**Full Paper**

# The Interaction of Iodide Film with Platinum Microparticles on Different Electrode Materials for Various Electrocatalytic Reactions

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**Abstract**
The electrochemical depositions of Pt microparticles and KI film were successfully carried out on glassy carbon electrodes (GCE), gold electrodes (GE), and indium tin oxide electrodes (ITO). The electrochemical studies of Pt micro/KI film on GCE show that the film was stable, active at pH 1.5 electrolyte solutions. The Pt microparticle/KI film modified ITO electrodes were examined by using scanning electron microscopy (SEM) and atomic force microscopy (AFM) techniques. The SEM and AFM results show that the Pt particle sizes were in the range of 120 nm – 1.4 μm, respectively. The proposed film on GCE shows efficient electrocatalysis for oxygen, $Cr_2O_7^{2-}$ reduction by using cyclic voltammetry. Further the electrochemical oxidation of sodium *meta*-arsenite (As(III)), $H_2O_2$ were successfully carried out and the detection of $H_2O_2$ in real samples has been validated.

**Keywords:** Pt microparticles, Iodide film, As(III) oxidation, $Cr_2O_7^{2-}$ reduction, $H_2O_2$ oxidation

## 1. Introduction

Metal micro/nanoparticles have proved their specific importance comparing with their bulk metals. The fabrication process of micro/nanoparticles can be generated by numerous techniques like sono chemical reduction [1] or microwave dielectric heating methods [2]. In electrochemistry, the electrodes covered with metallic nanoparticles are widely studied. For example, the preparation of spatially distributed noble metal particles deposited on high surface area metal oxides [3, 4], activated carbon supports [5, 6], or in polymeric films on electrodes [7 – 10] and fabrication on passive metal surfaces [11] exhibited excellent catalytic activities. Further these types of electrodes offers improved catalytic activities for various technologically important reactions such as hydrogen evolution, methanol oxidation and the four-electron reduction of oxygen to water.

In these studies, the platinum particles have been recognized as powerful electrocatalysts for many important electrode reactions [12]. Platinum microparticles modified glassy carbon electrode (GCE) for the electrooxidation of ethanol in acidic medium [13], Pt modified GCE in perchloric acid solutions to investigate the electrochemical behavior of ascorbic acid [14] are reported. It was also interesting to study the electrocatalytic properties of Pt microparticles incorporated into polymer films [15]. Electrochemically deposited spherical Pt microparticles dispersed in a polymeric film electrode exhibited higher electrocatalytic activity towards the generation of hydrogen and reduction of oxygen [16]. Poly aniline/poly (acrylic acid) modified platinum microparticles for the reduction of hydrogen and oxidation of methanol [17], platinum microparticles in inorganic/organic mono layers modified carbon electrode for the arsenic(III) oxidation reactions [18] too reported. Further in halogens, the iodine has an important role in electrode modification. It has the highest polarizability and binds strongly with transition metal electrodes. The $I^-$ adlayer modified electrodes applied for the enhanced electrochemical oxidation [19], reduction of $H_2O_2$ [20, 21] and the cathodic detection of $H_2O_2$ in iodide-modified gold electrode [22] were reported.

The oxygen reduction reaction (ORR) is an imperative topic for electrochemical studies. This reaction is very slow with the characteristic of numerous different reaction paths, intended primarily by the catalytic effect of the electrode material [23]. Recently, this reaction is particularly interesting as a main cathodic reaction in fuel cells [24]. It's kinetics and mechanism was usually scrutinized primarily on platinum, known as its best electrocatalyst [25, 26]. The other metals, for example Ag and Au, under fixed conditions, may display effectiveness in oxygen reduction close to that of platinum [26, 27].

Next the environmentally perilous materials like chromium, arsenic detection and determination is more important in the new Era. They are important target compounds in biological and environmental systems. Chromium(III) is an

essential trace element in the metabolism of lipids and proteins and is vital for maintenance of a normal glucose tolerance factor. The use of chromates, i.e., hexavalent chromium oxygenic compounds, in the industrial sector has led to serious concern about workers' exposure to Cr (VI), which is now classified as a human carcinogen [28]. By using electroanalytical methods, the detection of chromium has been done on carbon paste electrodes (CPEs) in which complex-forming agents can be mixed as modifiers [29]. Further the carbon paste modified electrodes [30], potentiometric titrations [31], chitin modified electrodes [32] also have used for the chromate detection. All these methods demonstrates the advantages of direct modification of the electrode material which were capable to detect Cr(III), and enabled their use for analysis in selected samples and having their specific disadvantages. On the other hand, the arsenic exists in many different chemical forms in nature; particularly, in ground water they are found almost exclusively as arsenite and arsenate. Many arsenic compounds are known to be toxic and have been associated with many health problems such as skin lesions, keratosis (skin hardening), lung cancer, and bladder cancer [33]. Their direct exposure to humans and animals and the side effect to the ecosystem remain international problems. Further the electrochemical oxidation of arsenic at various metal electrodes like Pt, Au shows very interesting studies in the field of electroanalytical chemistry. Only few electrochemical methods have been reported for arsenite detection [34, 35]. Metal electrodes, such as gold, platinum electrodes or modified glassy carbon, pyrolytic graphite electrodes with metal films have successfully detected arsenic by using anodic stripping potentiometry and anodic stripping voltammetry techniques. However, still these types of modified electrodes facing problems such like limited sensitivity, poor precision, low electron-transfer reaction, high overvoltages, low stability, and no reproducibility for the arsenic detection [36].

The hydrogen peroxide is an essential product for biological processes, food production, and in sterilization process. There are numerous possible chances for hydrogen peroxide to affect the biological systems [37]. Hydrogen peroxide acts as a powerful oxidizing agent so it could be applied in so many organic compounds synthesis reaction [38]. Thus, the detection of $H_2O_2$ is important in clinical, environmental applications and in enzyme reactions [39]. Therefore, it is essential to prepare a sensor to determine the $H_2O_2$. In electrochemical method, at metallic electrodes the reduction or oxidation of hydrogen peroxide, have been found as great interest. For example, pulse electrochemical detection of $H_2O_2$ on gold electrode [40], electrochemical reduction and oxidation of $H_2O_2$ at gold electrodes [19, 41] and amperometric detection of $H_2O_2$ at Pt and Au electrodes [42] has been reported. However, at bare electrodes, it shows the slow electrode kinetics and high over potentials were required for the redox reaction. To overcome this problem, the modified electrodes have been widely applied to decrease the over potentials. Further in modified electrodes, hemoglobin-immobilized dopamine-oxidation polymer/Prussian blue/Au electrode [43], Prussian blue-complex

membrane modified catalytic layer [44], myoglobin/arylhydroxylamine film modified glassy carbon electrode [45] are some of the few examples for $H_2O_2$ detection process. Even though modified electrodes have shown interesting ability toward hydrogen peroxide detection, they also linked with many problems such like film deposition process, toxicity, poor repeatability, and stability. For these reason, there is a need to develop a simple and reliable methods for the fabrication of novel sensor for hydrogen peroxide detection at lower concentrations. Also there is a need to develop a film modified electrode which could be used in multiple aspects to detect and determine the oxygen, chromium reduction, arsenic, and hydrogen peroxide oxidation processes. From the above literature reports we can elucidate that the combination of Pt microparticles with KI film will show efficient electrocatalytic reactions comparing with their separate analysis. Thus, the combination of Pt particles with iodide as a bilayer film was more interesting in this era. This type of film modified electrodes will exhibit obvious electrocatalytic properties for various compounds.

For the first time, our study is staged with the aim to make a detailed study about the interactions between the platinum microparticles with iodide film for electrocatalytic applications. The proposed Pt-iodide bilayer film could efficiently reduce the oxygen and chromium. In addition, it is also employed for the arsenic and hydrogen peroxide oxidation reactions. Further the Pt-iodide bilayer film was characterized by using SEM and AFM techniques. To evaluate the practical analytical utility of this type of bilayer film, the real sample analysis for $H_2O_2$ electrooxidation has been examined in micromolar concentrations, respectively.

## 2. Experimental

### 2.1. Reagents

All the chemicals and reagents used in this work were of analytical grade and were used as received without further purification. $K_2PtCl_6$ was purchased from Strem Chemicals (USA). Potassium iodide (KI) was obtained from Wako chemicals (USA). Sodium *meta*-arsenite was purchased from (Sigma-Aldrich, USA). All the solutions were prepared with double distilled water. The experimental results were obtained at room temperature. The buffer solutions for the electrocatalysis were pH 1.5 $H_2SO_4$ solutions containing $1 \times 10^{-3}$ M KI. For real sample analysis, commercially available antiseptic (30% $H_2O_2$), contact lens cleaner solutions (3% $H_2O_2$) were used.

### 2.2. Apparatus

Electrochemical measurement like cyclic voltammetry (CV) was carried out using CHI 410a, CHI 750 potentiostats (CH Instruments, Austin, TX, USA). A conventional three-electrode system was used throughout the experiments. The BAS glassy carbon electrodes (GCE) ($\varnothing = 0.3$ cm), was in

the form of disk sealed in a teflon jacket having an exposed geometric surface area of 0.07 cm$^2$, respectively. The working electrode was a bare or Pt particles/iodide film modified GCE, 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 morphological characterizations of the film were examined by means of scanning electron microscopy (SEM) (Hitachi S-3000H) and atomic force microscopy (AFM) (Being Nano-Instruments CSPM-4000). For our convenience, the indium tin oxide (ITO) thin film coated electrodes were used for SEM and AFM analysis. For FIA analysis, the screen printed carbon electrodes (SPCE) (from Zensor (Taiwan)) were used.

### 2.3. Film Preparation

Prior to film deposition process, the GCE was polished with the help of BAS polishing kit by using aqueous slurries of finer alumina powder (0.05 μm), rinsed and ultrasonicated in double distilled deionized water. All the experimental solutions were purged with purified $N_2$ gas. Platinum was electrochemically deposited on GCE by using CV in 0.5 M $H_2SO_4$ solution containing $2.5 \times 10^{-3}$ M $K_2PtCl_6$ and the potentials were in the range of 1.1 to $-0.2$ V (vs. Ag /AgCl, at 0.1 V/s) for 15 cycles. Further the modified GCE was immersed in pH 1.5 $H_2SO_4$ solution containing $1 \times 10^{-3}$ M KI for the electrochemical deposition of iodide layers on the Pt modified GCE. Here the iodide film on Pt modified GCE was electrochemically active and stable in presence of KI solution. Therefore, all the electrocatalysis experiments were carried out in presence of $1 \times 10^{-3}$ M KI in pH 1.5 $H_2SO_4$ solutions, respectively.

### 3. Results and Discussion

### 3.1. Characterization of Pt$_{micro}$/KI Film Modified GCE

Figure 1A shows the cyclic voltammograms (CVs) of Pt deposition process on GCE surface. From the cyclic voltammograms, we can see that the reduction and oxidation peaks of platinum occur at 0.5 and 0.8 V, respectively. Further the remaining two peaks at 0.16 V shows the hydrogen adsorption and desorption process. On continuous cycling, all these peaks were found growing which confirms the deposition of Pt on the GCE surface. Here the morphological nature of the Pt deposition on GCE has been considered as microparticles by comparing with similar type Pt microparticles deposition on GCE from the previous literature reports [9, 46, 47]. Thus hereafter, we consider electrodeposition of Pt as Pt microparticles on GCE surface for further electrochemical activities. Also this prediction has been supported by the Pt particles deposition on ITO electrode surface [48]. Next the Figure 1B shows the cyclic voltammograms (CVs) of iodide film deposition 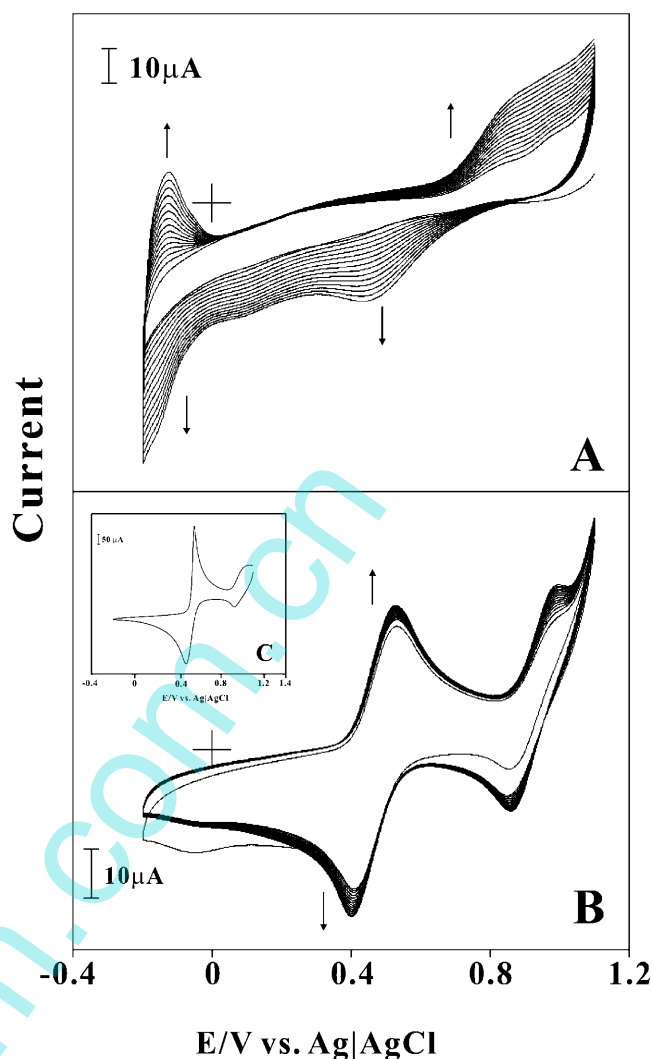on Pt microparticles modified GCE. During the cathodic potential scan, two peaks were observed at 0.94 and 0.4 V, and in anodic potential scan, two peaks were observed at 0.6 and 1.0 V. Further the growth of these two obvious redox couples show the successive formation of the iodide film on Pt particles modified GCE. Hereafter the electrode covered with Pt microparticles and KI film was called as Pt$_{micro}$/KI film modified GCE. Furthermore Figure 1C shows the cyclic voltammetric response of bare GCE in pH 1.5 $H_2SO_4$ solutions containing $1 \times 10^{-3}$ M KI. Next the Pt$_{micro}$/KI film modified GCE was transferred to pH 1.5 $H_2SO_4$ solution containing $1 \times 10^{-3}$ M KI for different scan rate studies (Fig. 2A). In different scan rate studies, the film exhibits the oxidation peak of platinum at 1.1 V, respectively. At the same time we can clearly see the two peaks of KI film in oxidation side at 0.5 and 0.9 V. Then the reduction peaks of



Fig. 1. A) Consecutive CVs of Pt particles deposition on GCE from 0.5 M $H_2SO_4$ containing $2.5 \times 10^{-3}$ M $K_2PtCl_6$ in the potential range of 1.1 V to $-0.2$ V. B) Consecutive CVs of KI film growth behavior on Pt particles modified GCE from pH 1.5 $H_2SO_4$ containing $1 \times 10^{-3}$ M KI in the potential range of $-0.2$ and 1.1 V (scan rate: 100 mV s$^{-1}$). C) CVs of bare GCE in pH 1.5 $H_2SO_4$ containing $1 \times 10^{-3}$ M KI (scan rate: 100 mV s$^{-1}$).
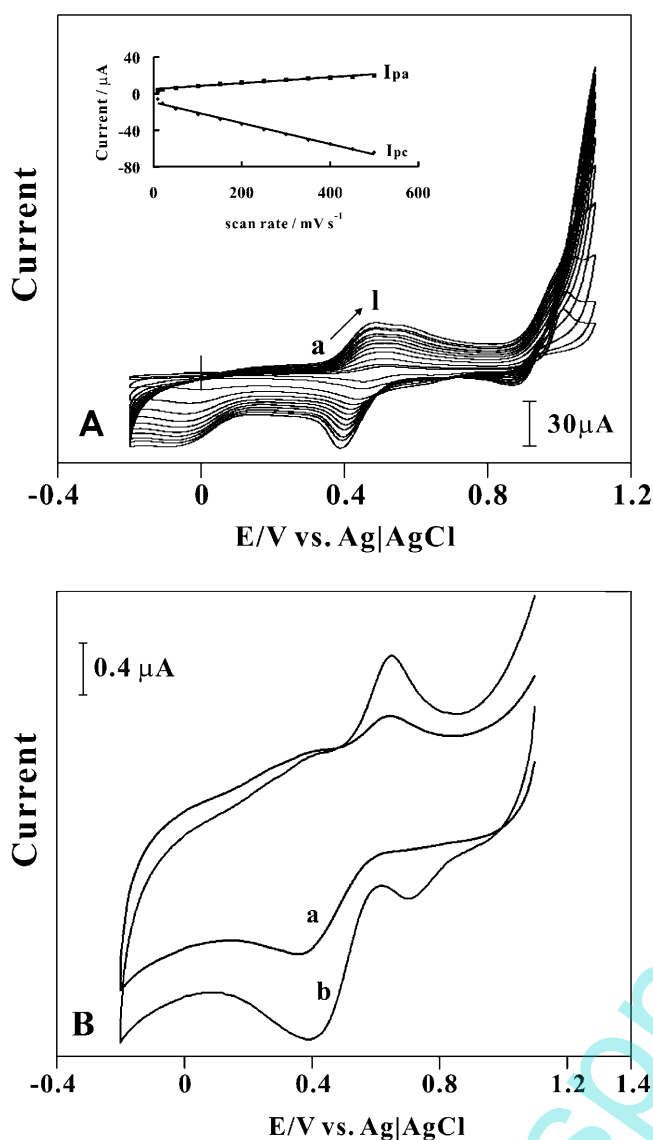
Fig. 2. A) CVs of Pt$_{micro}$/KI film on GCE in presence of $1 \times 10^{-3}$ M KI in pH 1.5 H$_2$SO$_4$ solution with various scan rates: a) 10, b) 20, c) 50, d) 100, e) 150, f) 200, g) 250, h) 300, i) 350, j) 400, k) 450, and l) 500 mV s$^{-1}$. Inset shows the current vs. scan rate. B) CVs of KI film at GCE in the absence of $1 \times 10^{-3}$ M KI (a), presence of $1 \times 10^{-3}$ M KI in pH 1.5 H$_2$SO$_4$ (b) (scan rate: 100 mV s$^{-1}$).

Pt and KI film occurs at the same potential (0.4 V) which can not be distinguished from the CV. From this result it shows that the first redox peak of KI film is obvious and stable, the other peak is quasireversible. Furthermore the anodic and cathodic peak currents of Pt$_{micro}$/KI film increases linearly with the increasing scan rates up to 500 mV s$^{-1}$. The inset of Figure 2A shows the $I_{pc}$ and $I_{pa}$ vs. scan rate current increase in the first redox couple of the proposed film. Finally, these results illustrate that Pt$_{micro}$/KI film on GCE was electrochemically active in pH 1.5 H$_2$SO$_4$ solution.

To validate the important role of KI present in pH 1.5 H$_2$SO$_4$ solutions, the electrodeposited KI film on GCE was examined in absence and presence of KI in pH 1.5 H$_2$SO$_4$

solutions, respectively. Figure 2B, curve a shows the cyclic voltammetric response of electrochemically deposited KI film on GCE in pH 1.5 H$_2$SO$_4$ solution, curve (b) in pH 1.5 H$_2$SO$_4$ solution containing $1 \times 10^{-3}$ M KI. Comparing these two cyclic voltammetric responses of KI film on GCE, it was concluded that the presence of KI in the electrolyte solution (pH 1.5 H$_2$SO$_4$) shows the obvious electrochemical activities of KI film. At the same time, in absence of KI it shows a nullified response for KI film, respectively. Thus, all the electrocatalytic experiments were performed in presence KI solution. Further the cyclic voltammetric response of only Pt$_{micro}$ film/GCE has been examined (figure not shown). Here the cyclic voltammogram of Pt$_{micro}$ film on GCE shows only the electrochemical response of the platinum (Pt reduction at 0.48 and oxidation at 0.89 V). Finally, above these examination results illustrate the importance of platinum microparticles and KI film as a bi-layer for the further electrochemical processes, respectively.

## 3.2. EQCM Measurements for Pt$_{micro}$ Film

EQCM is a powerful technique capable of detecting very small mass changes at the electrode surface which accompanies with the electrochemical process. Here the EQCM and CV techniques were used to study the in situ growth of the Pt microparticles. Figure 3A shows the consecutive CVs of Pt particles deposition on the gold electrode surface. The Pt particles were electrochemically deposited from 0.5 M H$_2$SO$_4$ solutions containing $2.5 \times 10^{-3}$ M K$_2$PtCl$_6$, the potentials in the range of 1.1 to $-0.2$ V vs. Ag /AgCl for fifteen cycles. Further the Figure 3B shows the change in the EQCM frequency recorded during the first fifteen cycles of consecutive CVs. Here the increase in the voltammetric peak current in Figure 3A and the decrease in frequency (or increase in mass) in Figure 3B were found consistent with the growth of a Pt microparticle film on the gold electrode. These results showed that the deposition potential was obviously between 1.1 and $-0.2$ V (versus Ag | AgCl). In the EQCM experiment, the mass change at the gold electrode from the frequency change (assuming the film to be a rigid resonator) was derived from the Sauerbrey equation.

$$\text{Mass change } (\Delta m) = -1/2 \ (f_o^{-2}) \ (\Delta f) \ A \ (k\rho)^{1/2}$$

where $\Delta f$ is the observed frequency change, $A$ the area of the gold disk coated onto the quartz crystal, $\rho$ the density of the crystal, $k$ the shear modulus of the crystal and $f_o$ is the oscillation frequency of the crystal. Here 1 Hz frequency change is equivalent to 1.4 ng mass change. During the first CV scan, about 1364.16 ng/cm$^2$ of Pt microparticles was deposited on the gold electrode and a total of about 20 462.4 ng/cm$^2$ of Pt microparticles were deposited after the fifteen scan cycles. Furthermore the inset shows the plot of frequency change versus the scan cycle (no of cycles during the film formation) and this curve was linear as expected.
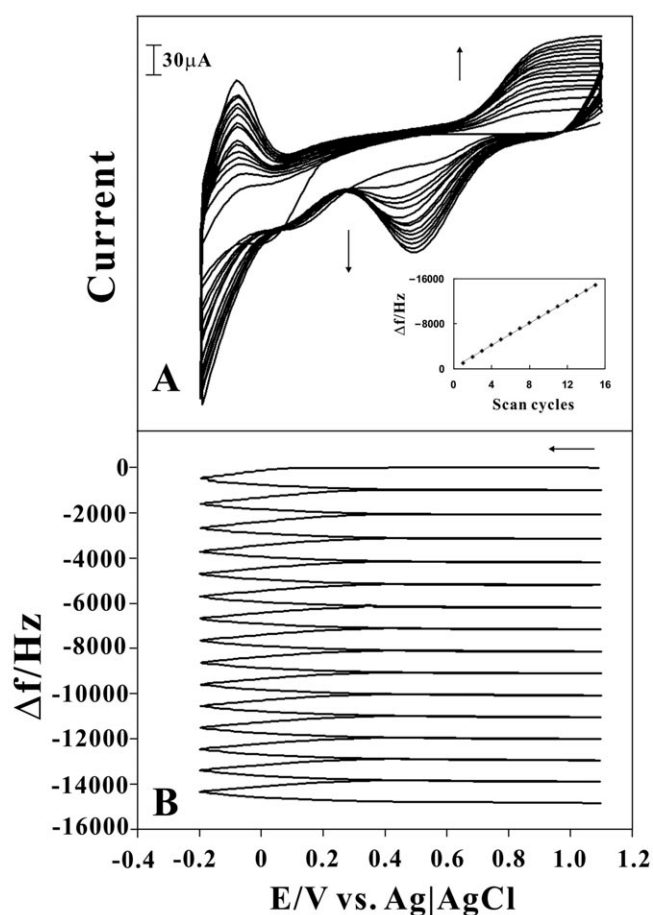
Fig. 3. A) Consecutive CVs of gold electrode modified with Pt microparticles from 0.5 M $H_2SO_4$ containing $2.5 \times 10^{-3}$ M $K_2PtCl_6$. B) The change in EQCM frequency was recorded concurrently with the fifteen consecutive cyclic voltammograms between 1.1 and $-0.2$ V. The inset shows frequency change $\Delta F$ vs. scan cycle.

### 3.3. SEM and AFM Analysis

Figure 4A and B shows the typical SEM micrographs of $Pt_{micro}$/KI film on ITO. From the Figure 4A and B, we can see the electrochemical depositions of Pt microparticles on the electrode surface as bright and round shaped particles in the size range of 120 nm – 1.4 μm, respectively. Here the Pt particles size varies from nano- to micrometer size range. Therefore, we consider the Pt particle as microparticles. Here the Pt particles exceeds the nanoscale range, however it partially exhibits the nanoscale property for the electro-catalysis reactions. Here all the Pt particles will exhibit as active centers for this type of modified electrode. At the same time, from these results we can not elucidate the KI film which was deposited as a very thin layer on the Pt microparticles surface. Next, Figure 4B shows the 60 deg angle view of same $Pt_{micro}$/KI film on ITO. Figure 4C shows the size distribution graph of Pt particles deposited on the electrode surface. On the other hand, the same film has been examined by using atomic force microscopic techniques (figure not shown). Here the film was characterized by the employing the atomic force microscopy in tapping mode.
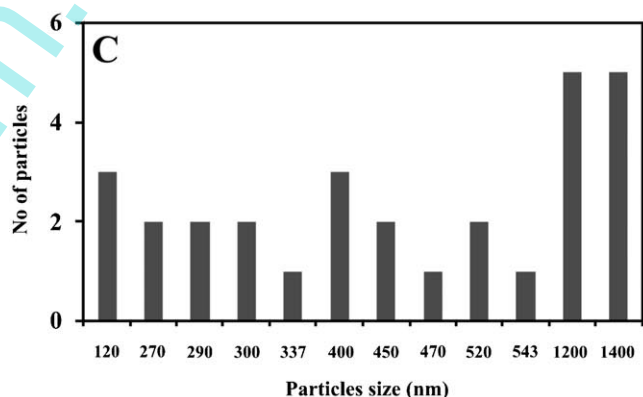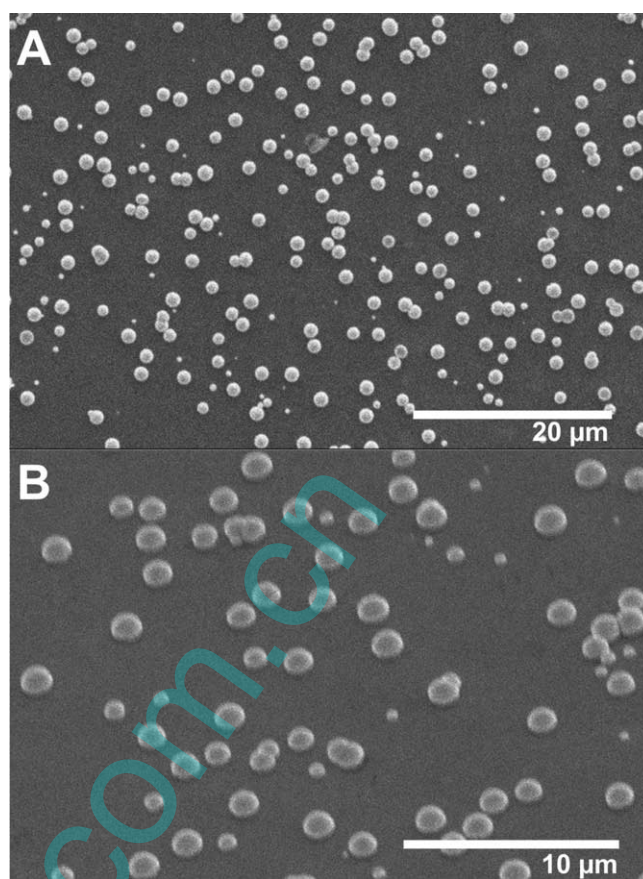


Fig. 4. A) SEM images of electrochemically deposited $Pt_{micro}$/KI film (view angle 90 degree, 20 μm). B) Close view of the same film (view angle 60 degree, 10 μm). C) Pt particle size distribution graph.

The AFM results show that spherical shaped Pt micro-particles were widely spread over the electrode surface. Furthermore, from the AFM results we can notice only the presence of Pt microparticles in very clear manner. At the same time, the electrochemical deposition of KI film which was formed as very thin layer can not be observed from the AFM result. Here the morphological characteristics of $Pt_{micro}$/KI film observed from AFM were consistent with their SEM images. The AFM parameters obtained for the $Pt_{micro}$/KI film were listed in Table 1. Finally, these SEM and

Table 1. AFM parameters obtained for the $Pt_{micro}$/KI film.

| Parameters | Measurements |
|---|---|
| Average roughness (AR) | 8.17 nm |
| Skewness (Sk) | −0.123 |
| Kurtosis (Ku) | 2.88 |

AFM results validate the presence of Pt microparticles on the electrode surface.

### 3.4. $Pt_{micro}$/KI Film Modified GCE Response for Oxygen Reduction and Water Oxidation Process

Figure 5A exhibits the CVs of $Pt_{micro}$/KI film in pH 1.5 $H_2SO_4$ aqueous solutions saturated with oxygen purging. In the absence of oxygen, the cyclic voltammograms of $Pt_{micro}$/KI film does not show any cathodic reduction peak for $O_{2-}$ shown as curve a in Figure 5A. At the same time, in presence of $O_2$ in pH 1.5 $H_2SO_4$ aqueous solution the cyclic voltam-mograms of $Pt_{micro}$/KI film exhibited a new cathodic reduction peak which was appeared at around 0.35 V. This cathodic peak corresponds to the electrochemical reduction reaction (ORR) of $O_2$ at the $Pt_{micro}$/KI film modified GCE (Fig. 5A, curve b). Further the bare GCE does not show any cathodic peak for the electrochemical reduction of $O_2$ (Fig. 5A, curve a′). According to the above results, it was found that the bare GCE fails to produce the $O_2$ reduction peak and same time the $Pt_{micro}$/KI film modified GCE efficiently shown good electrocatalytic activities for the electrochemical reduction of $O_2$. Next the Figure 5B shows the water oxidation process at $Pt_{micro}$/KI film modified electrode. Here the oxidation of water into oxygen was resolved by using $Pt_{micro}$/KI film by cyclic voltammetry by applying different working electrode potential ranges in pH 1.5 $H_2SO_4$ (containing $1 \times 10^{-3}$ M KI) at deoxygenated conditions. The results showed of a new cathodic wave found between 0.4 to 0.8 V depending on the positive potential limit. The peak current of the new cathodic wave was found to be increased with the increasing positive potential limit. Further the results showed that $O_2$ evolved during the electrocatalytic oxidation of water which was got reduced on reverse scan. Finally, the above results show the electro-catalytic activities of the $Pt_{micro}$/KI film for the oxygen reduction and water oxidation reactions.

### 3.5. Electrocatalytic Reduction of $Cr_2O_7^{2-}$ at $Pt_{micro}$/KI Film Modified GCE

The electrochemical reduction process of chromate occurs at the $Pt_{micro}$/KI film modified GCE was shown in Figure 6. Here the electrocatalytic reduction of chromate to chro-mium(III) was carried out in pH 1.5 $H_2SO_4$ electrolyte solutions. From the Figure 6, it shows that the bare GCE fails to reduce the chromate (curve a′). At the same time, the $Pt_{micro}$/KI film modified GCE exhibits a broad reduction
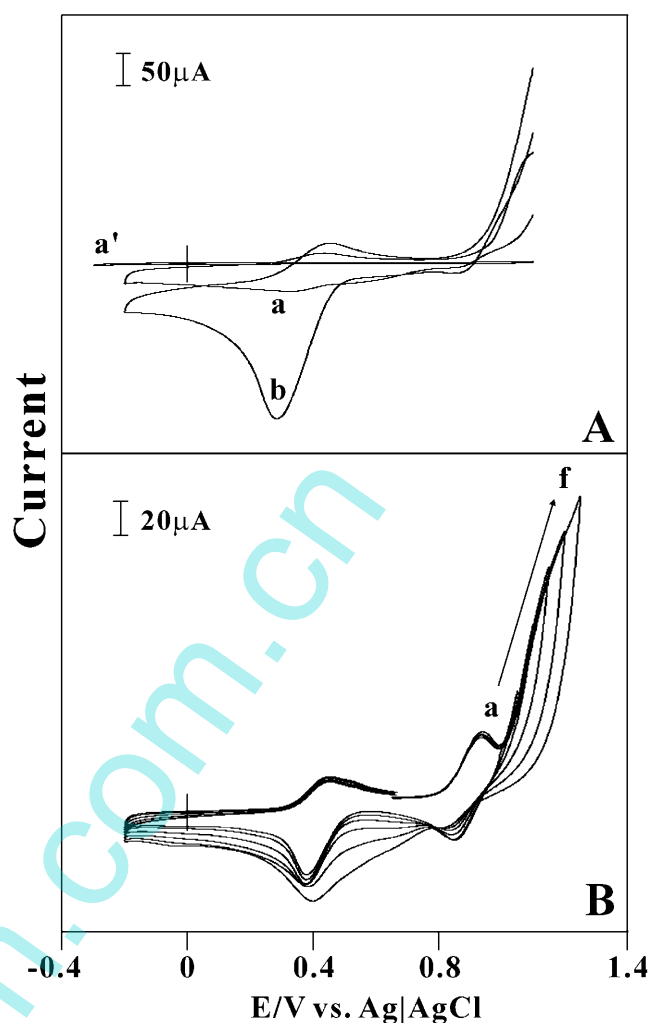


Fig. 5. A) CVs of $Pt_{micro}$/KI film on GCE in presence of $1 \times 10^{-3}$ M KI in pH 1.5 $H_2SO_4$ with concentration of $[O_2] = $ a) 0, b) $2 \times 10^{-4}$ M; a′) bare GCE and $[O_2] = 2 \times 10^{-4}$ M. B) CVs of $Pt_{micro}$/iodide film on GCE in presence of $1 \times 10^{-3}$ M KI in pH 1.5 $H_2SO_4$ for water oxidation process; potential change is from −0.2 to a) 1.0, b) 1.05, c) 1.1, d) 1.15, e) 1.2, and f) 1.25 V.

peak for $Cr_2O_7^{2-}$ which appears at 0.38 V. Further the concentrations of $Cr_2O_7^{2-}$ examined for the reduction process were in the linear range of $2 \times 10^{-4}$ to $1 \times 10^{-3}$ M. The reduction peak current increases linearly with the increasing concentrations of $Cr_2O_7^{2-}$ (curve a–f). The inset in Figure 6 shows the calibration plot for the chromate reduction on $Pt_{micro}$/KI film modified GCE. Here the linear plot response between the concentrations of dichromate and the peak current indicates that the $Pt_{micro}$/KI film modified GCE could be efficient for the detection of chromium. Further the linear regression equation of reduc-tion current vs. concentration calibration plot was found as $Y = -0.732x - 6.138$, with correlation coefficient of 0.9. These results validate the electrocatalytic activity of $Pt_{micro}$/KI film for the direct chromate reduction process. Further the electrochemical reduction of chromate on $Pt_{micro}$/KI film modified GCE might be rationalized as a one-step reduction
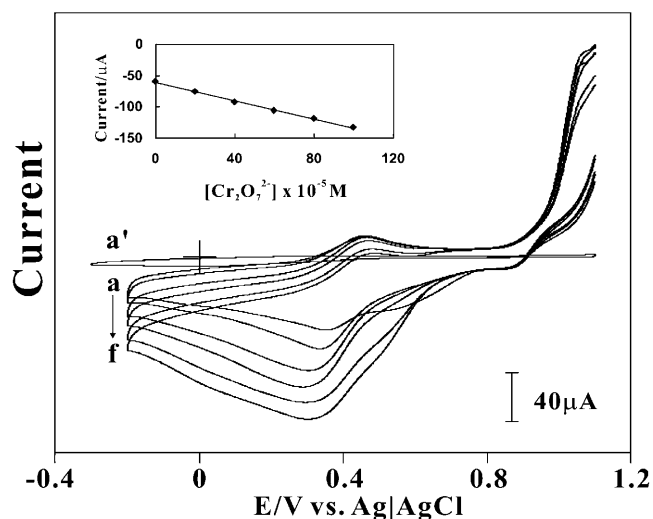
Fig. 6. CVs of $Pt_{micro}$/KI film on GCE in presence of $1 \times 10^{-3}$ M KI in pH 1.5 $H_2SO_4$ with various concentrations of $[Cr_2O_7^{2-}] =$ a) 0, b) $2 \times 10^{-4}$, c) $4 \times 10^{-4}$, d) $6 \times 10^{-4}$, e) $8 \times 10^{-4}$; and f) $10 \times 10^{-4}$ M; a') bare glassy electrode and $[Cr_2O_7^{2-}] = 10 \times 10^{-4}$ M.

of Cr (VI) to Cr(III). Furthermore the repeatability measurements using $Pt_{micro}$/KI film was investigated. As ascertained by experiments with 10 replicates in model solutions containing 5 µM dichromate, the signal of interest at the same electrode surface could be repeated with a relative standard deviation from 2 to 5%. Such diversity may be reasonable and negligible.

## 3.6. Electrocatalytic Oxidation of As(III) at $Pt_{micro}$/KI Film Modified GCE

To examine the electroanalytical performance of $Pt_{micro}$/KI film modified GCE for As(III) oxidation, the cyclic voltammetry was employed. Shown in Figure 7A is the typical cyclic voltammetric response of As(III) addition on Pt microparticles/KI film modified GCE in pH 1.5 $H_2SO_4$ electrolyte solution containing KI. Here the As(III) oxidation was examined in the linear range of $2 \times 10^{-4}$ to $1 \times 10^{-3}$ M, respectively. From the Figure 7A, the curve a' represents the oxidation process of As(III) ($1 \times 10^{-4}$ M) on bare GCE. It can be seen that there was no evident peak observed for As(III) oxidation at bare GCE. At the same time, the anodic peak currents of As(III) oxidation were increased linearly with the additions of As(III) on $Pt_{micro}$/KI film modified GCE. The enhanced oxidation peak current of As(III) clearly indicates the electrocatalytic oxidation process of As(III) at $Pt_{micro}$/KI film modified GCE. Further the calibration plot for the As(III) oxidation (figure not shown) and the linear regression equation was found as $y = 0.3134x - 8.771$, with correlation coefficient of 0.9980. Furthermore the $Pt_{micro}$/KI film modified electrode was finally examined for the As(III) detection by using FIA measurements (Inset of Fig. 7A). Here it is possible to detect the As(III) at very low concentration range on $Pt_{micro}$/KI film
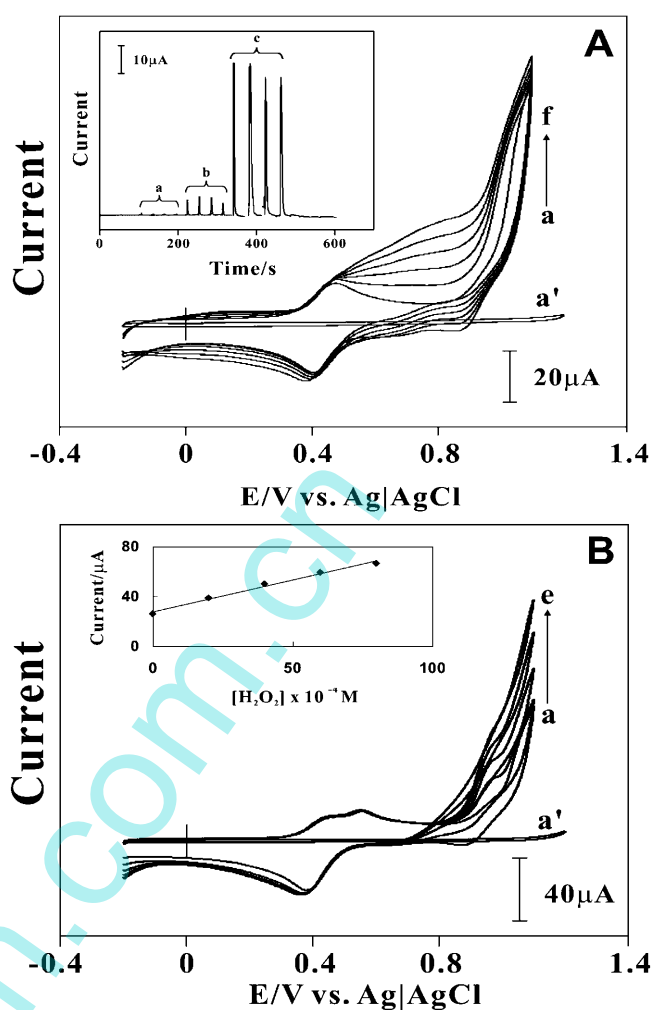




Fig. 7. A) CVs of $Pt_{micro}$/KI film on GCE in presence of $1 \times 10^{-3}$ M KI in pH 1.5 $H_2SO_4$ with various concentrations of $[As(III)] =$ a) 0, b) $2 \times 10^{-4}$, c) $4 \times 10^{-4}$, d) $6 \times 10^{-4}$, e) $8 \times 10^{-4}$, and f) $10 \times 10^{-4}$ M; (a') bare GCE and $[As(III)] = 10 \times 10^{-4}$ M. The inset shows the As(III) detection by using FIA technique. The concentrations were in the range of A) $1 \times 10^{-9}$, B) $1 \times 10^{-8}$, and C) $1 \times 10^{-6}$ M. B) CVs of $Pt_{micro}$/KI film on GCE in presence of $1 \times 10^{-3}$ M KI in pH 1.5 $H_2SO_4$ with various concentrations of $[H_2O_2] =$ a) 0, b) $2 \times 10^{-3}$, c) $4 \times 10^{-3}$, d) $6 \times 10^{-3}$, e) $8 \times 10^{-3}$ M; (a') bare GCE and $[H_2O_2] = 8 \times 10^{-3}$ M.

by using FIA measurements. The FIA measurements were carried out by injecting 12 successive additions of As(III) in different concentration range $1 \times 10^{-8}$ to $1 \times 10^{-6}$ M, respectively. Further the FIA responses increased rapidly just after injection of the sample and returned to baseline within about 5s, shown in the inset of Figure 7A. Here the set A ($1 \times 10^{-8}$ M) FIA signal shows a very little current response for the As(III) detection. However the set B and C shows obvious signals for the As(III) detection for $1 \times 10^{-7}$ and $1 \times 10^{-6}$ M concentrations, respectively. In addition, the reproducibility of the system was very good for 10 successive additions and the RSD was found as 2%. From the above results, the possible detection of As(III) on $Pt_{micro}$/KI film modified GCE in two different techniques were validated.

### 3.7. Electrocatalytic Oxidation of $H_2O_2$ at $Pt_{micro}$/KI Film Modified GCE

Generally, the bare GCE has a very poor activity towards the electrocatalytic oxidation of $H_2O_2$. Thus there is a need of electrochemically modified electrodes which have already shown their enhanced electrocatalytic oxidation of $H_2O_2$. The electrocatalytic oxidation process of $H_2O_2$ on $Pt_{micro}$/KI film modified GCE was investigated by CV. Figure 7B shows the cyclic voltammetric behavior of a bare GCE and the $Pt_{micro}$/KI film electrode in the presence of $H_2O_2$ in pH 1.5 $H_2SO_4$ solutions at the scan rate of 100 mV s$^{-1}$. For the bare GCE (curve a′), no oxidation peak current for $H_2O_2$ was obtained in the potential range of $-0.2$ to 1.3 V. At the same time on $Pt_{micro}$/KI film modified electrode, oxidation peaks are observed (curve a to e, at 1.1 V) which were assignable to the oxidation of $H_2O_2$. Further by adding $H_2O_2$ in the test solution, the oxidation current greatly increased in linear manner. This shows that the $Pt_{micro}$/KI films are suitable mediators to transfer the electron between $H_2O_2$ and the working electrode, to facilitate the electrochemical of oxidation of $H_2O_2$. Here the microsize Pt particles covered GCE surface will exhibit as active sites on electrode surface and made them easier to contact with $H_2O_2$ substrate for the electrocatalytic oxidation process. In addition the modified electrode composed of many microparticles without aggregation could be resulted for the enhanced electrocatalytic oxidation of $H_2O_2$. From the calibration plot (Inset of Figure 7B), the catalytic peak currents are proportional to the concentration of $H_2O_2$ in the range of $2 \times 10^{-3}$ to $8 \times 10^{-3}$ M. The linear regression equation for $H_2O_2$ oxidation was respectively expressed as $y = 0.051x - 2.770$ with the correlation coefficient of 0.9877. From the above results, it can be evaluated that the presence of the $Pt_{micro}$/KI film on GCE facilitates significant detection for $H_2O_2$ reduction.

### 3.8. Repeatability and Stability of the Proposed Electrode

The replicate measurements ($n = 10$) performed with the $Pt_{micro}$/KI film for the given $H_2O_2$ concentration within the linear range displayed high reproducibility (3%). Further the stability of the electrodes was investigated by monitoring the higher concentration of $H_2O_2$ ($1 \times 10^{-3}$ M) solution during for 6 hours. In all of these cases, the current signals appeared were stable (2.0%). These results show that $Pt_{micro}$/KI film modified GCE possess good repeatability and stability.

### 3.9. Selectivity of $Pt_{micro}$/KI Film for $H_2O_2$ Detection

Two interfering substances (acetic acid and L-tyrosine) were used to evaluate the selectivity of the $Pt_{micro}$/KI film. The current ratios were calculated by 1:2 ($H_2O_2$, interfering substance) ratio. From the experimental result it was observed that the error made by each interferent was less than 6%. Further the possible interferences from foreign ions were examined. No interference was observed for ions such as $Na^+$, $K^+$, $CO_3^{2-}$, $SO_4^{2-}$, and $Cl^-$ at concentration two fold higher than that of $H_2O_2$.

## 4. Real Sample Analysis

The practical validation of $Pt_{micro}$/KI film was assessed for the detection of $H_2O_2$ in two different types of real samples such like antiseptic and contact lens cleaner solutions by standard addition method using differential pulse voltammetry. Here differential pulse voltammetric technique has been employed and found as suitable for the detection of $H_2O_2$ in real samples. Further the analysis results have been listed in Table 2. From these analyses results it was concluded that $Pt_{micro}$/KI film have shown good electrocatalytic activity for $H_2O_2$ detection in two different types of real samples, respectively.

## 5. Conclusions

In conclusion, our studies show the successful electrochemical depositions of Pt microparticles and iodide film on different electrodes like GCE, GE, SPCE, and ITO, respectively. Further the EQCM, SEM, and AFM characterization results of $Pt_{micro}$/KI film illustrates the details about the gravimetric and surface morphological analysis of the modified electrode surface. The $Pt_{micro}$/KI film modified electrode could be used for the electrocatalytic reduction reactions such like oxygen, $Cr_2O_7^{2-}$ reduction, by using CV. It also shows the effective electrocatalytic oxidation reactions for As(III), $H_2O_2$ oxidation by using CV and FIA techniques. Further in this proposed film, the presence of Pt microparticles will act as active centers for all the electrocatalytic reactions. Finally from these results, it concludes that the $Pt_{micro}$/KI film modified electrode is efficient for the detection of environmentally hazardous materials and other biologically important compounds, respectively.

Table 2. $H_2O_2$ detection in real samples.

| Sample No. | Real samples | Added (μM) | Found (μM) | Recovery (%) |
|---|---|---|---|---|
| 1. | Contact lens cleaner | 2.0 | 2.1 | 105.0 |
| | | 4.0 | 3.9 | 97.5 |
| 2. | Antiseptic solution | 2.5 | 2.4 | 96.0 |
| | | 4.5 | 4.6 | 102.2 |

## 6. Acknowledgements

## 7. References

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