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Iodide Modified Electrodes for the Electrochemical Detection of Environmentally Hazardous Materials

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Electrochemical deposition and chemisorption studies of iodide film have been done on the glassy carbon electrode (GCE) and polycrystalline gold electrode (poly GE). The iodide film preparation under different conditions and its stability were examined. Further, the redox activity of the iodide modified film on GCE and poly GE was examined in different pH solutions. Here, the electrochemically deposited iodide film on GCE showed good stability and was electrochemically active at pH 1.5 and 4 solutions, while the chemisorbed iodide film on poly GE was found active and stable at pH 9 and 13 solutions. The iodide modified GCEs exhibits a good electrocatalytic activity for the oxidation of As (III) and the reduction of Cr (VI), respectively. A detailed study for As (III) oxidation has been done by using the rotating ring-disk electrode technique. Meanwhile, chemisorbed iodide film on poly GE shows electrocatalytic reduction reactions of IO_3^- by using different techniques like cyclic voltammetry and differential pulse voltammetry. To examine the practical analytical utility of the proposed electrode, the real sample analyses for arsenic and chromate detection have been examined and the results were found satisfactory.

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The development of a good analytical methodology for the detection of environmentally hazardous materials like chromium and arsenic is vital in analytical science. Generally, arsenic exists in different chemical forms in nature. Many arsenic compounds are known to be toxic. Particularly in ground water, they are found almost exclusively as arsenite and arsenate. Millions of people throughout the world use drinking water that contains both arsenite and arsenate in carcinogenic concentrations. Such toxic pollutants have been associated with many health problems such as skin lesions, keratosis (skin hardening), lung cancer, and bladder cancer.[1] Most people in the developing countries are still at risk for cancer due to chronic arsenic poisoning. Their direct exposure to humans and animals and the side effects to the ecosystem will persist as an international problem. According to the U.S. Environmental Protection Agency (EPA) and World Health Organization arsenic guidelines, the maximum contaminant level of arsenic in a community water system is 10 μg/L. The electrochemical oxidation of arsenic at various metal electrodes like Pt and Au is of great interest because As (III) is an important compound in waste water analysis. Therefore, it is important to develop a sensor to detect and monitor the arsenic level in the ecosystem. There are few electrochemical methods reported for the arsenic detection.[2-4] For example, in metal electrodes the gold and platinum or modified glassy carbon (GC) and pyrolytic graphite with such metal films have been used for the detection of arsenic by using anodic stripping potentiometry and voltammetry. However, there are still problems that make routine analysis inconvenient, such as limited sensitivity, poor precision, low electron-transfer reaction, high overvoltages, and low stability for the electrode surface between each measurement.[5]

Chromium is an important target analyte in biological and environmental systems. In inorganic oxides, chromium occurs with several coordination numbers, different oxidation states, and different molecular structures.[6,7] The different toxicities of Cr (III) and Cr (VI) are well known.[8] In practice, Cr (IV) and Cr (V) ions exist, but Cr (III) and Cr (VI) are the most common oxidation states in aqueous chemistry.[9] Further, chromium (III) is an essential trace element in the metabolism of lipids and proteins, and vital for the maintenance of a normal glucose tolerance factor. In particular, chromium (VI) was more biologically mobile than Cr (III) and known to be present in certain water systems due to industrial activities. Also, Cr (VI) is reported to be the second most inorganic contaminant in groundwater at hazardous waste sites. Further, the use of chromates (hexavalent chromium oxygenic compounds) in the industrial sector has led to serious concern about workers' exposure to Cr (VI), which has been classified by the U.S. EPA as a human carcinogen in Group A.[10,11] In the human being, the molecular debris associated with the process of Cr (VI) to Cr (III) reduction induces the critical changes in DNA. Evidence supporting that idea came from in vitro studies showing that chromate alone does not damage DNA in the absence of reducing agents.[12] Based on the above discussion, there is a need to develop a sensor for the detection of chromate. Several methodologies including spectral and chromatographic techniques have been developed for the detection of Cr (VI). In electroanalytical methods, carbon paste electrodes,[13-16] potentiometric titrations,[17,18] and chitin modified electrodes[19] are some examples which have been reported already. All these methods demonstrate the advantages of the direct modification of electrode material which was capable of differentiating between Cr (VI) and Cr (III), which enabled their usage for analysis in selected samples and have their specific disadvantages.

In most of the countries, the table salt is iodized with potassium iodate or iodine. The iodized salt is accepted as the way of choice and the most successful strategy for the prevention of iodide deficiency disorders. An excess of iodine or iodate can produce goiter and hypothyroidism as well as hyperthyroidism.[20,21] Also, the iodate (IO_3^-) is reported as a toxic anion and it may form during the ozonization process.[22] Several techniques have been applied for the determination of iodate, including chromatography coupled with spectrophotometry, mass spectrometry, chemiluminescence, spectrofluorometry, and amperometry.[23-26] In modified electrodes, ruthenium oxide/hexacyanoferrate/silicomolybdate hybrid films,[27] polymerized new fuchsin film,[28] and polymerized neutral red film[29] were reported for the IO_3^- reduction. Although these methods were of interest for iodate detection, they need several reaction steps involving the number of reagents and time-consuming processes. Hence, there is a need for simple and easier films for the electrode modification process to detect the iodate.

The environmentally friendly and technologically suitable electrode, its simplification, and fabrication method for various purposes have become imperative in contemporary research in analytical chemistry. For example, in halogens, the iodine has added an innovation in the electrode modification technology, as it is chemically stable and economically low cost, environmentally green, and technologically perfect to fix onto electrodes. The chemisorption species derived from the iodide ion at typical solid–metal electrodes provides an interesting case study because the strong surface activity of this ligand brings about profound changes in the redox chemistry of the iodine/iodide couple in the surface-bound state. Further, this system is important because: (*i*) the iodide ion can be used as a model

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for a strong surface active electrolyte, and (*ii*) the kinetics of redox processes of unadsorbed species can be altered when the working-electrode surface is pretreated with a full monolayer of iodine.[30] The structure of I^- layers has been investigated by many techniques such as electrochemical quartz crystal microbalance,[31,32] scanning tunneling microscopy,[33-36] atomic force microscopy,[37] and low X-ray photoelectron spectroscopy.[38,39] The I^- adlayer modified electrodes have become remarkably viewed at different metallic electrodes,[30,38] especially in the synthesis of nanoparticles rich in expected facets.[40] The underpotential deposition of metallic adlayers of a desired structure,[41,42] the formation of highly ordered arrays of organic molecules,[43,44] the protection of highly sensitive surfaces of metal single crystals,[45,46] cathodic detection, and the electrochemical oxidation of H_2O_2 using an iodine modified electrode[47,48] have been reported.

In the present work, we report the iodide layers electrodeposition and chemisorption process on glassy carbon electrode (GCE) and polycrystalline gold electrode (poly GE) in the presence of KI solution. The electrochemical properties of the iodide films on two different electrodes have been examined in different pH solutions. The two proposed types of iodide modified electrodes show an attractive performance toward the electrochemical oxidation of As (III) and the reduction of Cr (VI) and iodate by using the cyclic voltammetry (CV), differential pulse voltammetry (DPV), and rotating ring-disk electrode (RRDE) techniques. To validate the practical usage of the proposed electrode, the real sample analyses for Cr (VI) and As (III) in real drinking water sources such as mineral water and tap water have been examined.

Experimental

Reagents and apparatus.— Sodium meta arsenite was purchased from Sigma-Aldrich, USA. KI and KIO_3 were obtained from Wako Chemicals (USA). Other reagents were of analytical grade. All the solutions were prepared with double-distilled water. All the experimental results were obtained at room temperature. The buffer solutions for electrocatalysis were pH 1.5 H_2SO_4 and KOH (pH 13) solutions containing 1×10^{-3} M KI. The electrochemical measurements such as CV and DPV were carried out using CHI 410a and CHI 900 potentiostats (CH Instruments, Austin, TX). A conventional three-electrode system was used throughout the experiments. The Bioanalytical Systems, Inc. (BAS, USA) GCEs ($\varphi = 0.3$ cm diameter) GE ($\varphi = 0.16$ cm diameter) were in the form of disks sealed in a Teflon jacket having an exposed geometric surface area of 0.07 and 0.02 cm^2, respectively. The working electrode was a bare or iodide film modified GCE or GE, the auxiliary electrode was a platinum wire, and an Ag/AgCl electrode was used as a reference. All the potentials mentioned in this paper were referred to this reference electrode. The RRDE experiments were performed by a Pine Instruments Co. (USA) electrode in conjunction with a CHI-750 potentiostat that was connected to a model AFMSRX analytical rotator. The RRDE containing a GC disk electrode and a GC ring electrode was used for hydrodynamic studies.

Preparation of the iodide film on GCE and poly GE.— Prior to modification, the bare GCE and GE were polished by using a BAS polishing kit with aqueous slurries of finer alumina powder (0.05 μm), rinsed, and ultrasonicated in double-distilled deionized water. All the solutions were deaerated by passing high-purity nitrogen before the electrochemical experiments. The iodide film was electrochemically deposited on GCE from pH 1.5 H_2SO_4 solution containing 1×10^{-3} M KI by cycling the potential between −0.75 and 1.2 V vs (Ag/AgCl) at the scan rate of 100 mV s^{-1} for 30 cycles. Further, the GE was electrochemically pretreated by repeating the potential scan in the range of −0.2 to 1.5 V vs (Ag/AgCl) at 100 mV s^{-1} for 60 cycles in 0.05 M H_2SO_4 solution to attain the CV characteristic of a clean GE. The electrochemically pretreated GE is called poly GE, which was immersed in 0.1 M KOH solution containing 1×10^{-3} M KI to accomplish the chemisorptions of iodide adlayers. Finally, the iodide modified poly GE was fabricated.

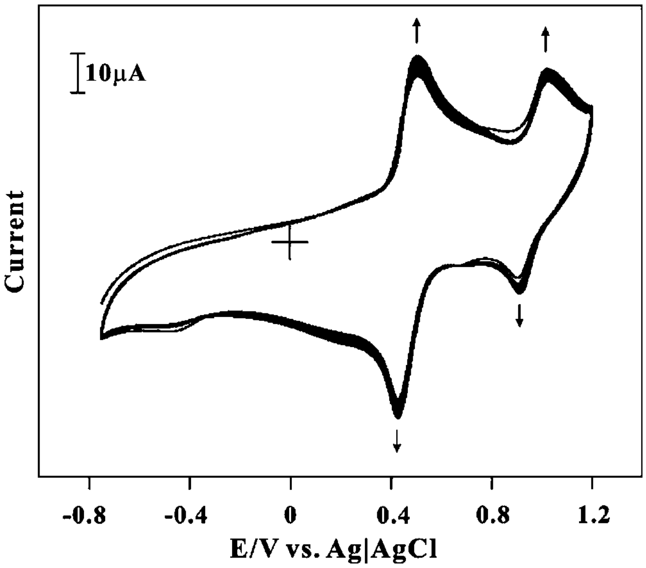

Figure 1. CVs of a GCE modified with an iodide film synthesized from H_2SO_4 solution (at pH 1.5) containing 1×10^{-3} M KI. Switching potential between −0.75 and 1.2 V.

Results and Discussion

Characterization of iodide film on GCE and poly GE.— Figure 1 shows the repetitive CV response of GCE in pH 1.5 H_2SO_4 solutions containing 1×10^{-3} M KI. From Fig. 1, the cathodic peaks at 0.42 and 0.90 V and the anodic peaks at 1.05 and 0.50 V were observed for the iodide film growth process on GCE. In subsequent cycles, all the peaks were found growing. Further, the significant growth of these two obvious redox couples clearly suggests the successive formation of the iodide film on GCE. To examine the electrochemical properties of the iodide film modified GCE, it was transferred to pH 1.5 H_2SO_4 solutions containing 1×10^{-3} M KI for different scan rate studies. Figure 2A represents the CVs of iodide film at different scan rates from 50–300 mV s^{-1}. Here, the anodic and cathodic peak currents of the iodide redox system linearly increased with the increasing scan rates up to 300 mV s^{-1} (Fig. 2A). Further, Fig. 2B and C shows the cathodic and anodic peak currents vs the scan rate plot for the iodide film modified GCE. These results show that the cathodic and anodic peak currents of the iodide film were linearly increasing, and that the charge transfer within the iodide was fast compared with the time scale of the potential scan, respectively.

To modify the poly GE with chemisorptions of iodide film, it was immersed in KOH solution (pH 13) containing 1×10^{-3} M KI. Then, the chemisorbed iodide film modified GE was examined for different scan rate studies (50–300 mV s^{-1}) in the same solution. Figure 3 shows the different scan rate studies of the iodide film modified GE. Figure 3 shows that the linear increase in the peak currents of the redox couples at various scan rates confirms the chemisorbed iodide layer on poly GE. The inset of Fig. 3 shows the anodic and cathodic peak currents vs the scan rate plot of the iodide redox couple at −0.4 V. In particular, the redox couples of iodide film were obtained at around −0.4 and −0.8 V, showing the preferential chemisorptions of iodide onto the poly GE. Also, the CV obtained here for the chemisorptions of the iodide adlayer is similar to that obtained by Stickney et al.[39] Further, the sharp peak and broad peak obtained at −0.4 and −0.8 V proves the cathodic adsorption/desorption of the iodide layer on the poly GE, respectively. In particular, the sharp peak at −0.4 V is attributed to the adsorption process, and the broad cathodic peak obtained was due to more desorption of iodide from the electrode surface and change in the structure.[48] Besides, the chemisorbed iodide adlayers are more

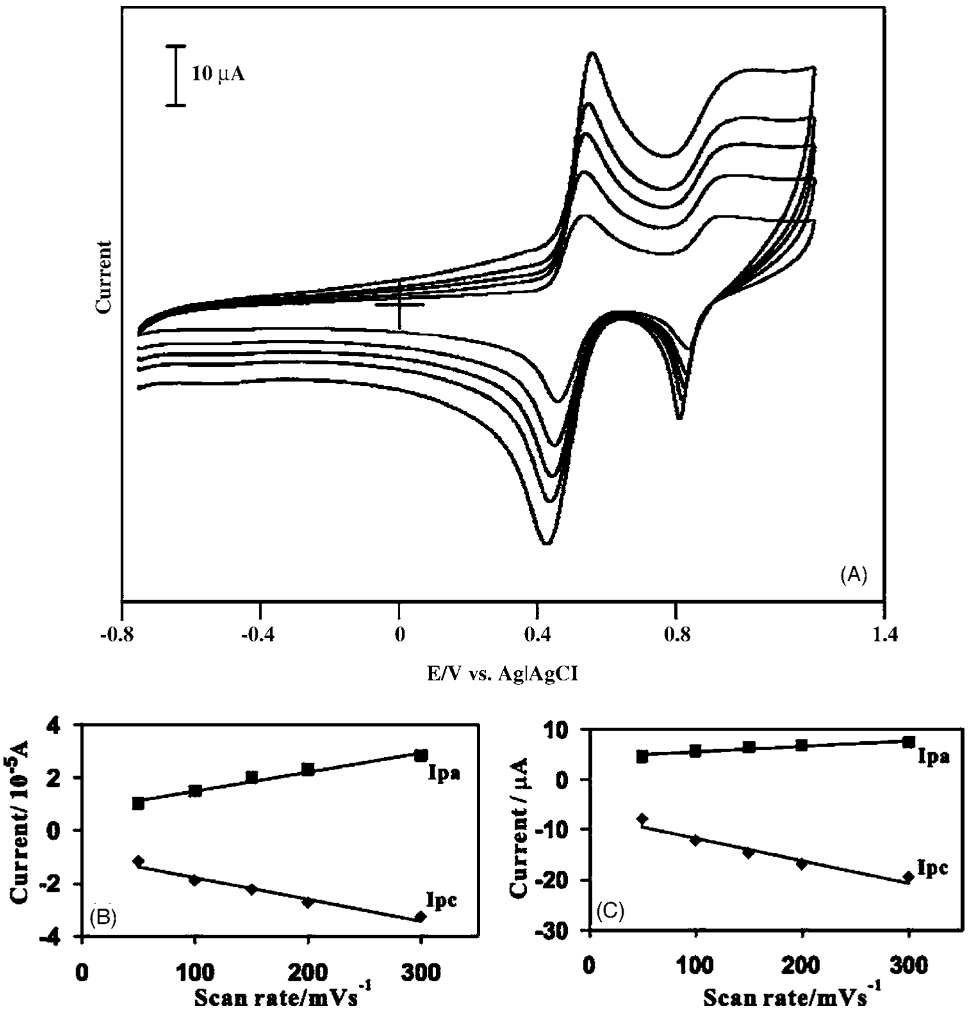

Figure 2. (A) CVs of iodide layer on GCE in the presence of 1×10^{-3} M KI in pH 1.5 H_2SO_4 solution with various scan rates: 50, 100, 150, 200, and 300 mV s^{-1}. Inset (B and C) shows the plot of the cathodic and anodic peaks current vs the scan rate.

electronegative and highly polarizable than Au, and the iodide adlayers induce a partial positive charge on the poly GE surface and they become partially negative charged.[47] Finally, the above results clearly illustrate the successful modification process of iodide layers by the electrodeposition and chemisorption processes on the GCE and poly GE surface.

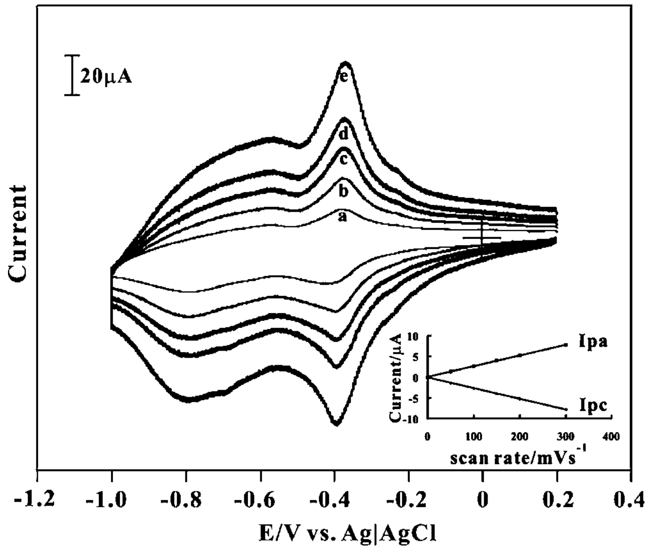

Figure 3. CVs of iodide layer on poly GE in the presence of 1×10^{-3} M KI in pH 13 KOH solution with various scan rates: (a) 50, (b) 100, (c) 150, (d) 200, and (e) 300 mV s^{-1}. Inset shows the plot of the cathodic and anodic peaks current vs the scan rate.

Electrochemical activities of iodide film in different pH solutions.— The electrochemical responses of the iodide film on GCE in different pH solutions have been examined. Figure 4 demonstrates the iodide film (on GCE) in different pH buffer solutions (1.5, 4, 7, and 9) in the presence of 1×10^{-3} M KI. In pH 1.5 electrolyte solution, the film exhibited two significant and clear redox couples at 0.4 and 0.9 V, which was compatible with the original redox activities of the iodide film. Further, in pH 4 buffer solutions, it shows the two redox couples whose peak separation was very low when compared with the same film's property in pH 1.5 solutions. Here, the redox couple at 0.4 V appeared as the obvious one. Next, in pH 7 buffer solutions, the two redox couples of the iodide film appeared as quasi-reversible peaks and very close to each other. Finally, in pH 9 buffer solution, the iodide film exhibits one irreversible peak. From the above results, it can be seen that, as the solution pH increases, there is a change in the redox peak potentials and at a higher pH it fails to produce the redox couples of the iodide film. Generally the redox couples of the iodide film were not pH dependent. However, in the different species such a pH change in the film will exhibit different properties. From these pH studies, it was fournd that pH 1.5 and 4 are the optimized pH conditions for the iodide film modified GCE.

At the same time, the cathodic chemisorptions of iodide film at poly GE also reveals different properties in various pH buffer solu-

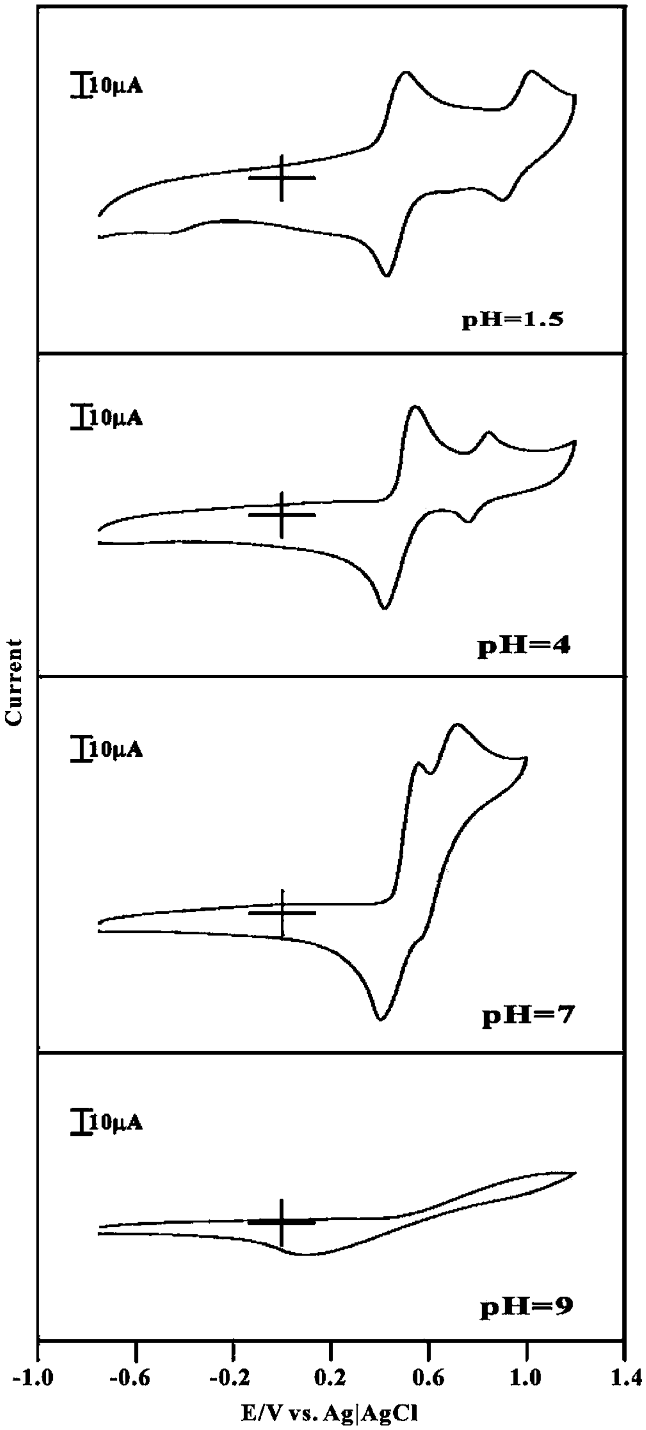

Figure 4. CVs of iodide film on GCE in the presence of 1×10^{-3} M KI in various buffer solutions.

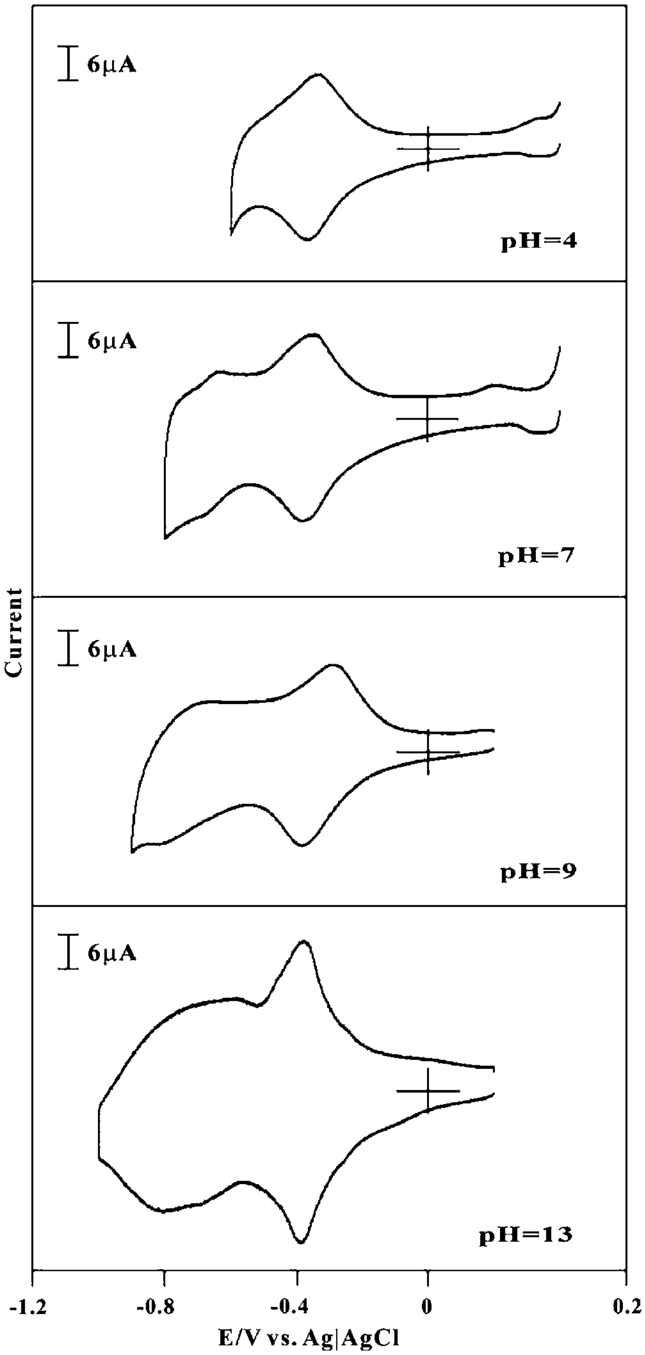

Figure 5. CVs of iodide film on poly GE in the presence of 1×10^{-3} M KI in various buffer solutions.

tions. The electrochemical behavior of chemisorbed iodide film on poly GE was examined in various pH buffer solutions (4, 7, 9, and 13) and the results are shown in Fig. 5. In pH 4 buffer solution, the chemisorbed iodide film exhibits only one obvious redox couple at −0.4 V. Next, in pH 7 buffer solution, it shows one perfect redox couple at the same potential like in the pH 4 solution and additionally one broad redox peak at −0.7 V which was not apparent. Further, in pH 9 buffer solutions, the iodide film shows two redox couples at −0.4 and −0.8 V, respectively. In that, the redox couple at −0.4 V was the obvious one and another couple at −0.8 V exhibits as a broader one. Finally, in pH 13 buffer solutions, the chemisorbed iodide film exhibits two redox couples at 0.4 and −0.8 V potentials, respectively. Here, the redox couple at −0.4 V was sharp and the other one at −0.8 V appeared in the wide range. From these results, the chemisorbed iodide on poly GE shows its own electrochemical activities in different pH solutions. However, during the pH change, there is no potential shift for the redox couple at −0.4 V. But, there is an interesting broad peak found at −0.8 V in alkaline pH conditions. Finally, we have ascertained the electrochemical activities of the iodide films (on GCE, poly GE) by examining them in various pH solutions.[48]

Electrocatalytic oxidation of As (III) on iodide modified GCE.— The fine performance of iodide film modified GCE toward the detection of As(III) makes it attractive for the fabrication of

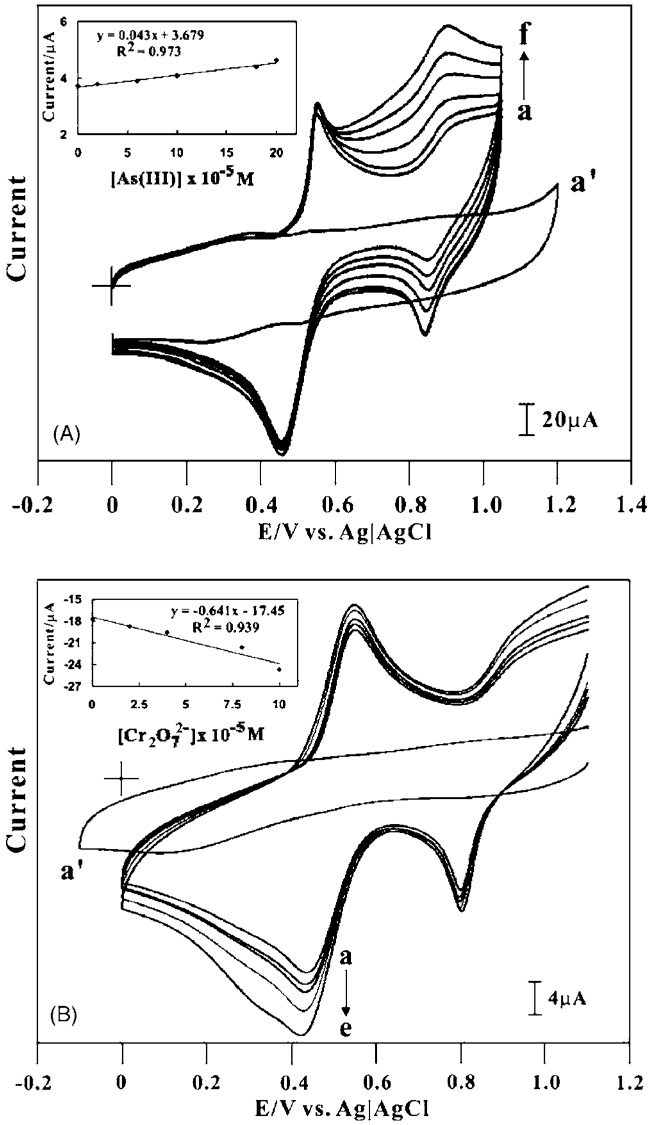

Figure 6. (A) CVs of iodide film on GCE in the presence of 1×10^{-3} M KI in a pH 1.5 H_2SO_4 with various concentration of [As (III)]= (a) 0, (b) 2×10^{-5}, (c) 6×10^{-5}, (d) 1.0×10^{-4}, (e) 1.8×10^{-5}, and (f) 2×10^{-4} M; (a′) bare GCE and [As (III)] = 2×10^{-4} M. Inset is the plot of I_{pa} vs concentration. (B) CVs of iodide film on GCE in the presence of 1×10^{-3} M KI in a pH 1.5 H_2SO_4 with various concentrations of [$Cr_2O_7^{2-}$] = (a) 0, (b) 2×10^{-5}, (c) 4×10^{-5}, (d) 8×10^{-5}, and (e) 1.0×10^{-4} M; (a′) bare GCE and [$Cr_2O_7^{2-}$] = 1×10^{-4} M. Inset is the plot of I_{pc} vs concentration.

iodide-based sensors. Figure 6A shows the typical CV response of iodide film modified GCE for the successive additions of As (III) in the range of 2×10^{-5}–2×10^{-4} M. Further, the important factor for the performance of iodide film 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, the As (III) oxidation has been done in the presence of 1×10^{-3} M KI in pH 1.5 H_2SO_4 solution. From Fig. 6A, it can be seen that the oxidation peak current increases linearly at 0.8 V with the increasing concentrations of As (III). 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 indicates the electrocatalytic oxidation of As (III) at iodide modified GCE. Further comparing with bare GCE [for 2.0×10^{-4} M of 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 vs concentration plot for As (III) oxidation. From the calibration plot, the linear regression equation for As (III) oxidation was found as $y = 0.043x + 3.679$, with a correlation coefficient of 0.9730. Finally, the above results validate the electrocatalytic oxidation of As (III) on iodide modified GCE.

Electrocatalytic reduction of $Cr_2O_7^{2-}$ on iodide film modified GCE.— We have examined the electrocatalytic activity of $Cr_2O_7^{2-}$ reduction on iodide film modified GCE. Figure 6B shows the CVs of electrocatalytic reduction of Cr (VI) to Cr (III) on iodide film modified GCE in pH 1.5 H_2SO_4 containing 1×10^{-3} M of KI. Here, the reaction process on iodide film modified GCE might be rationalized as the one-step reduction of Cr (VI) to Cr (III). Further, the electrocatalytic reduction peaks of $Cr_2O_7^{2-}$ were obtained at 0.42 V. The iodide film on GCE shows a linear current increase response for the $Cr_2O_7^{2-}$ reduction in the concentration range of 2×10^{-5}–1×10^{-4} M. When $Cr_2O_7^{2-}$ was added to the solution, the charge under the reduction peak was found to increase with a decrease in the oxidation peak currents. This behavior is typical of that expected for a reduction of $Cr_2O_7^{2-}$ at the iodide modified GCE. At the same time, the electrocatalytic reduction of $Cr_2O_7^{2-}$ on unmodified bare GCE was examined and it fails to reduce the chromate (curve a′). Further, by plotting the reduction current vs concentration, the linear regression equation for chromate reduction was found as $y = -0.641x - 17.45$, with a correlation coefficient of 0.939. Finally, the above results confirm the successful reduction of $Cr_2O_7^{2-}$ at iodide modified GCE.

RRDE measurements.— To evaluate the electrocatalytic properties of iodide modified film on GCE, the electrochemical oxidation of As (III) was studied by the hydrodynamic method. Here, the RRDE technique was the enhanced technique for the electrochemical oxidation of As (III) on rotating GC ring disk electrode. Figure 7A shows the RRDE voltammograms for the redox behavior of As (III) at the iodide modified GC ring disk electrode in pH 1.5 H_2SO_4 aqueous solution (containing 1×10^{-3} M of KI) with different concentrations of As (III). Here, the As (III) was spiked in the linear range of 1×10^{-4}–7×10^{-4} M and the rotation rate of the electrode was fixed at 2500 rpm. Well-defined voltammograms with a mass transport-limited current were observed at each addition of As (III). Further, the ring current (I_R) and the disk current (I_D) were found to increase with the increasing concentration of As (III). The inset of Fig. 7A shows the linear relationship between the concentration and catalytic currents, which clearly indicates that the iodide modified electrode catalyzes the As (III). Meanwhile Fig. 7B represents the RRDE voltammograms of iodide modified GCE for the electrocatalytic oxidation of As (III) (7×10^{-4} M) at iodide film in pH 1.5 H_2SO_4 solution (containing 1×10^{-3} M of KI) at different rotation rates (200–2500 rpm). Figure 7B shows that both the oxidation current at the disk and the reduction current at the ring increased with the rotation speed. The linear properties of the Levich plot show that the catalytic reaction is exclusively controlled by the mass transfer process in the solution. The collection efficiency was calculated from the ratio between I_R and I_D (inset of Fig. 7B). Here, the maximum ratio obtained was 0.18, which slightly decreased with the rotation speed. The theoretical collection efficiency was calculated by using the geometry of RRDE ($r_1 = 0.269$ cm, $r_2 = 0.313$ cm, and $r_3 = 0.383$ cm) and the reversible redox reaction of $[Fe(CN)_6^{3-}]/[Fe(CN)_6^{4-}]$. Here, the RRDE experiments of $[Fe(CN)_6^{3-}]/[Fe(CN)_6^{4-}]$ redox reactions were carried out under different rotation speeds by fixing the ring potential at 0.5 V. In particular, from the present investigation it was found that the theoretical efficiency calculated was 0.35. Furthermore, the constant value of the I_R/I_D ratio at a different electrode rotation rate points out the absence of any chemical reaction couple with electron transfer pro-

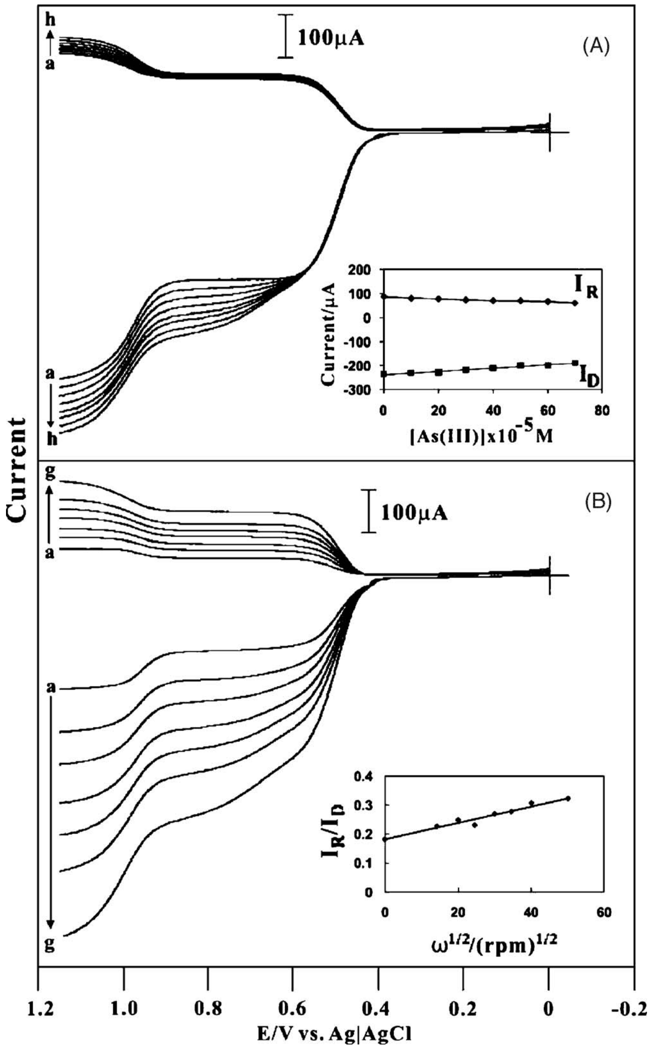

Figure 7. (A) RRDE voltammograms of iodide film on GCE in the presence of 1×10^{-3} M KI in a pH 1.5 H_2SO_4 with various concentrations of [As (III)]= (a) 0, (b) 1×10^{-4}, (c) 2×10^{-4}, (d) 3×10^{-4}, (e) 4×10^{-4}, (f) 5×10^{-4}, (g) 6×10^{-4}, and (h) 7×10^{-4} M; electrode rotation speed = 2500 rpm. $E_R = 0$ V. Inset is the plot of I_R and I_D vs [As (III)]. (B) RRDE voltammograms of iodide film on GCE in the presence of 1×10^{-3} M KI in a pH 1.5 H_2SO_4 with 7×10^{-4} M of As (III) at different rotation speeds: (a) 200, (b) 400, (c) 600, (d) 900, (e) 1200, (f) 1600, and (g) 2500 rpm. $E_R = 0$ V. Inset is the plot of variation of I_R and I_D vs rotation rate.

cess. Here, the collection efficiency of As (III) at an iodide modified electrode was found to be somewhat less than that of the theoretical value.

Detection of As (III) and Cr in real samples.— For the real sample analysis, the As (III) and chromate detection has been conducted in real-world drinking waters like mineral water and tap water (Taipei Water Department, Taiwan). The drinking mineral water source used here for the analysis was well characterized and furnished detailed information about the various minerals it contained (Ca = 14.8 to 27.6, Mg = 8.8 to 16.4, Fe < 0.018, F < 0.1, and Na = 2.7–11.3 mg/L; pH 6.0–8.0). The certification shows that there were probably no other toxic metals in the mineral water. Further, the tap water analysis reports from Taiwan says it contains various substances which affect the palatability (Fe = 0.019, Cu = 0.00068, Zn = 0.00243, chloride = 5.63, sulfate = 11.8, pH 7.1). Also, the report was clear that it does not have any toxic metals like As, Pb, Se, Cr, Cd, Ba, Sb, Ni, and Hg in it. Both the water sources have been examined for the As (III) and Cr detection by using iodide modified electrodes. Figure 8A shows the background subtracted DPVs for the detection of As (III) obtained from the mineral water. Here, the catalytic oxidation peaks of As (III) were detected in mineral water by spiking 0.2 nM, 0.02 μM, and 0.2 μM concentrations. Further, the oxidation peak currents increased linearly with the increasing concentrations of As (III). Similar type results were reported in the literature.[5,49] From these results, it was ascertained that the iodide modified GCE shows a good electrocatalytic activity for the detection of As (III) in the mineral water. Furthermore, Fig. 8B exhibits the DPVs of As (III) detection in tap water. Here, the As (III) oxidation peaks were detected in the tap water for 0.2 nM, 0.02 μM, and 0.2 μM concentrations. In addition, the results obtained from the tap water were significantly higher than the level obtained for the mineral water. In terms of peak height, the response of the iodide modified electrode for spiked As (III) in tap water was higher than the mineral water. Next, Fig. 8C and D shows the detection of Cr in the mineral water and tap water. Here, the reduction peaks of Cr (Fig. 8C) in mineral water were obtained by spiking the chromate concentration in the range of 0.2–2 μM. Further, the linear increase in the reduction peak currents of Cr reveals the electrocatalytic nature of the iodide modified GCE. In the case of Cr detection in tap water, it shows obvious reduction peaks for 2 nM and 0.2 μM concentrations (Fig. 8D). These results validate the minimal possible detection of As and Cr in real drinking water sources like mineral water and tap water. Finally, these results support the minimal possibility of using iodide modified electrodes for real sample analyses in sub-micromolar levels.

Electrocatalytic reduction of IO_3^- on poly GE.— Generally, the electrocatalytic reduction reaction of IO_3^- requires higher overpotentials at bare electrodes. To overcome this problem, the modified electrodes were applied for the electrocatalytic reduction of IO_3^-. Here, we have utilized the chemisorbed iodide film on poly GE for the electrocatalytic reduction reactions of IO_3^-; the results are shown in Fig. 9A. The electrocatalytic reduction of IO_3^- was carried out on iodide modified poly GE in pH = 13 KOH buffer solution (containing 1×10^{-3} M KI) with various concentrations of KIO_3. The chemisorbed iodide film on poly GE showed the reduction peak for IO_3^- at −0.8 V. Here, the linear additions of KIO_3 in the buffer solution were in the range of 2×10^{-5}–1×10^{-4} M. For each addition of IO_3^-, the cathodic reduction peak current increases significantly and the anodic current concomitantly decreases, showing the electrocatalytic reduction of IO_3^-. At the same time, there is no obvious response at the bare poly GE electrode for the IO_3^- reduction in the same condition, as shown. Thus, it indicates that IO_3^- was strongly reduced by the chemisorbed iodide layer on poly GE. Further, the reduction current of IO_3^- vs concentration was plotted and the linear regression equation was found as $y = -10.88x - 0.318$, with a correlation coefficient of 0.998. Finally, Table I shows the comparison of the present work with previous reports for the reduction of the IO_3^- .

DPV studies.— DPV is known to be sufficiently sensitive, fast, and reliable for iodate determination. Although the peak heights and sensitivity were slightly higher in DPV, lower background currents and better peak resolution were obtained by DPV. The electrocatalytic reduction of IO_3^- at iodide modified poly GE was carried out in the potential range of 0 to −1.2 V, and well-defined reduction peaks at −0.8 V were obtained (Fig. 9B). The linear ranges for the detection of IO_3^- using DPV were 2×10^{-5}–2×10^{-4} M, respectively. Here, the reduction peak currents of IO_3^- increased linearly with increasing the concentrations of the IO_3^-. Further, the inset of Fig. 9B shows the calibration plot for the current vs concentration of IO_3^- catalysis. The calibration plot for IO_3^- reduction shows the uniform electrocatalytic activity of the chemisorbed iodide film for the IO_3^- reduction. The linear regression equation obtained from the calibration plot was found as $y = -0.404x - 0.673$, with a correlation coefficient of 0.998. Finally, from these two different types of tech-

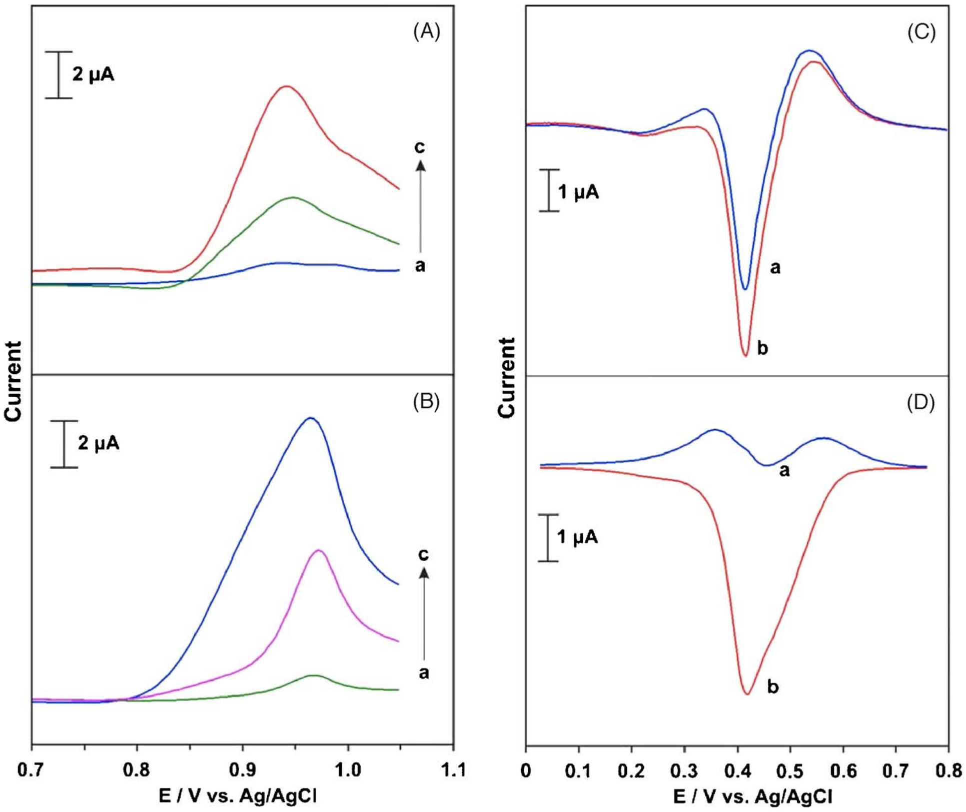

Figure 8. (Color online) (A) DPVs of As (III) detection in mineral water ($a = 0.2$ nM, $b = 0.02$ μM, and $c = 0.2$ μM). (B) As (III) in tap water ($a = 0.2$ nM, $b = 0.02$ μM, and $c = 0.2$ μM). (C) DPVs of chromate detection in mineral water ($a = 0.2$ μM, $b = 2$ μM). (D) Chromate detection in tap water ($a = 2$ nM, $b = 0.2$ μM).

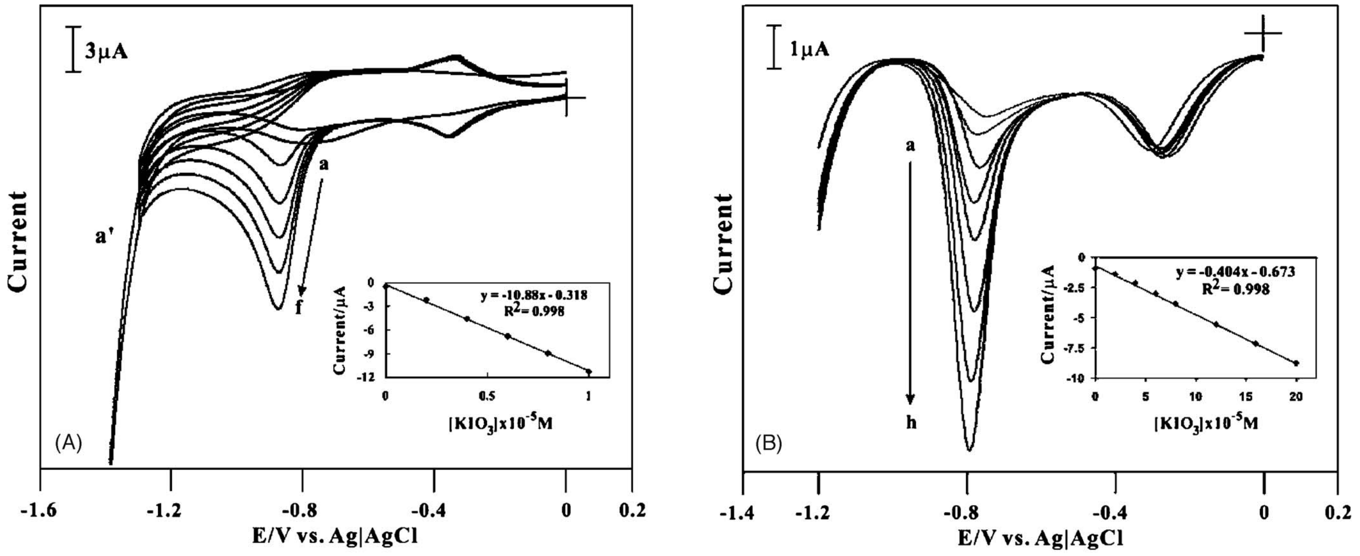

Figure 9. (A) CVs of iodide film on poly GE in the presence of 1×10^{-3} M KI in a pH 13 KOH with various concentration of $[\mathrm{KIO_3}]$= (a) 0, (b) 2×10^{-5}, (c) 4×10^{-5}, (d) 6×10^{-5}, (e) 8×10^{-5}, and (f) 1×10^{-4} M; (a′) bare poly GE and $[\mathrm{KIO_3}] = 1 \times 10^{-4}$ M. Inset is the plot I_{pc} vs concentration. (B) DPVs of iodide film on poly GE in the presence of 1×10^{-3} M KI in a pH 13 KOH with various concentrations of $[\mathrm{KIO_3}]$= (a) 0, (b) 2×10^{-5}, (c) 4×10^{-5}, (d) 6×10^{-5}, (e) 8×10^{-5}, (f) 1.2×10^{-4}, (g) 1.6×10^{-4}, and (h) 2×10^{-4} M. Inset is the plot of I_{pc} vs concentration.

Table I. Comparison of chemisorbed iodide film/poly GE with other methods for $\mathrm{IO_3^-}$ reduction.

Electrode	Linear range (mol $\mathrm{L^{-1}}$)	Detection limit (mol $\mathrm{L^{-1}}$)	E_{pc} (V)	Reference
Poly luminol film	2.5×10^{-3}–5.0×10^{-3}	—	−0.2	50
Poly fuchsin film	6.0×10^{-4}–1.8×10^{-3}	—	−0.3	28
Poly neutral red film	3.3×10^{-4}–1.0×10^{-3}	—	−0.4	29
$(\mathrm{RuO/Fe(CN)_6^{3-}/SiMo_{12}O_{40}^{4-}})$ film	2.0×10^{-4}–8.0×10^{-4}	—	0.1	27
Iodide film	2.0×10^{-5}–10×10^{-5}	1.447×10^{-5}	−0.8	Proposed method

nique results (CV and DPV), we conclude that the chemisorbed iodide film on poly GE shows satisfactory results for the electrocatalytic reduction of IO_3^-.

Conclusion

In conclusion, our studies illustrate the electrochemical deposition and chemisorption of iodide film on different electrodes like GCE and poly GE. The properties of the iodide film for different deposition methods at two different types of electrode surfaces were examined. Further, the electrochemical activities of the proposed electrodes in different pH solutions have been examined. The proposed iodide modified electrodes have shown their maximum electrocatalytic activities for As (III) oxidation, $Cr_2O_7^{2-}$ and IO_3^- reduction in different buffer solutions. In particular, the electrocatalytic applications of the iodide modified film on GCE showed good results for As (III) oxidation in CV and RRDE studies. The chemisorbed iodide film on poly GE showed a successful reduction of IO_3^- and $Cr_2O_7^{2-}$ by using CV and DPV techniques. The minimal practical analytical utility of the proposed electrodes have been examined for Cr and As (III) detection in tap water and mineral water, and the results were found satisfactory. Moreover, the preparation of iodide film is very easy and eco-friendly for the determination of environmentally hazardous materials. Finally, the important conclusion from this study was an easy reproduction of the iodide film from KI solution for different types of electrodes, economically cheaper than other types of modified electrodes. Further, the effect of interaction of nanoparticles with iodide film is part of our ongoing work.

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