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Electrochemical Behavior of Iodine on Nano Gold Doped in H_2TiO_3

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In this paper the nano gold doped in H_2TiO_3 were prepared, and the electrochemical catalysis for iodine at the modified electrode was studied. It was demonstrated that when the pH is less than 9, the I^- at the modified electrode can be oxidized to be I_2 and then IO_3^-, and the reduction peaks of I_2 and IO_3^- at the modified electrode were also found; when the pH is more than 9, the I^- is oxidized to be IO_3^- directly, and the reduction product of IO_3^- at the modified electrode is I^-.

Keywords: nano gold, H_2TiO_3, iodine, catalysis

1. INTRODUCTION

The metatitanic acid (H_2TiO_3) like hydrous titania, has weak acid properties, but it sorbs hydrolysable multicharged cations from aqueous solutions, thus H_2TiO_3 is a perspective sorbent for extraction of multivalent elements from aqueous solutions. H_2TiO_3 was successfully prepared from lithium metatitanate Li_2TiO_3 through exchange of lithium cations for hydrogen ions in acetic acid [1].

Nano-Au and its composites have been extensively utilized in recent years, owing to their extraordinarily catalytic activities [2-5]. Taking account of the advantages of Nano-Au and porous-H_2TiO_3, depositing Nano-Au on matrix of sorbent H_2TiO_3 will be a promising composite.

Iodine is one of the essential trace elements for human body, which is an "Intelligence element". Iodine plays an important physiological role in the human body. The iodine can promote biological oxidation, adjust the protein synthesis and decomposition, promote the metabolism of sugar and fat, adjust the water and salt metabolism, promote the absorption of vitamin, enhance the enzyme activity, promote growth and development and maintain the normal structure of the central nervous system. However, the excessive iodine can also cause hyperthyroidism [6]. One of the best and least expensive methods of preventing iodine deficiency disorder is by simply iodizing table salts, which is currently done in many countries [7]. The forms of iodine not only control the content in food and food cooking but also influence to the physiological function in human body. Therefore, to control the content and forms of iodine in food is very important and meaningful.

In present work, the electrochemical sensor was prepared with gold electrode (GE) modified by the Au@H_2TiO_3, and the electrochemical behavior of iodine at the modified electrode was studied.

2. EXPERIMENTAL

2.1. Regents

KI was purchased from Aldrich. 0.1 mm titanium foil was obtained from Guoyao Co., Ltd. (China). Double-distilled water was used throughout. 0.1M phosphate buffer solution (PBS) was prepared by dissolving 0.1mol NaCl and 0.1mol Na_2HPO_4 in the double-distilled water of 1000mL and adjusted desired pH values with 6 mol.L^{-1}HCl or 1mol.L^{-1}NaOH. 0.5 M Na_2SO_4-0.2 M NaF aqueous solution was prepared for the synthesis of H_2TiO_3. All reagents were analytical grade.

2.2. Instrument and Characterization

For all electrochemical experiments a CHI660D Electrochemical Analyzer (CHI, USA) was employed. The electrochemical cells consisted of a three electrode, a 3 mm GE modified by Au@H_2TiO_3 was used as working electrode. A platinum wire and a Ag/AgCl(3M KCl) electrode were served as the counter electrode and the reference electrode, respectively. The synthetic material was characterized by scanning electron microscopy (SEM) (QUANTA FEG 450, USA.) with energy dispersive spectrometer (EDS) (QUANTAX 400, Bruker, German), and UVspectrophotometer (UV-1750, Shimadzu, Japan). Powder X-ray diffraction (XRD) spectra were recorded on a Switzerland ARL/ X‘TRA X-ray diffractometer rotating anode with Cu-Ka radiation source (l = 1.54056 Å). IR spectra were measured by a NICOLET NEXUS470 spectrometer in the frequency range 4,000–400 cm^{-1}. The electrochemical impedance spectroscopy (EIS) was measured at the open-circuit potential over the frequency range of 10^5 to 0.02 Hz with an a.c. amplitude of 5 mV.

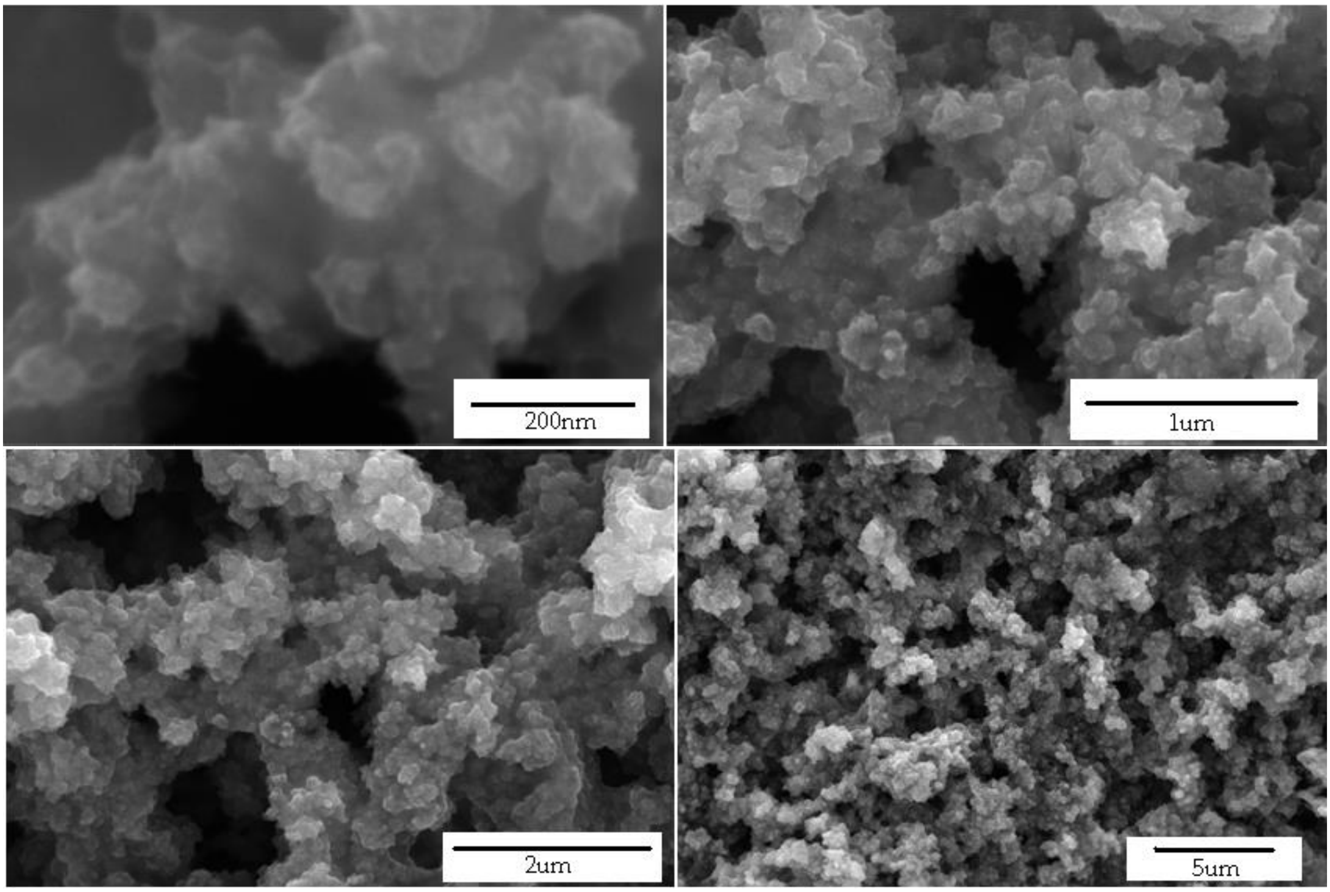
2.3 Prepared modified electrode

H_2TiO_3 was prepared by anodic oxidation of 0.1 mm×2cm×3cm titanium foil in the aqueous solution containing 0.5M Na_2SO_4-0.2M NaF. Prior to any electrochemical treatment, the titanium foil was sonicated in ether, ethanol and then in distilled water for 10 min each. Anodic oxidation was carried out in a stirred electrochemical cell working at room temperature. To drive the anodization a DC power supply was used whereas to record the resulting current a multimeter was employed. The applied anodic oxidation potentials at 30 V for 6 h were maintained constant during the anodization.

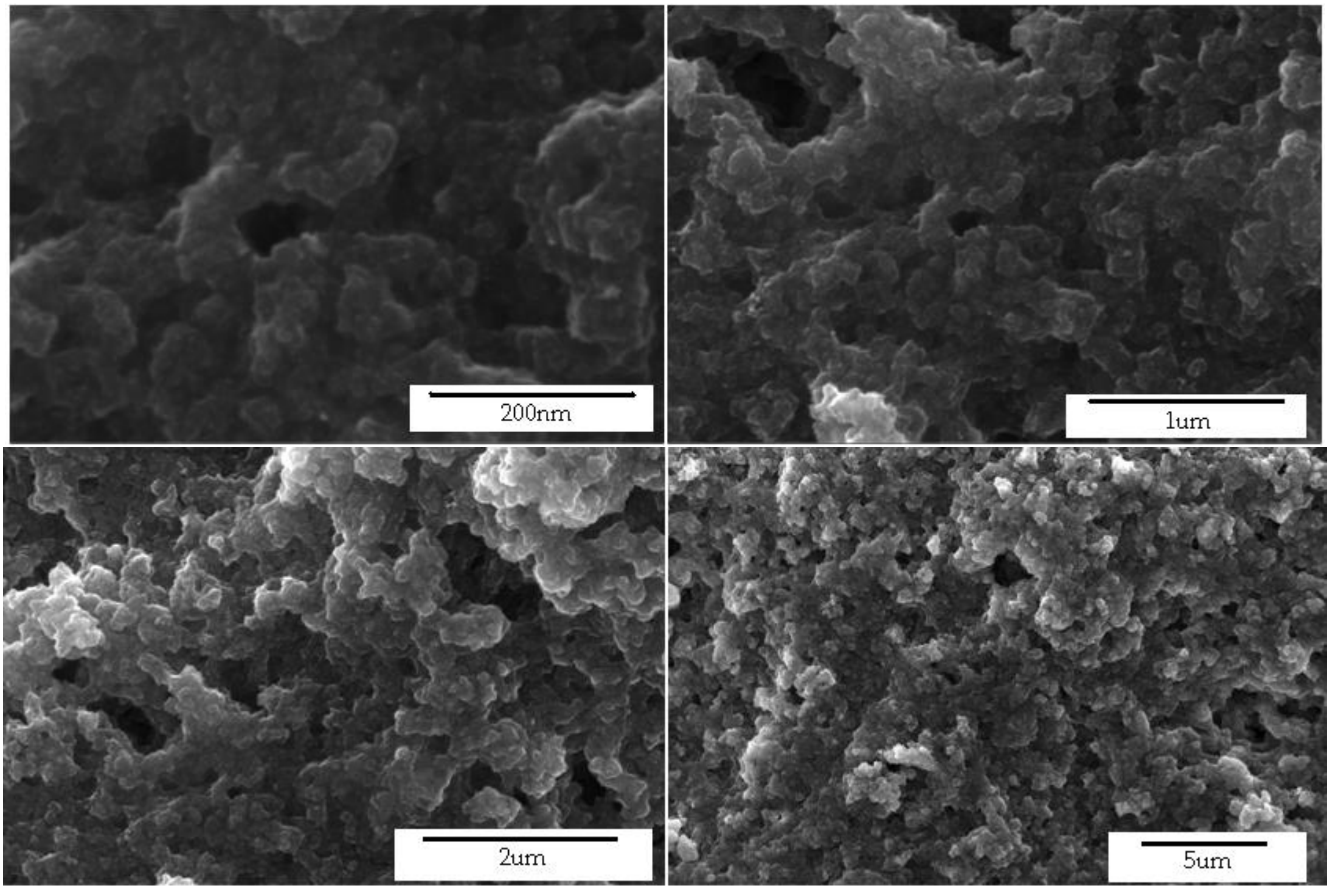
Thus the white H_2TiO_3 was obtained. The H_2TiO_3 was washed with distilled water and ethanol, respectively, and tried in atmosphere at 60℃. 0.150 g of $NaBH_4$ were dissolved in the mixture of 10 ml containing 1.0 $mg{\cdot}mL^{-1}$ $HAuCl_4$, 0.005M Na_2CO_3 and 1.0 $mg{\cdot}mL^{-1}$ H_2TiO_3. The mixture was stirred with a magnetic stirrer for 10 min to ensure that the $NaBH_4$ completely dissolved; the red and white Au@ H_2TiO_3 were soon produced, and followed by centrifugal separation, washing with distilled water and absolute alcohol, respectively, and then drying in vacuum at 40 °C for 6 h. The modifier suspension was prepared by dispersing the 10.0mg Au@ H_2TiO_3 in 10.0 ml of ethanol under sonication for 10 min. The Au@ H_2TiO_3 modified GE was prepared by casting 2μl of the mentioned above red and white suspension on the surface of GE using a micropipette and left to dry at room temperature. Before the voltammetric measurements, the modified electrode was cycled between -1 and 1 V (scan rate 100 mV. s^{-1}) in 0.1 M phosphate buffer solution (PBS) for several times until acquiring the reproducible responses. In order to compare with the response of iodine at H_2TiO_3/GE, the H_2TiO_3/GE is also prepared with the H_2TiO_3 at same method.

3. RESULTS AND DISCUSSION

3.1 SEM imagine and EDS pattern of Au@H_2TiO_3



A



B

Figure 1. SEM imagines of H_2TiO_3 (a) and Au@H_2TiO_3 (b)

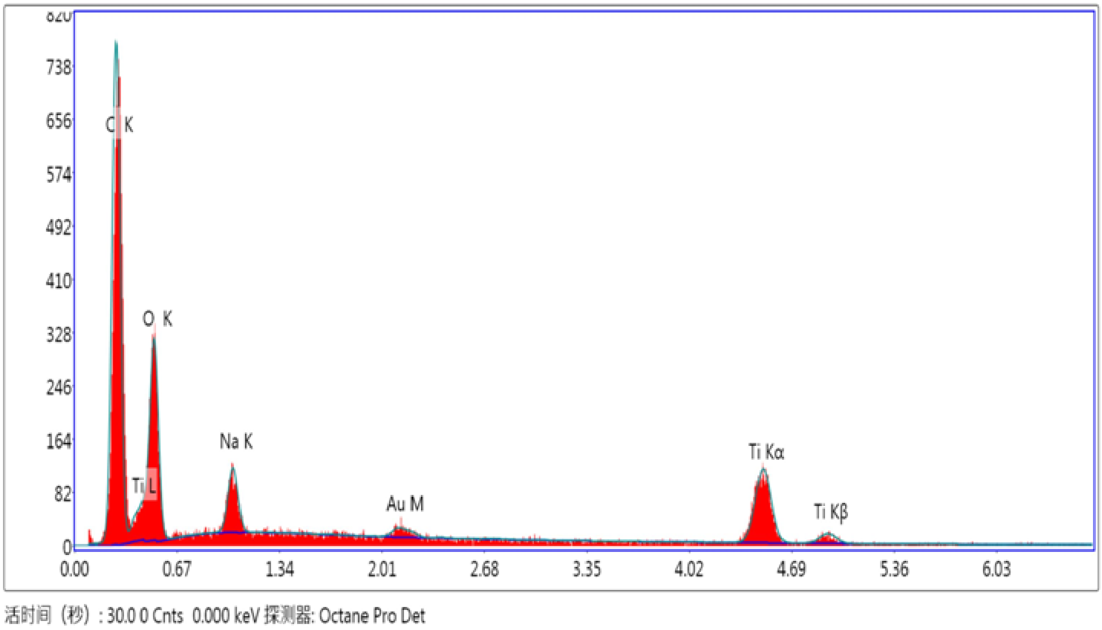


Figure 2. EDS pattern of Au@H_2TiO_3

SEM is applied to confirm the formation of a layer of the film on the surface of bare GE. The SEM imagines of Au@H_2TiO_3 and H_2TiO_3 on the surface of GE are shown in Fig.1, the sheet H_2TiO_3 and faveolate Au@H_2TiO_3 were observed.

EDS pattern and element analysis are shown in Fig.2 and Table 1, respectively. It can be seen that the Mole ratios of Ti and O and Na for Au@H_2TiO_3 on the carbon carrier are 1: 0.40: 3.24, and the molecular formula can be deduced as $H_{1.7}N_{a0.30}TiO_3$, indicating that some H^+ in H_2TiO_3 were replaced by the Na^+.

Table 1. Composition and distribution of element for Au@H_2TiO_3

Element	Weight%	Atom%	Intensity	Error %
C K	38.29	56.91	335.59	6.38
O K	25.29	28.22	141.29	11.07
Na K	4.46	3.46	51.42	10.71
Au M	1.82	0.16	9.14	12.97
Ti K	30.15	11.24	96.77	7.07

3.2 XRD pattern of Au@H_2TiO_3

The powder XRD pattern of the H_2TiO_3 and Au@H_2TiO_3 is shown in Fig. 3. Compared with H_2TiO_3, the major diffraction peaks can be indexed as the gold face centered cubic (fcc) phase based on the data of the JCPDS file (JCPDS no. 04-0784). The peaks appeared at 39.0°, 47.4° and 62.9°can be assigned to (111), (200) and (220) crystalline plane diffraction peaks of gold, respectively [8].

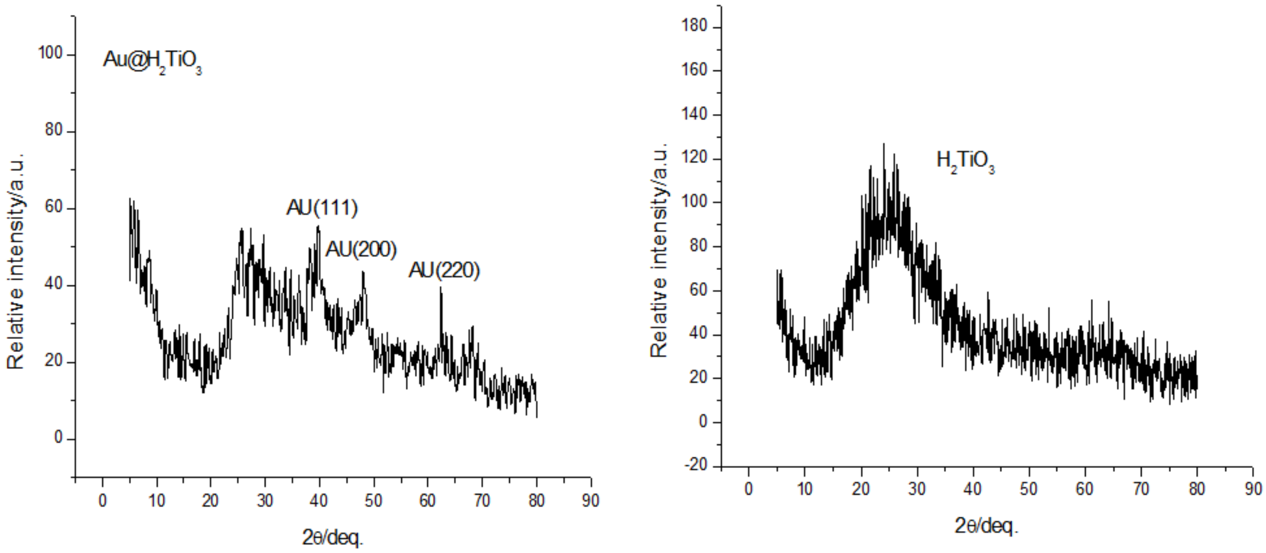


Figure 3. XRD pattern of the Au@H_2TiO_3 and H_2TiO_3

The UV spectrum of Au@H_2TiO_3 is shown in Fig. 4, a band centered at ca. 552 nm appears, characteristic of surface plasmon absorption on the nano Au [9].

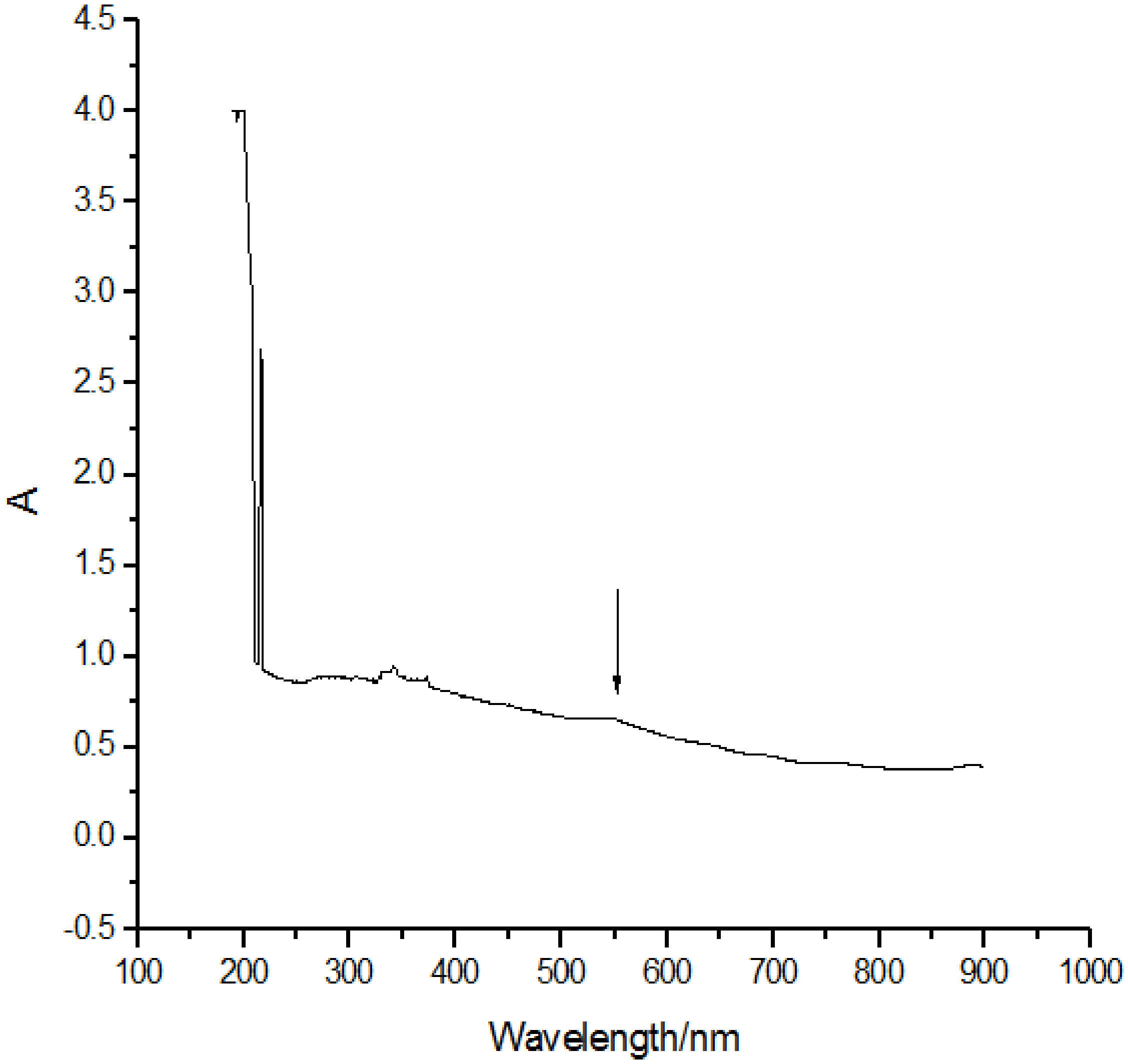


Figure 4. UV spectra of Au@H_2TiO_3

3.3 IR spectrum of Au@H_2TiO_3

IR spectrum of Au@H_2TiO_3 and H_2TiO_3 are shown in Fig. 5, the peaks at 3417cm^{-1} could be assigned to the stretching vibration of –OH, and the bands of 1620 and 1547 cm^{-1} and Ti-O corresponding to stretching vibration of Ti-O were also observed. The similar stretching vibrations of H_2TiO_3 were found. However, the peaks at 1007and 891 cm^{-1}for H_2TiO_3 disappeared in Au@H_2TiO_3, and the peak at 817 cm^{-1} for H_2TiO_3 shifted to 806 cm^{-1} in Au@H_2TiO_3 due to the absorption of nano gold.

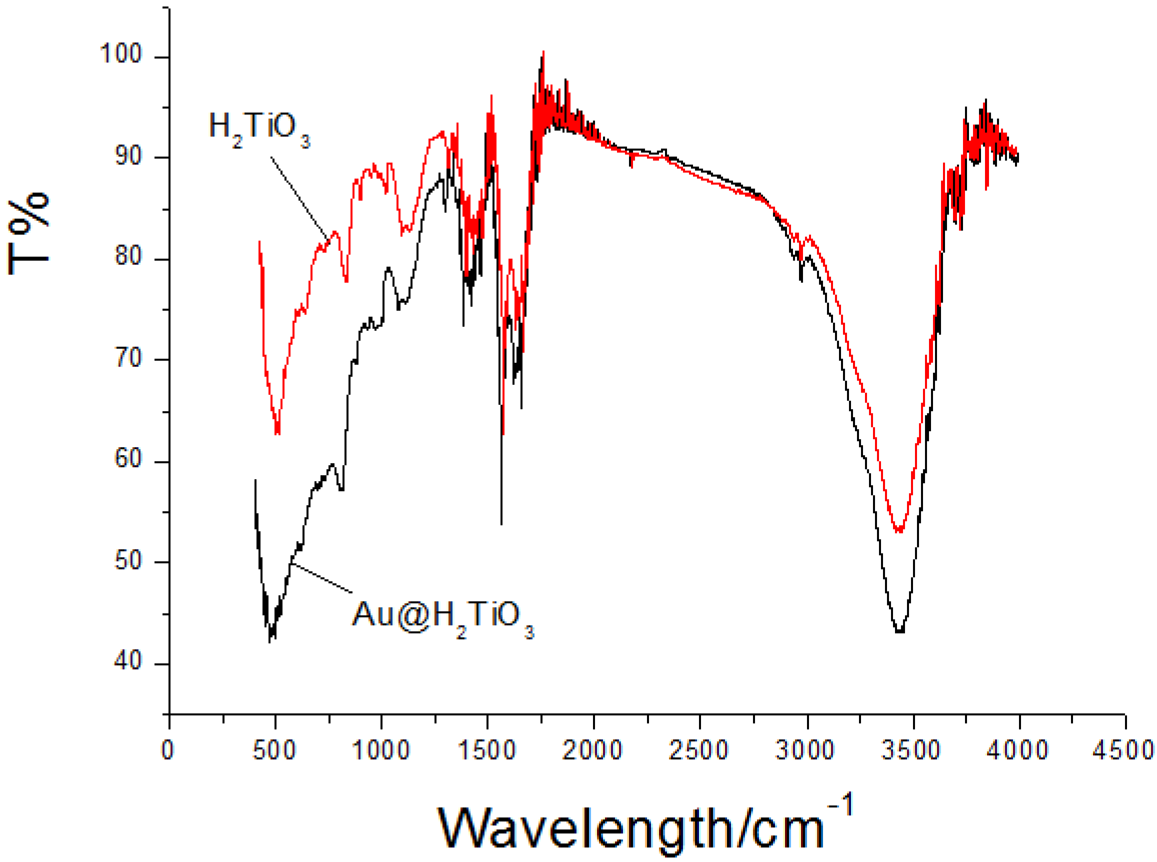


Figure 5. IR spectra of Au@ H_2TiO_3 and H_2TiO_3

3.4 EIS of Au@H_2TiO_3

EIS is an effective way to measure the electron-transfer resistance. EIS measurements were carried out at bare, H_2TiO_3 and Au@H_2TiO_3 composite film modified GE and the results are shown in Fig. 6. The supporting electrolyte used was 0.1KCl containing 5mM $Fe(CN)_6^{3-/4-}$. The semicircle portion observed at higher frequencies in a Nyquist plot corresponds to electron-transfer-limited process and diameter of the semicircle corresponds to interfacial electron-transfer resistance (Ret). Linear part of the spectrum is characteristic of lower frequency range and represents diffusional-limited process [10]. In Fig. 6, the EIS of GE implied the redox of $Fe(CN)_6^{3-/4-}$ at bare GE was controlled by the diffusional-limited process. After a modification with H_2TiO_3 layer, the electron-transfer resistance reached a higher value (curve b, *R*et =2.04KΩ), however, the modification of nano Au@H_2TiO_3 film modified electrode reached a lower value of electron-transfer resistance (curve c, *R*et =1.07KΩ), indicated that the high conductivity of Au@H_2TiO_3 film increases the electrical properties of the redox processes.

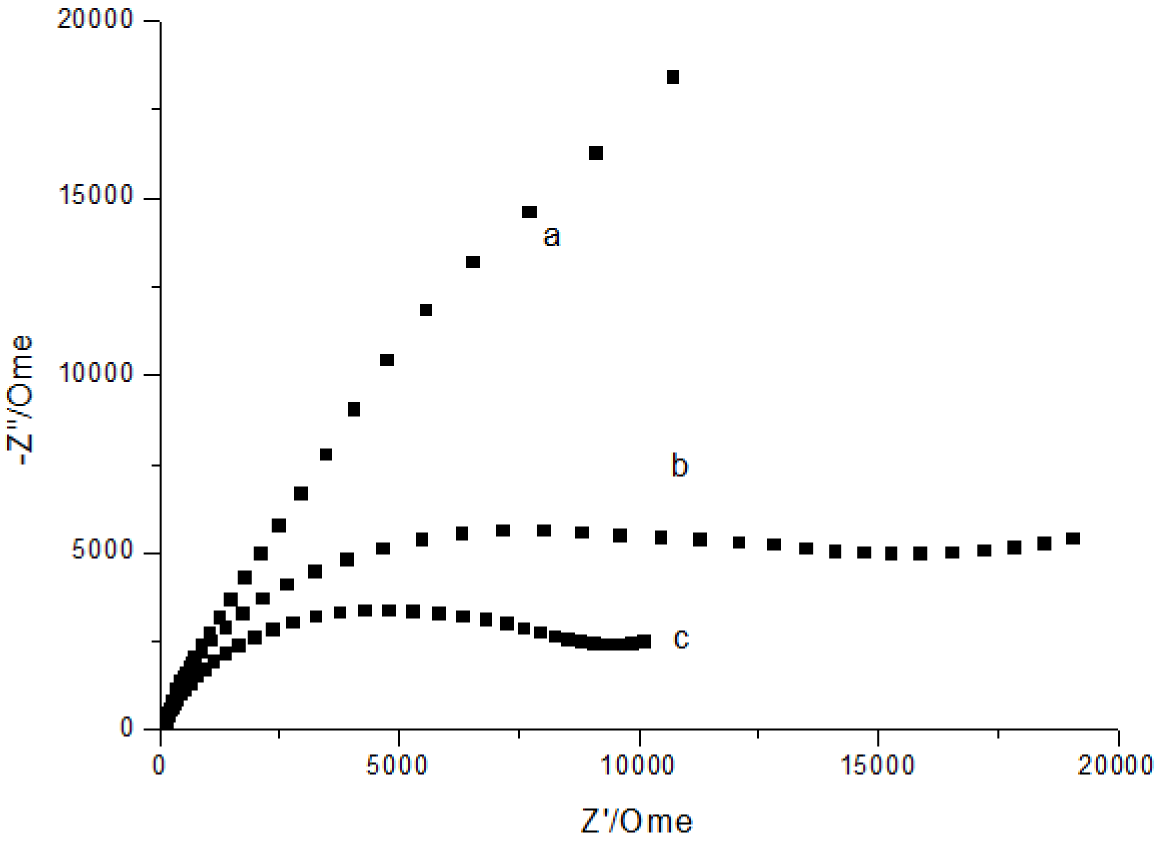
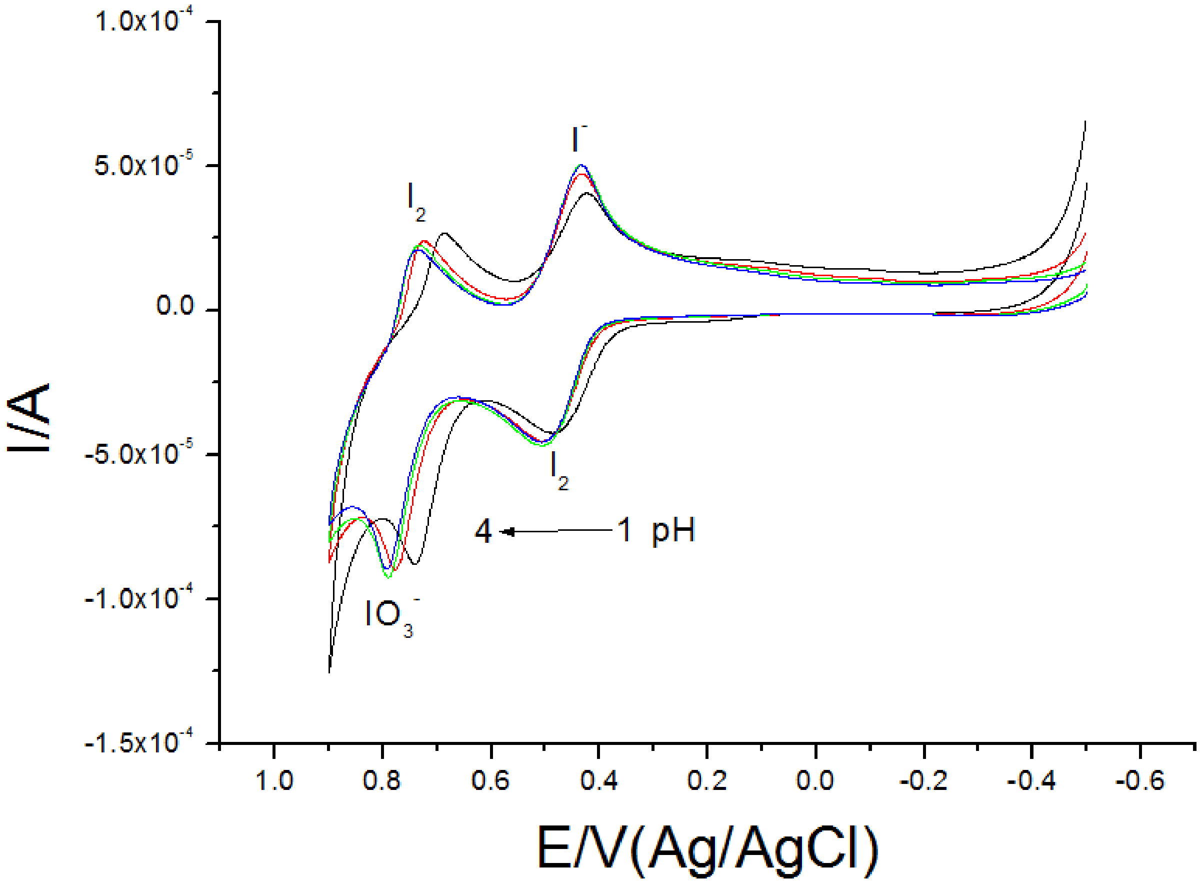
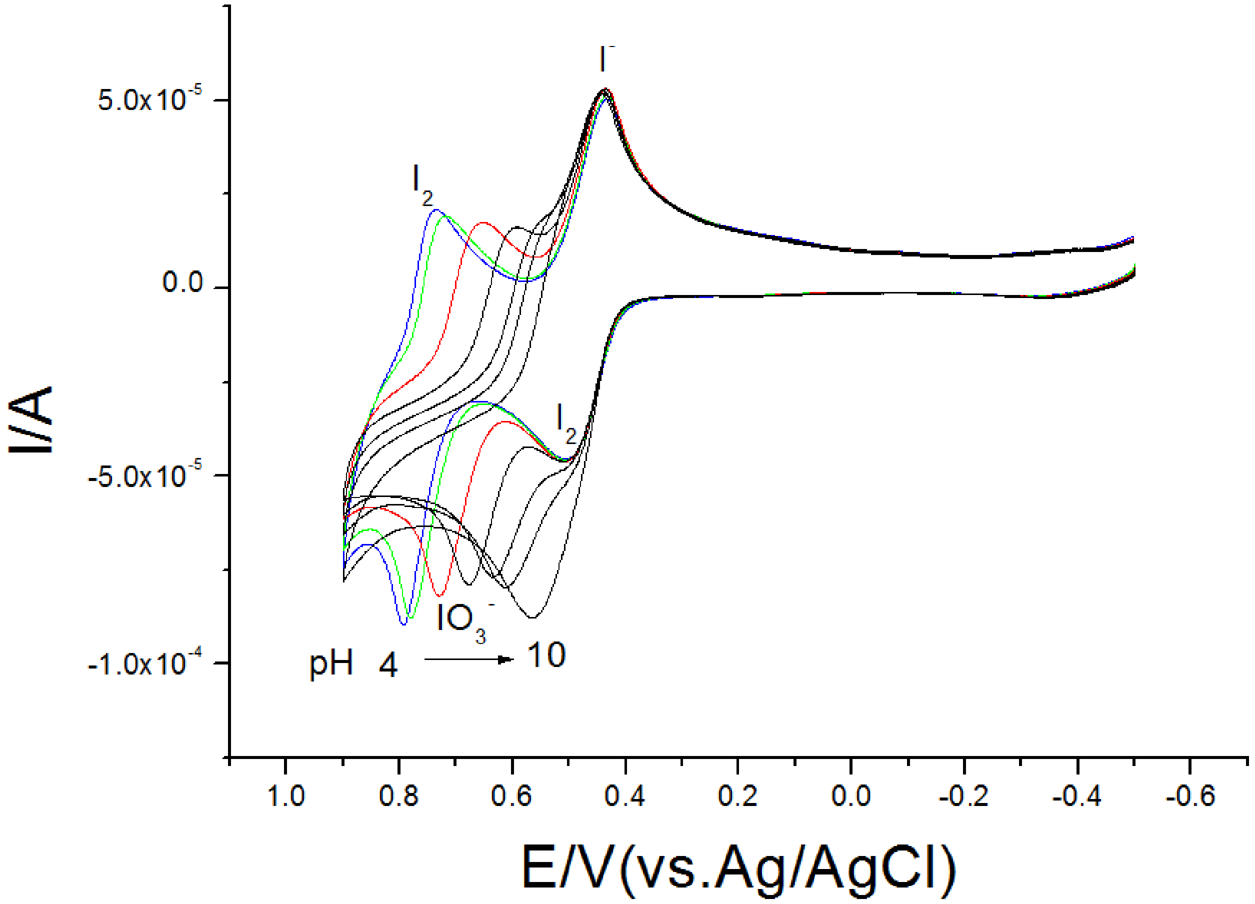


Figure 6. Electrochemical impedance spectra of (a) bare GE, (b) H_2TiO_3/GE and (c) Au@H_2TiO_3/GE in 5 mM $[Fe(CN)6]^{3-/4-}$ +0.1M KCl.

3.5 Behavior of iodine at Au@H_2TiO_3/GE

The influence of pH on the electrochemical behavior of iodine at Au@H_2TiO_3/GE in PBS was investigated at different pH values in the range of 1.0 to 13.0. Fig. 7 shows the CVs of 1.0×10^{-3} M iodine on the surface of the modified electrode over the discussed pH range at scan rates of 100 mV.s^{-1}. Two couple of redox peaks in the range of pH 1～8 were observed, the stable oxidation peak was found at about 0.500 V, and the reduction peak appeared at 0.430V, which could be ascribes the redox peaks of I^-/I_2.It was found that another oxidation peak potential shifted negatively with pH increasing and a good linear relationship was observed between the Ep and pH values in the range of 5.0 to 10.0, and a equation is obtained as Ep(V) =-0.04495 pH+1.00625 with the correlation coefficients (R) of -0.99645 in Fig. 8, which could be ascribe to the reaction of $I_2+3H_2O=2IO_3^-+6H^++10e^-$, and a value of about -44.85 mV per pH unit indicates that reaction of 10 electrons and 6 protons are involved in the electro-reduction of iodine on the surface of the modified electrode. When the pH is more than 9, the oxidation peak at 0.500 V disappeared, indicating that the I^- at the modified GE was transformed into IO3$^-$. The oxidation mechanisms was consistent with that reported by others [11–15].


1.0x10^-4
5.0x10^-5
0.0
-5.0x10^-5
-1.0x10^-4
-1.5x10^-4
I/A
I^-
I2
I2
4 ← 1 pH
IO3^-
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
E/V(Ag/AgCl)


5.0x10^-5
0.0
-5.0x10^-5
-1.0x10^-4
I/A
I^-
I2
I2
IO3^-
pH 4 → 10
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
E/V(vs.Ag/AgCl)

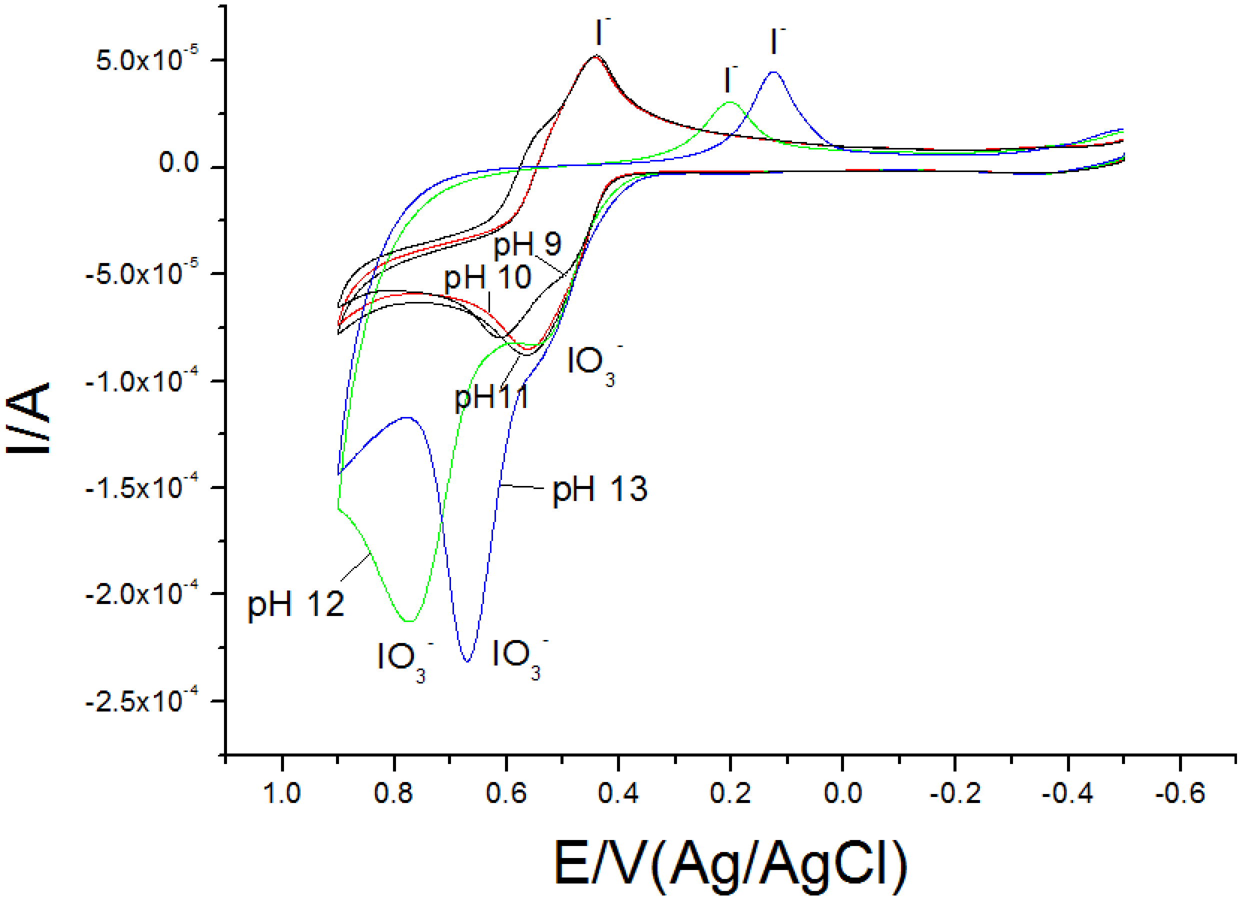


Figure 7. CVs of 1.0×10^{-3} M iodine in the range of pH 1.0～13.0; Scan rate:100mV/s; Supporting electrolyte: 0.1 mol L^{-1} PBS.

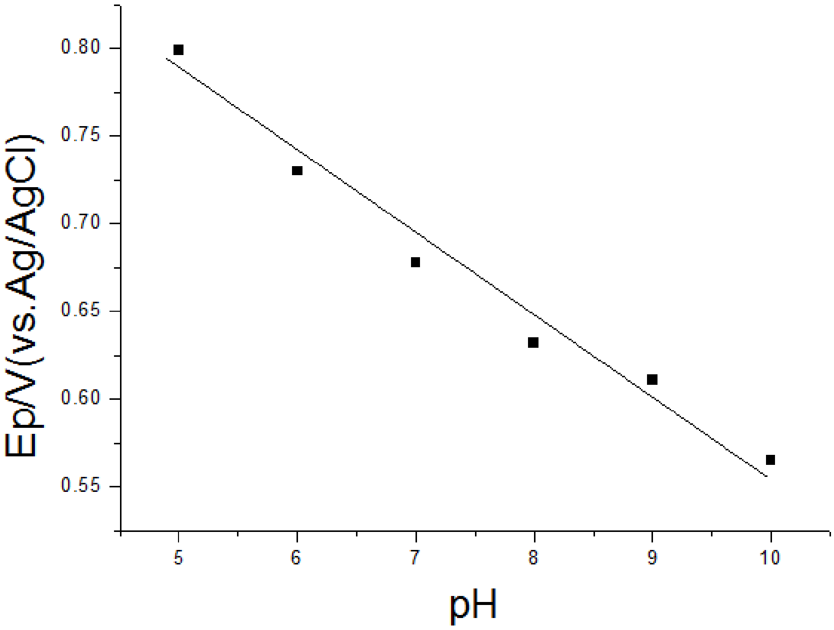


Figure 8. Plot of the peak potential against pH

The electrochemical response of iodine at the modified electrode in 0.1 M PBS of pH 13 is shown in Fig.9. The oxidation peaks of H_2TiO_3/GE and Au@H_2TiO_3/GE were found at 0.605 and 0.580V, respectively, the oxidation currents of Au@H_2TiO_3/GE are more than that of H_2TiO_3/GE, and the reduction peaks corresponding to the oxidation peaks were 0.077 and 0.093V, respectively. An oxidation peak for iodine at Au@H_2TiO_3/GE was observed at 0.672V, and a weak reduction peak appeared at 0.127V. The similar peaks of iodine at H_2TiO_3/GE were observed, however, their peak currents decrease. These results indicated that the Au@H_2TiO_3 modified electrode markedly promoted the electrochemical redox of iodine by considerably accelerating the rate of electron transfer due to the functional groups of Au@H_2TiO_3.

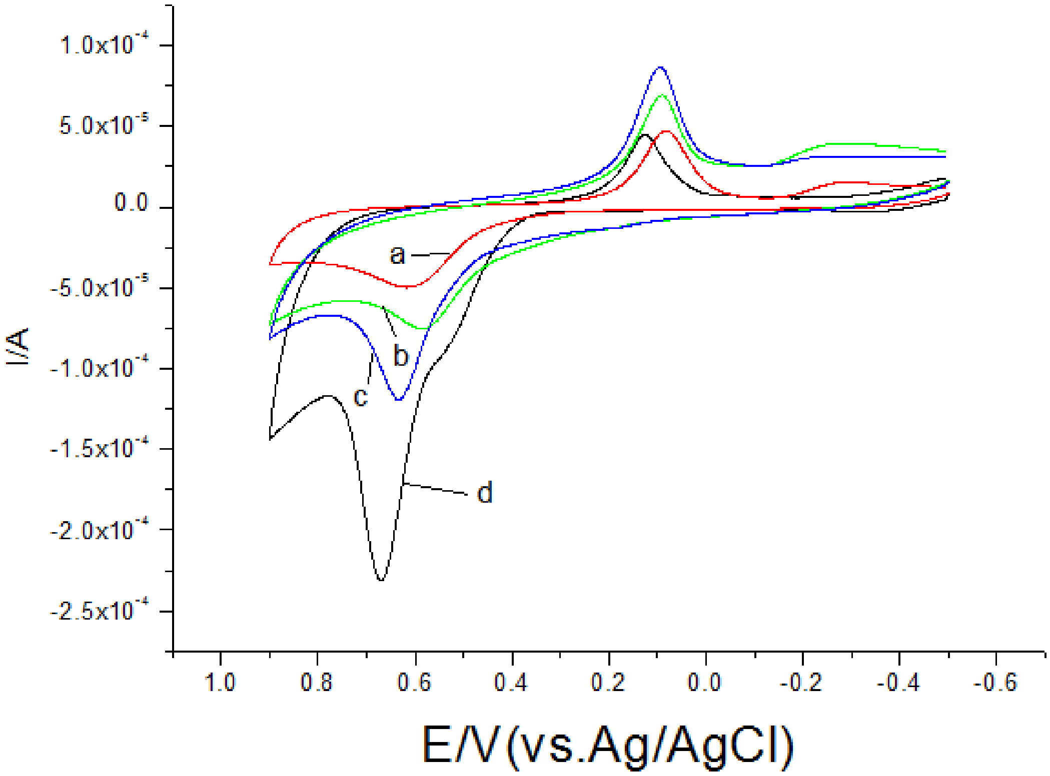


Figure 9. CVs of H_2TiO_3/GE（a）Au@H_2TiO_3/GE（b）and 1.0×10^{-3} M I^- at H_2TiO_3/GE（c）and Au@H_2TiO_3/GE （d）. Scan rate: 100.0 mV. s^{-1}. Supporting electrolyte: 0.1 mol L^{-1} PBS of pH 13.

The information involving electrochemical mechanism usually can be obtained from the investigation of CVs in the different potential sweep rates. Therefore, the CV investigations for 1.0×10^{-3} M iodine were performed on the surface of the Au@H_2TiO_3/GE in PBS of pH 13.0 at different potential sweep rates. Fig. 10 illustrates the influence of scan rate on the CVs of 1.0×10^{-3} M iodine in the range of 10 to 1000 mV.s^{-1}. Two regression equation for the relationship between the peak potentials and scan rate (ν) were obtained as $Ep_1(V)=3.80179\times10^{-4}\ \nu$ (mV/s)+0.65086 with the R values of 0.99183 and $Ep_2(V)=7.1\times10^{-5}\ \nu$ (mV/s)+ 0.71273 with the R values of 0.98496, and the condition potentials (E^{of}) were 0.614V (vs.Ag/AgCl), according to Nernst' equation the standard potentials were calculated to be 0.740V (vs.Ag/AgCl) and 0.968V(vs.SHE), which is close to the standard potentials of 1.085V for IO_3^-/I^- [16].

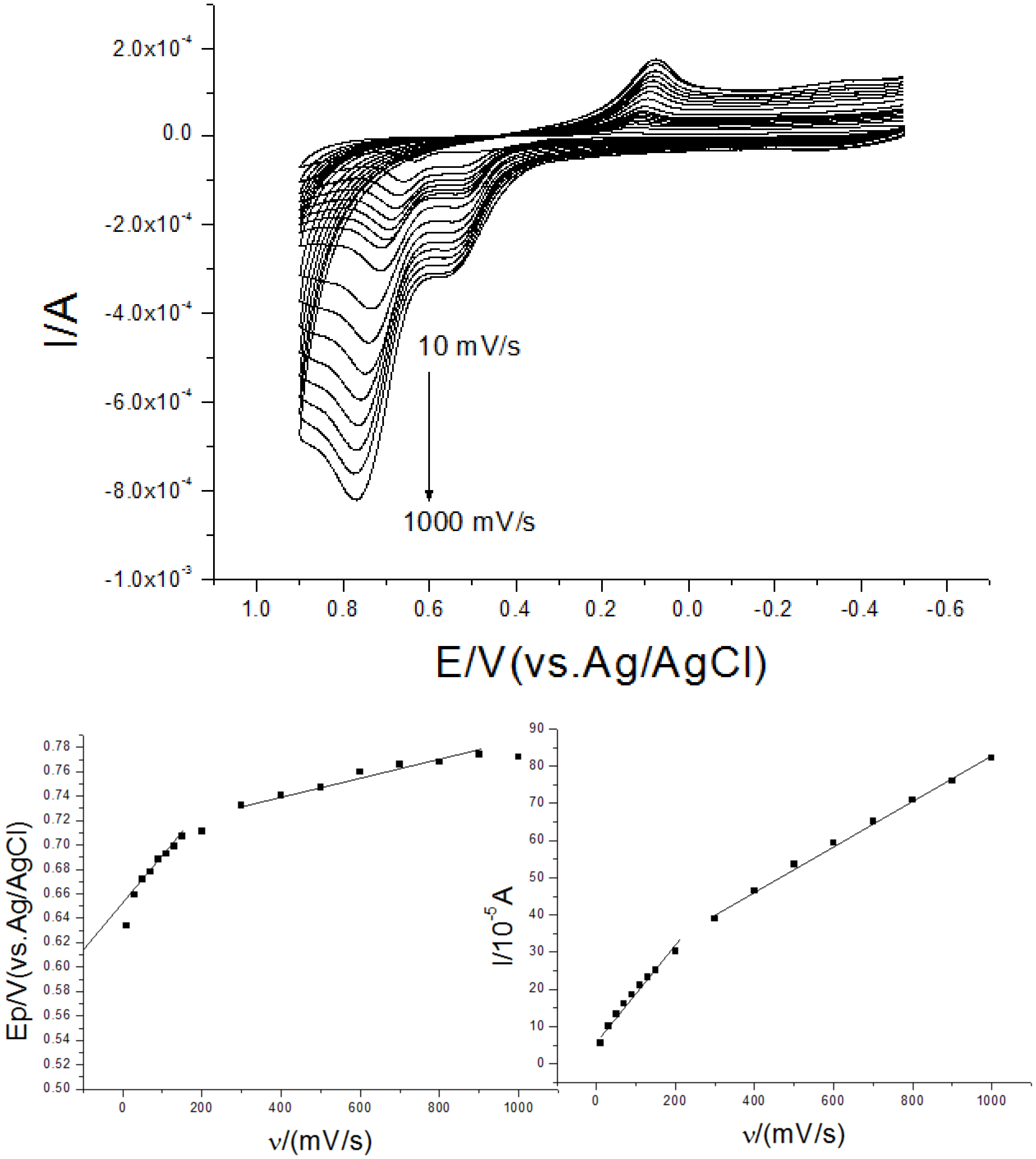


Figure 10. Influence of scan rate on the CVs of 1.0×10^{-3} M iodine; Supporting electrolyte: 0.1 mol L^{-1} PBS of pH 13.0.

Two regression equation for this relationship is obtained as $I(\times10^{-5}A)= 0.12643\ \nu$（$mV.s^{-1}$）$+6.39923$ with the R values of 0.99034 and $I(\times10^{-5}A)= 0.06037\ \nu$（$mV.s^{-1}$）$+22.3806$ with the R values of 0.99834, indicating a mixed adsorption-diffusion controlled process on the surface of the modified electrode.

The relationship between the oxidation current and the concentration was examined by CVs of iodine at Au@H_2TiO_3/GE in 0.1M PBS, and the results were shown in Fig.11. Under the previous conditions, the oxidation peak currents were proportional to iodine concentrations over two intervals in the range of 2.00×10^{-5} to 3.60×10^{-4} M and 3.6×10^{-4} to 1.68×10^{-2} M in 0.1 M PBS of pH 13.0. Two linear regression equations were obtained as I($\times10^{-5}$A)= 0.23723 c+8.83812 （2×10^{-6}M, R=0.99078) and I($\times10^{-5}$A)= 0.0068c+ 16.91108（2×10^{-6}M, R= 0.9904), respectively. The I^- in the range of 2.00×10^{-5} to 3.60×10^{-4} M at the modified GE in PBS of pH 13 was transformed into IO_3^-. However, when the concentration of I^- in PBS of pH 13 is more than 3.60×10^{-4}, a oxidation peak was found at 0.443 V, indicating that the I- was transformed into I_2 at the modified GE. The linear range of I^- in the 1 M $NaClO_4$ on the boron doped diamond electrodes was 0.2 ～0. 8mM [17], the sensitivity is less than that of this work.

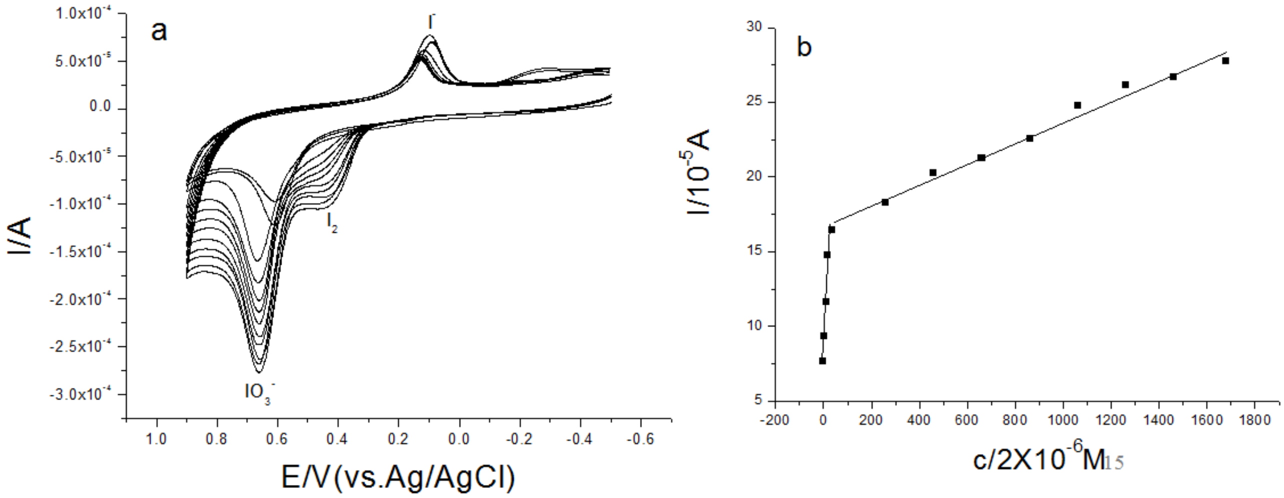


Figure 11. CVs of different concentration iodines (a) and plot of the peak currents against the concentration (b); Scan rate: 100mV/s; Supporting electrolyte: 0.1 mol L^{-1} PBS of pH 13.0.

4. CONCLUSIONS

In present work, the H_2TiO_3 was prepared by the anodic oxidation of titanium foil in the aqueous solution containing 0.5M Na_2SO_4-0.2M NaF. It was demonstrated that modification of GE with the Au@H_2TiO_3 is a simple and effective method for obtaining highly sensitive electrodes for determination of iodine forms. When the pH is less than 9, the I^- at the modified GC can be oxidized to be I_2 and then IO3$^-$, and the reduction peaks of I_2 and IO_3^- were also found; when the pH is more than 9, the I^- is oxidized to be IO_3^- directly, and the reduction product of IO_3^- at the modified GE is I^-.

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