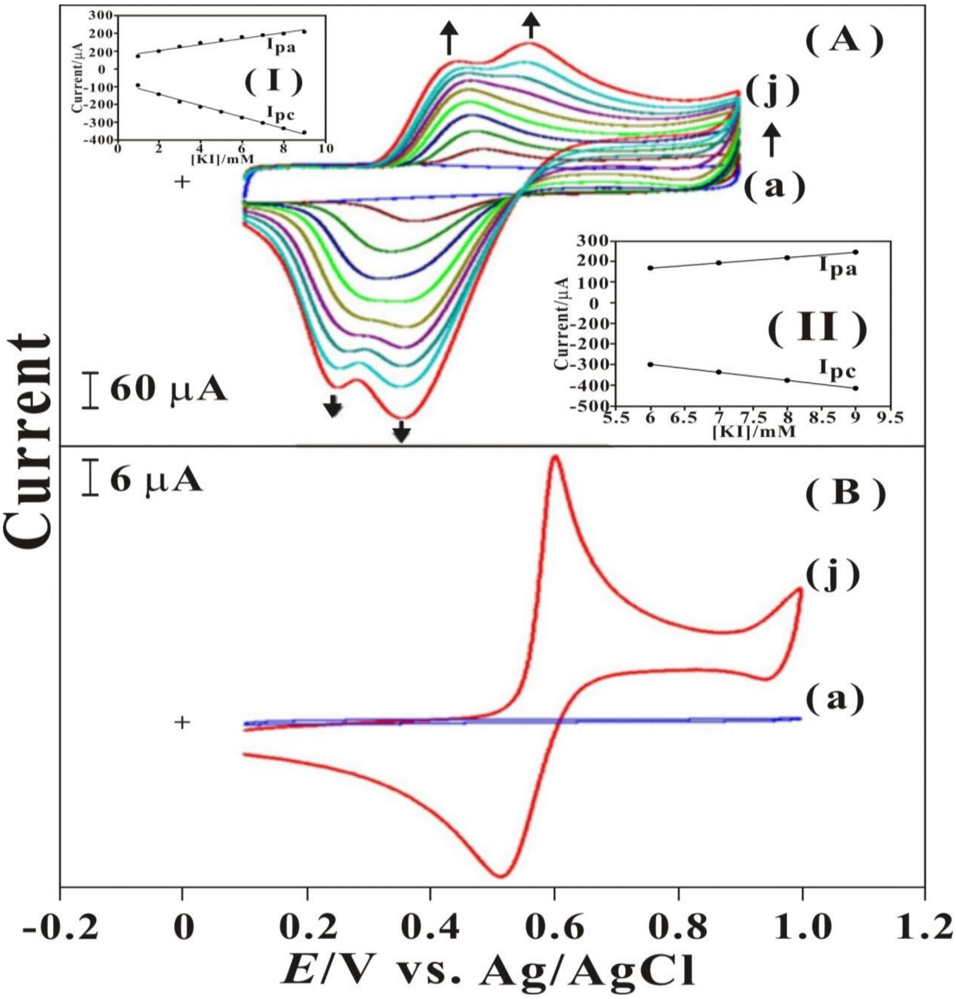


Figure 3. Cyclic voltammograms of (A) 5-PEDOT/GCE and (B) bare GCE examined in 0.1 M H_2SO_4 solution (pH 1.5) containing [KI] = (a) 0 M, (b) 1×10^{-3} M, (c) 2×10^{-3} M, (d) 3×10^{-3} M, (e) 4×10^{-3} M, (f) 5×10^{-3} M, (g) 6×10^{-3} M, (h) 7×10^{-3} M, (i) 8×10^{-3} M, and (j) 9×10^{-3} M, respectively. Scan rate = 100 mV s^{-1}. Insets: (I) and (II) were the plots of peak current (I_{pa} and I_{pc}) versus KI concentration.

3.3. SEM analysis for iodine doped on PEDOT film modified electrodes

Regarding the monitoring result of KI concentration using PEDOT/GCE by voltammetry, it can be supposed that the iodine formation involving I_3^-/I_2 process proceeded in the positive charge PEDOT film. Here, a new film type was supposed as iodide-doped-PEDOT or iodine-doped-PEDOT. In order to see the film type of PEDOT/GCE after scanning in the of higher KI concentration, the morphology of PEDOT/GCE was investigated by SEM. Fig. 4 showed the SEM images of the 5-PEDOT/GCE and the I_2-PEDOT/GCE (prepared by 5-PEDOT/GCE with 10 scanning cycles of 0.1-0.9 V in the presence of 6×10^{-3} M KI). By comparison, the I_2-PEDOT/GCE exhibited significant image with the specific rectangular shape (Fig. 4B). It seems that the iodine crystalline covered over PEDOT film. The length of iodine crystalline was evaluated in 30–100 μm by the white shape in Fig. 4B. It may provide the evidence of iodine formed in PEDOT/GCE when controlled with the sufficient positive potential and the higher iodide molar ratio.

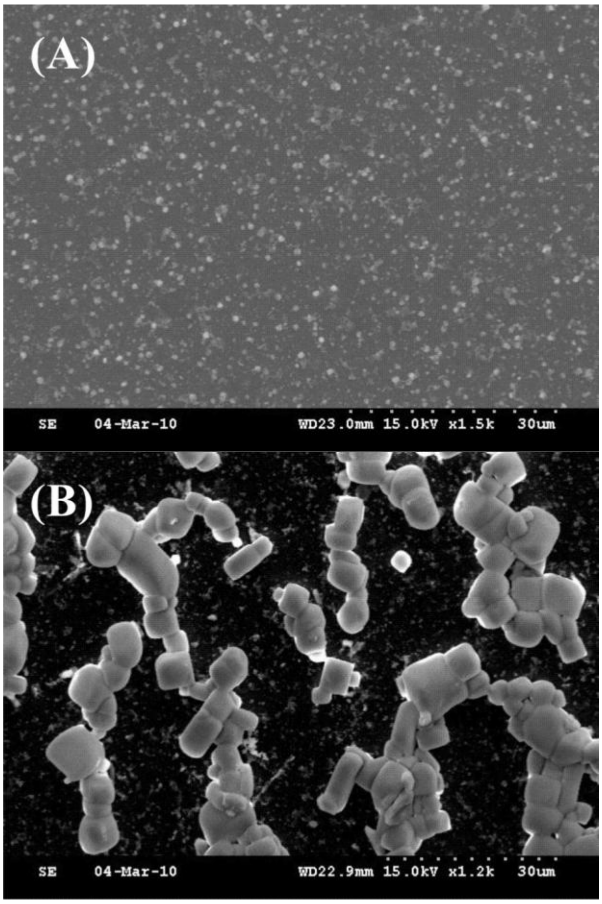


Figure 4. SEM images of (A) 5-PEDOT/GCE and (B) I_2-PEDOT/GCE (prepared by 10 scanning cycles of 0.1–0.9 V using 5-PEDOT/GCE in 0.1 M H_2SO_4 solution containing 6×10^{-3} M KI, scanning rate = 100 mV s^{-1}).

3.4. In-situ UV-Vis spectroelectrochemistry of iodide through PEDOT modified ITO electrodes

The spectroelectrochemical behaviors of iodide were studied by PEDOT modified ITO electrodes. Fig. 5 showed the UV-Vis spectra of iodide electro-switched by PEDOT/ITO using UV-Vis spectroelectrochemical method. When PEDOT/ITO was applied potential at $E_{appl.}$ = 0.2 V in a pH 1.5 aqueous buffer solution containing 10^{-2} M iodide, it exhibited one main absorbance peak at 373 nm (Fig. 5A(a)). This peak absorption increased as PEDOT/ITO was gradually applied to more positive potential at $E_{appl.}$ = 0.5 V and 0.7 V (Fig. 5A(b) & (c)). In addition, the solution color was gradually changed to yellowish as shown in the photos (a')-(c'). It may prove that iodine was the product of iodide (electro-switched by PEDOT/ITO) due to this solution color was similar to the solution of iodine dissolving in the same aqueous buffer solution. Inset of Fig. 5A shows the SEM image of I_2-PEDOT/ITO after the case of Fig. 5A(c). Moreover, the main absorption peak (373 nm) was significantly increased with the increase of the applied potential while decreased with the decrease of the applied potential. This means that iodide can be reversibly electro-switched by PEDOT/ITO. The main absorption peak (at 373 nm) was slightly shifted to 377 nm. Fig. 5B displayed the UV-Vis spectrum of 10^{-2} M iodine with a main absorption peak at 377 nm and a minor absorption peak at 463 nm. It was noticed that the same maximal absorption peak between iodide and iodine spectra. This may be the evidence of iodine formation in PEDOT film. One can conclude that iodide can be reversibly electro-switched to form iodine through PEDOT film modified electrode and iodine can be formed in PEDOT/GCE with sufficient positive potential and the higher iodide concentration.

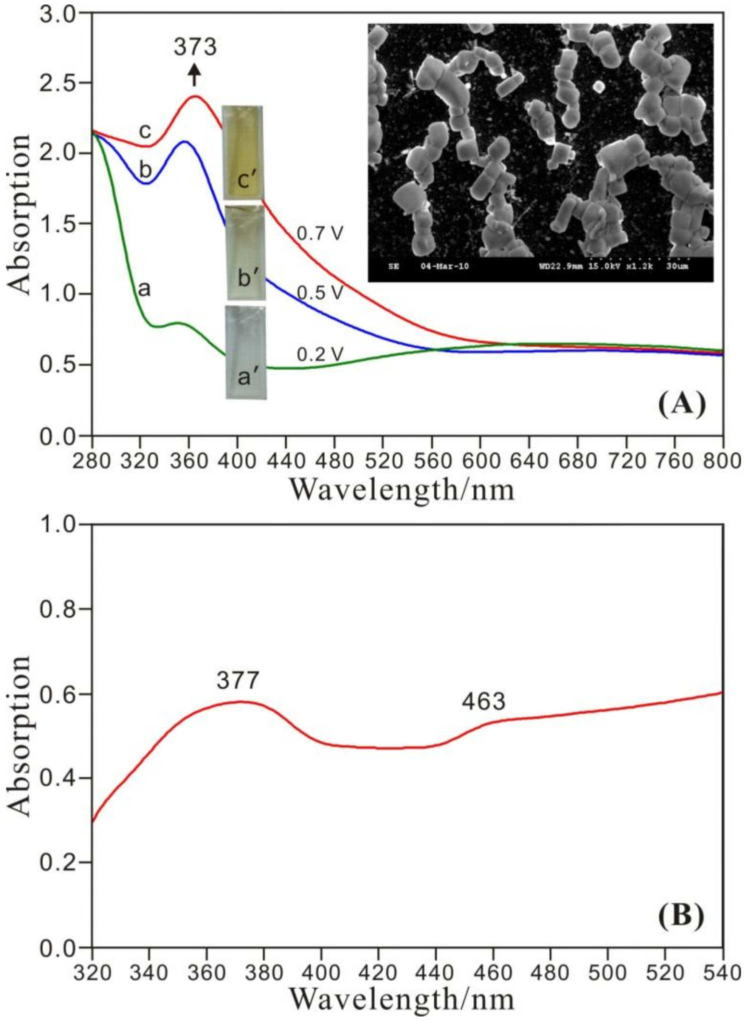


Figure 5. (A) In-situ UV-Vis spectra of 10^{-2} M KI (0.1 M H_2SO_4, pH 1.5) electro-switched by PEDOT/ITO electrode at the potential of (a) 0.2 V, (b) 0.5 V, and (c) 0.7 V, respectively. (B) The UV-Vis spectrum of 10^{-2} M I_2 in 0.1 M H_2SO_4 solution (pH 1.5). Inset of (A) was the SEM image of I_2–PEDOT/GCE and the photos of (A) were the sample cells corresponded to each case of (a)-(c).

3.5. Electrocatalytic oxidation of As(III) to As(V) at the preparative scale

In the present study aiming at developing novel arsenic remediation strategies, we have performed preliminary experiments combining electrocatalytic oxidation at the modified electrode. In a typical experiment, a solution of arsenite in the presence of iodide (at a KI:As(III) molar ratio of 10 : 3, where As(III) was 3 mM, KI was 0.9 mM) was submitted to electrocatalytic oxidation (E_{pa} = +0.8 V).

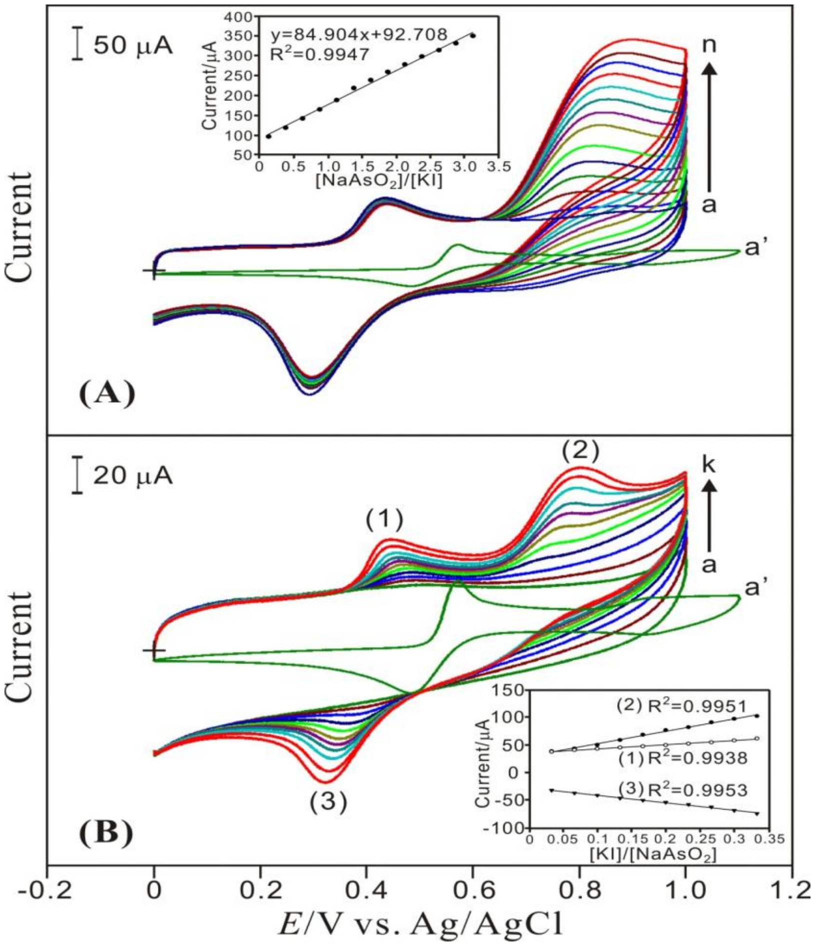


Figure 6. Cyclic voltammograms of PEDOT/GCE examined in 0.1 M H_2SO_4 solution (pH 1.5) with the case of: (A) 4×10^{-3} M KI in the presence of [$NaAsO_2$] = (a) 0 M, (b) 5×10^{-4} M, (c) 1.5×10^{-3} M, (d) 2.5×10^{-3} M, (e) 3.5×10^{-3} M, (f) 4.5×10^{-3} M, (g) 5.5×10^{-3} M, (h) $6.5\times10^{-}$ M, (i) 7.5×10^{-3} M, (j) 8.5×10^{-3} M, (k) 9.5×10^{-3} M, (l) 1.05×10^{-2} M, (m) 1.15×10^{-2} M, and (n) 1.25×10^{-2} M; and (B) 3×10^{-3} M $NaAsO_2$ in the presence of [KI] = (a) 0 M, (b) 1×10^{-4} M, (c) 2×10^{-4} M, (d) 3×10^{-4} M, (e) 4×10^{-4} M, (f) 5×10^{-4} M, (g) 6×10^{-4} M, (h) 7×10^{-4} M, (i) 8×10^{-4} M, (j) 9×10^{-4} M, (k) 1×10^{-3} M; respectively. Insets were the plots of the peak current (I_{pa1}, I_{pa2}, I_{pc3}) versus the molar ratio of KI and $NaAsO_2$. Scanning rate = 100 mV s^{-1}.

Electrocatalytic oxidation of As(III) can be performed by PEDOT modified GCE in the presence of iodide. The fine performance of iodide film modified GCE toward the detection of As(III) makes it attractive for the fabrication of iodide-based sensors. Fig. 6A shows the voltammetric response of PEDOT/GCE for the successive additions of As(III) in the range of 5×10^{-4} –1.25×10^{-2} M. Further, the important factor for the performance of PEDOT/GCE was the presence of KI in the buffer solution. According to this behavior of iodide film, all the catalysis has been done in the presence of KI in the corresponding buffer solutions. Here, As(III) oxidation has been done in the presence of 5×10^{-4} M KI in pH 1.5 H_2SO_4 solution. The oxidation peak current increases linearly at 0.8 V with the increasing concentrations of As(III) (Fig. 6A). When As(III) was added, the anodic peak current increased noticeably while that of the cathodic current decreased substantially. The decrease of the cathodic and the enhancement of the anodic currents clearly indicate the electrocatalytic oxidation of As(III) at PEDOT/GCE through iodide redox process.

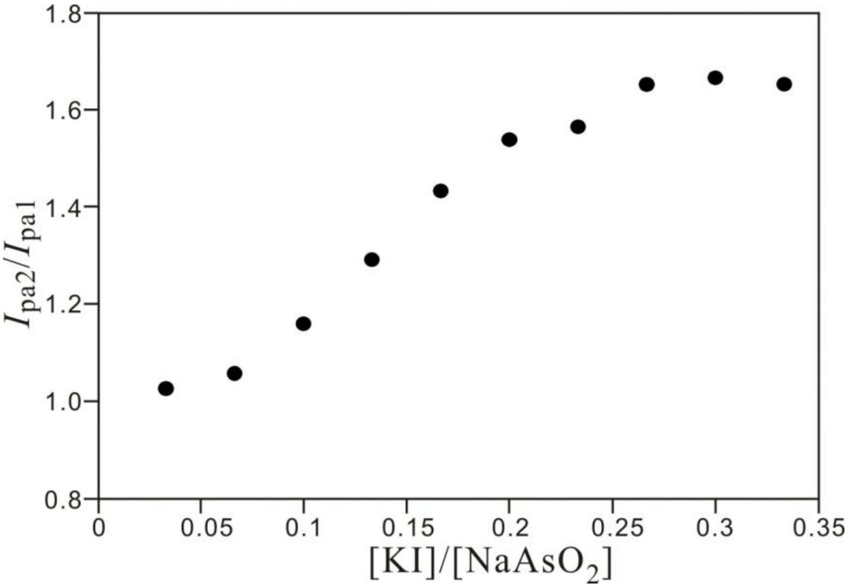


Figure 7. Plot of the current ratio of peak 1 & 2 (I_{pa2}/I_{pa1}) versus concentration ratio of iodide and arsenite ($[KI]/[NaAsO_2]$) obtained from Fig. 6B.

Further comparing with bare GCE for 1.25×10^{-2} M As(III), it can be seen that unmodified bare GCE fails to oxidize the As(III). Furthermore, the inset in Fig. 6A shows the anodic peak currents versus concentration plot for As(III) oxidation. From the calibration plot, the linear regression equation for As(III) oxidation was found as y = 84.904x + 92.708, with a correlation coefficient of 0.9947. Finally, the above results validate the electrocatalytic oxidation of As(III) on PEDOT/GCE in the presence of iodide. The reaction may be expressed as following:

$$\text{PEDOT/GCE} \rightarrow \text{PEDOT}^{+}\text{/GCE} + e^{-} \quad (12)$$

$$\text{PEDOT}^{+}\text{/GCE} + I^{-}_{(aq)} \rightarrow \text{PEDOT}^{+}I^{-}\text{/GCE} \quad (13)$$

$$\text{PEDOT}^{+}I^{-}\text{/GCE} + I^{-}_{(aq)} \rightarrow \text{PEDOT-}I_2\text{/GCE} + e^{-} \quad (14)$$

$$\text{PEDOT-I}_2\text{/GCE} + \text{As(III)}_{(aq)} \Rightarrow \text{(PEDOT)/GCE} + \text{As(V)}_{(aq)} + 2\text{I}^- \qquad (15)$$

Fig. 4B showed the cyclic voltammogram of 3×10^{-2} M As(III) with the additions of 1×10^{-4}–1×10^{-3} M KI. The current response of arsenite (peak 2) was increased with the increase of KI molar ratio.

The correlation can be seen in Fig. 7 which showed the plot of current ratio of peak 1 & 2 (I_{pa2}/I_{pa1}) of iodide and arsenit ([KI]/[As(III)]). The As(III) current response was obviously enhanced by increasing iodide molar ratio. In this case, the As(III) current response can be enhanced about 1.66 amplification while the molar ratio of As (III) /KI was 0.3.

4. CONCLUSION

In this paper, we used PEDOT modified electrodes to study the iodide electrochemical behaviors of. This PEDOT/GCE has lower over-potential and higher current response for iodide. Iodine formation is dependent on sufficient positive potential and the higher iodide concentration. Iodine crystalline located in PEDOT was accounted and verified by SEM images and in-situ UV-Vis spectra. The PEDOT modified electrode can determine iodide with good linear current response by cyclic voltammetry. Using PEDOT electrode through iodide redox process, it also can determine As(III) with good current response. Particularly, it can enhance As(III) current response by increasing iodide molar ratio in the solution. This system can be developed as a As(III) sensor.

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