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Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Interaction between gold (III) chloride and potassium hexacyanoferrate (II/III)—Does it lead to gold analogue of Prussian blue?

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ARTICLE INFO

Article history:

Received 29 December 2010

Received in revised form 12 April 2011

Accepted 13 April 2011

Available online 27 April 2011

Keywords:

Prussian blue

Interaction

Potassium ferrocyanide

Potassium ferricyanide

Gold (III) chloride

ABSTRACT

Prussian blue analogues are a class of compounds formed by the reaction between metal salt and potassium hexacyanoferrate (II/III). In our earlier report, the formation of Au@Prussian blue nano-composite was noticed on potential cycling the glassy carbon electrode in a medium containing gold (III) chloride and potassium hexacyanoferrate (III). Hence in this work, the formation of gold hexacyanoferrate was attempted by a simple chemical reaction. The reaction of gold (III) chloride with potassium hexacyanoferrate (II/III) was examined by UV–Vis spectroscopy and found that there is no redox reaction between gold (III) chloride and potassium hexacyanoferrate (III). However, the redox reaction occurs between gold (III) chloride and potassium hexacyanoferrate (II) leading to the formation of charge transfer band and the conversion of hexacyanoferrate (II) to hexacyanoferrate (III) was evidenced by the emergence of new absorption peaks in UV–Vis spectra. The oxidation state of gold in Au–Fe complex was found to be +1 from X-ray photoelectron spectroscopy. The stability of the Au–Fe complex was also studied by cyclic voltammetry. Cyclic voltammetric results indicated the presence of high spin iron in Au–Fe complex. Hence ‘as formed’ Au complex may be $\text{KFe}_x[\text{Au}(\text{CN})_2]_y$. The results revealed that the formation of gold hexacyanoferrate was not feasible by simple chemical or electrochemical reaction in contrast to other Prussian blue analogues.

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1. Introduction

Prussian blue (PB) was the first synthetic co-ordination compound having history for more than three centuries. This compound is still considered ‘hot’ in research because of its interesting ionic, electronic and electrochemical properties [1–4]. Various PB analogues are formed by precipitation of ferrocyanide ion with the transition metal ions like Co(II), Ni(II), Zn(II), Cd (II), Cu(II), Ag(I) etc., [5]. These PB analogues were also formed as thin films by electrochemical potential cycling of electrodes in a medium containing potassium ferricyanide and corresponding metal salts [6]. Among group IB metals, Cu and Ag analogues could be formed electrochemically on solid electrodes [7,8]. However Au analogue of PB could not be formed on glassy carbon (GC) electrode by electrochemical cycling in medium containing potassium ferricyanide and gold chloride. Instead it leads to the formation of Au–PB nanocomposite. The mechanism leading to the formation of Au–PB nanocomposite was studied in great detail by Senthil et al. [9]. Au nanoparticles have been used as catalyst in the electron transfer reaction between potassium ferrocyanide and thiosulfate [10] or borohydride [11].

However to the best of our knowledge, interaction between gold (III) chloride and either potassium ferrocyanide or ferricyanide has not been studied in detail. Liu et al. [12] reported the formation of Pt analogue on GC electrode by reacting potassium ferricyanide with chloroplatinic acid. Pt analogue formed on GC was characterized by the surface redox process occurring at 0.77 V (vs saturated calomel electrode) due to redox transition of low spin Fe (II/III). In this work, we have studied the interaction between the gold (III) chloride and potassium ferrocyanide or ferricyanide in the absence of electrochemical cycling. We found the reaction of gold (III) chloride with either potassium ferricyanide or ferrocyanide on GC led to the formation of PB in the former and a different charge transfer complex involving Fe (II)/(III) and Au(I) in the later case. We present here, the different mechanistic pathways of the chemical reaction between gold (III) chloride and potassium ferrocyanide or ferricyanide in detail. The two pathways of reaction were deciphered at using Ultraviolet–Visible (UV–Vis), X-ray photo electron spectroscopy (XPS) and cyclic voltammetry.

2. Experimental

HAuCl_4 (Sigma–Aldrich), $\text{K}_3[\text{Fe}(\text{CN})_6]$, $\text{K}_4[\text{Fe}(\text{CN})_6]$ (E–Merck) and NaBH_4 (Sigma–Aldrich) Analar grade were purchased. UV–Vis absorption spectra were collected using Cary 500 scan UV–Vis

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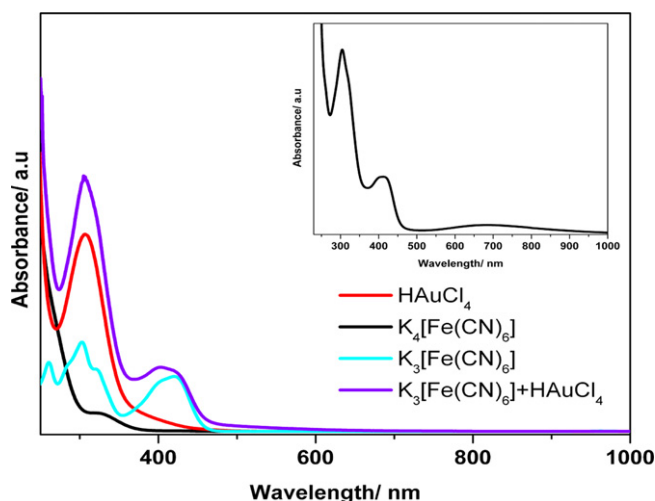


Fig. 1. UV-Vis spectra of 1 mM HAuCl_4 , $\text{K}_4[\text{Fe}(\text{CN})_6]$, $\text{K}_3[\text{Fe}(\text{CN})_6]$, $\text{K}_3[\text{Fe}(\text{CN})_6] + \text{HAuCl}_4$. Inset: $\text{K}_4[\text{Fe}(\text{CN})_6] + \text{HAuCl}_4$.

spectrophotometer with incident light normal to the 1 cm path length quartz cell. XPS was done by forming a thin film of charge transfer complex by drop casting 10 μl of 10 mM each of potassium ferrocyanide and gold chloride on 1 cm \times 1 cm non-conducting glass slide and analysed using the Multilab 2000 (Thermoscientific, UK) photoelectron spectrometer fitted with a twin anode X-ray source. 10 μl of 0.1 M NaBH_4 was dropped on the formed thin film for reducing gold ions. The Au 4f core-level photoemission spectra were recorded using the $\text{MgK}\alpha$ (1253.6 eV) source. Deconvolution of XPS was done using XPSpeak 4.1 software. Thermo-Nexus 670 model spectrometer with ATR attachment was used for fourier transform infra red (FT-IR) measurements and spectral range was limited to 2300–1800 cm^{-1} . Sample preparation for FT-IR measurement was similar to that of XPS analysis. Glassy carbon (GC) electrode of 3 mm diameter was used in this study and GC electrode was polished using 4/0 emery sheet and sonicated for 5 min before each experiment. 2.5 μl of 10 mM HAuCl_4 and 10 mM $\text{K}_4[\text{Fe}(\text{CN})_6]/\text{K}_3[\text{Fe}(\text{CN})_6]$ were placed on a GC electrode, the mixture of the reactants forms the charge transfer complex. The reactant mixture was allowed to dryness on the surface of the GC electrode for about 10 h and then washed with Millipore water to remove unreacted reactants, if any. An aliquot of 5 μl of 0.1 M NaBH_4 was dropped on the formed thin film on the GC electrode for reducing gold ions. Cyclic voltammetric experiments were done on a BAS-100B electrochemical system and all the potentials mentioned in this text are against Ag/AgCl (3 M NaCl) reference electrode, unless otherwise stated. The solutions were freshly prepared every time using Millipore water (18.2 $\text{M}\Omega\text{ cm}$).

3. Results

3.1. UV-Vis and FT-IR spectral studies

The electronic spectra of 1 mM gold chloride, potassium ferrocyanide, potassium ferricyanide, a mixture of potassium ferricyanide and gold chloride are shown in Fig. 1. The spectrum recorded in a mixture of potassium ferrocyanide and gold chloride is given in the inset of Fig. 1. The absorption wavelength (λ_{max}) values for the solutions are tabulated in Table 1. It is clear from Fig. 1 and Table 1 that there is no significant change in the absorption wavelength when potassium ferricyanide and gold chloride are mixed together. Even after keeping the mixture for a few hours, the solution did not show any visible color change indicating the absence of interaction between two anionic reactants. This obser-

Table 1

Observed λ_{max} value for each reactant from UV-Vis spectra.

Reactants ($1 \times 10^{-3} \text{ mol dm}^{-3}$)	λ_{max} (nm)
HAuCl_4	306
$\text{K}_4[\text{Fe}(\text{CN})_6]$	332
$\text{K}_3[\text{Fe}(\text{CN})_6]$	260, 303, 325, 421
$\text{HAuCl}_4 + \text{K}_3[\text{Fe}(\text{CN})_6]$	306, 414
$\text{AuCl}_4 + \text{K}_4[\text{Fe}(\text{CN})_6]$	305, 414, 692

vation is consistent with the results of Zhai et al. [13] in that they observed no change in the absorption band after the addition of ferricyanide to gold chloride, indicating that no bond was formed between gold chloride and ferricyanide. Freund et al. [10] studied the redox reaction between ferricyanide and thiosulfate catalysed by colloidal gold whereas Romero et al. [11] demonstrated that the gold nanoparticles act as an efficient catalyst in the reduction of ferricyanide ion to ferrocyanide ion by sodium borohydride.

Interestingly, in contrast to ferricyanide, we observed a redox reaction with intense green color formation when potassium ferrocyanide and gold chloride were mixed in equi-molar ratio. The UV-Vis spectra were marked by the absence of absorption corresponding to ferrocyanide ion. Instead, we noticed absorption corresponding to ferricyanide ion. When the oxidation state of Fe changes from 2+ to 3+, it is natural to expect concomitant changes in the oxidation state of Au in gold chloride but there was no absorption corresponding to the characteristic surface plasmon resonance band for Au_{nano} . Our attempts to reduce gold chloride in the presence of a stabiliser like sodium dodecylsulfate also did not indicate the formation of Au_{nano} . These observations indicate that Au^{3+} in gold chloride may undergo reduction to Au^+ . Incidentally, the formation of Au^+ from Au^{3+} on the addition of potassium ferrocyanide is known to occur [14]. In addition, a charge transfer band was also observed at 690 nm which is common in PB-like compounds [15]. Fig. 2 shows the FT-IR spectrum of Au-Fe complex, stretching vibration at 2168 cm^{-1} confirms the presence of cyanide ligand. Cyanide stretching vibration shifts to higher wave numbers, when compared to the that in $\text{KAu}(\text{CN})_2$ (2140 cm^{-1}). A similar shift was observed in PB type compounds [16].

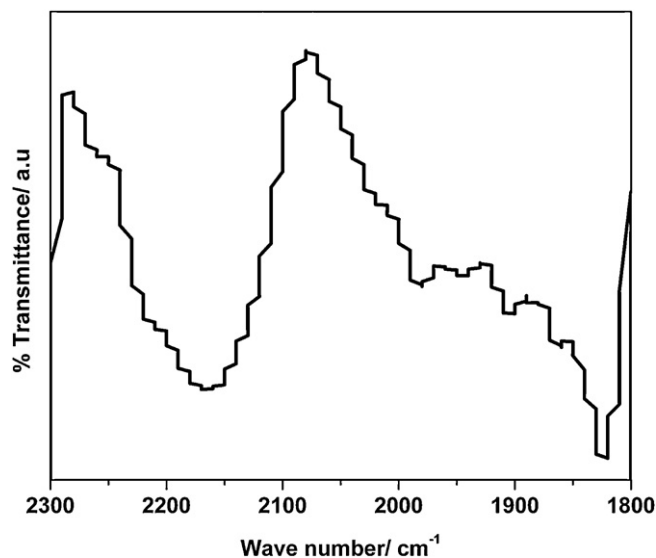


Fig. 2. FT-IR spectra of Au-Fe complex.

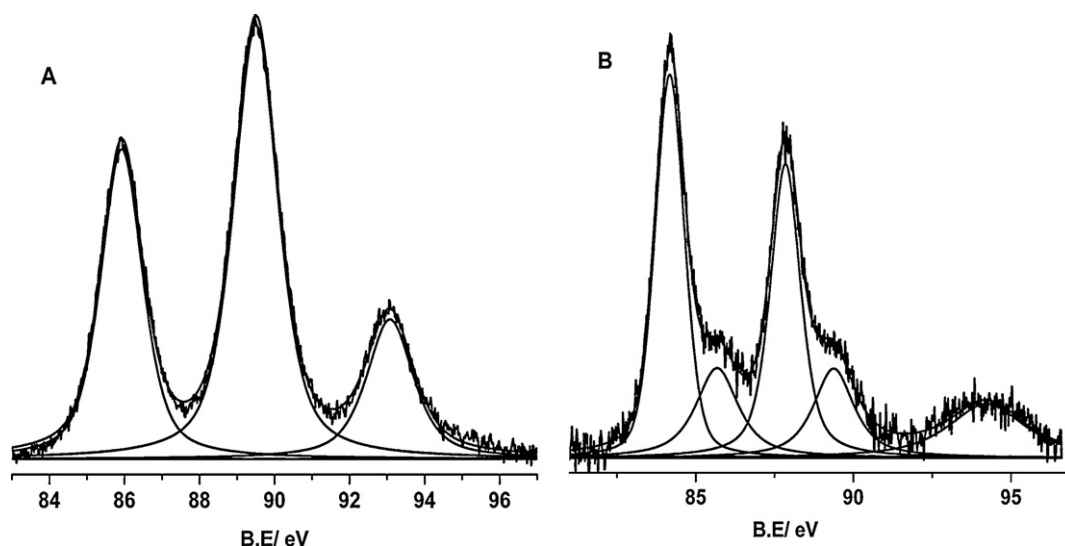


Fig. 3. XPS of Au-Fe complex (A) before and (B) after NaBH_4 reduction.

3.2. XPS studies

We have formed films of the charge transfer complex on a plain glass plate by drop casting a mixture of 10 mM potassium ferrocyanide and gold chloride and subsequent drying. XPS of this film showed $\text{Au } 4f_{5/2}$ and $4f_{7/2}$ peaks at 85.92, 89.50, 93.07 eV (Fig. 3A) which correspond to Au^+ in $[\text{Au}(\text{CN})_2]^-$ [17–21]. Relative shift in the binding energy values of Au^+ with reference to those of Au^0 was found to vary between 1.2 and 2.3 eV [19] and the shift was found to be consistent with the substrate interaction [22]. This observed shift [17–21] may be attributed to the above reasons and also to the influence of the chemical environment. In a control experiment, the complex is reduced using NaBH_4 and analysed for XPS. It showed a peak shift to lower binding energy values of 84.17 and 87.84 eV corresponding to metallic gold [23] (Fig. 3B).

3.3. Cyclic voltammetric studies

To characterize the interaction between potassium ferrocyanide and gold chloride, we have followed an unconventional approach of forming a film by drop casting the mixture on GC as described in the experimental section. This electrode showed a voltammetric response (Fig. 4) that clearly exhibits two redox processes; one at 0.29 V and the other at 0.63 V. The peak currents of both the processes decrease with increasing cycle number. However we obtain a stable redox at 0.15 V when the potential range is limited to 0.0–0.6 V (Fig. 5). Similar improvement in the stability was earlier achieved in the case of silver hexacyanoferrate modified electrode when the potential cycling was limited to 0.9 V [24]. The redox peak obeys characteristics of an ideal surface reaction as seen from the linear relation between the plot of peak current and scan rate [inset in Fig. 5]. Gold ion in Au-Fe complex formed on GC electrode was reduced using NaBH_4 (as followed by XPS analysis) to metallic gold. NaBH_4 -treated electrode in 0.5 M H_2SO_4 showed voltammetric peaks characteristic of gold oxide formation at 750 mV and gold oxide reduction at 430 mV versus $\text{Hg}/\text{Hg}_2\text{SO}_4$ reference electrode (Fig. 6).

A similar modification of GC surface by drop casting a mixture of potassium ferricyanide and gold chloride result in the formation of PB on the surface of electrode as seen from the two sets of redox process at 0.16 V and 0.837 V (Fig. 7). Both the redox couples remain stable on potential cycling. The origin of these redox processes in the case of films formed on the GC surface from

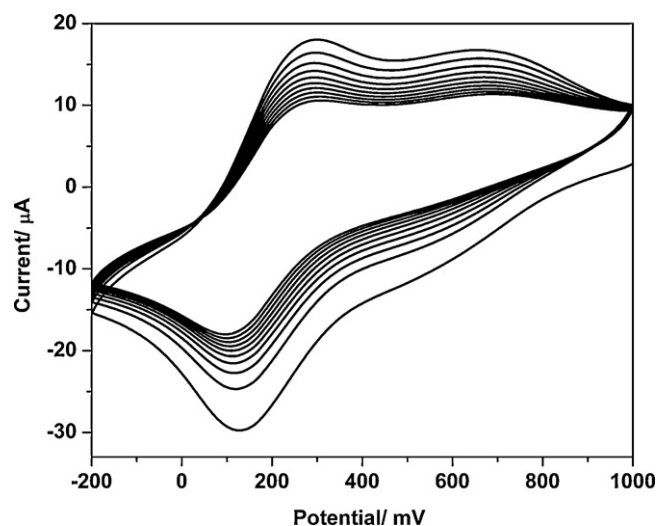


Fig. 4. Cyclic voltammogram shows the redox behavior of Au-Fe complex in 0.1 M KNO_3 at the scan rate of 50 mV s^{-1} .

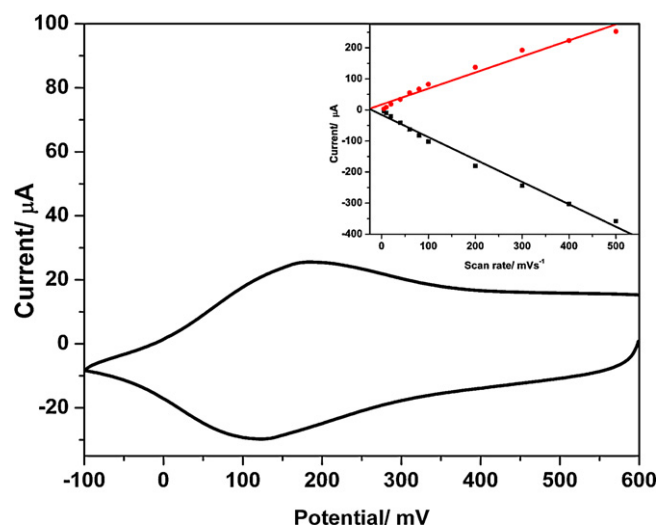


Fig. 5. Cyclic voltammogram shows the redox behavior of Au-Fe complex in 0.1 M KNO_3 at the scan rate of 20 mV s^{-1} . Inset figure: plot of peak current and scan rate.

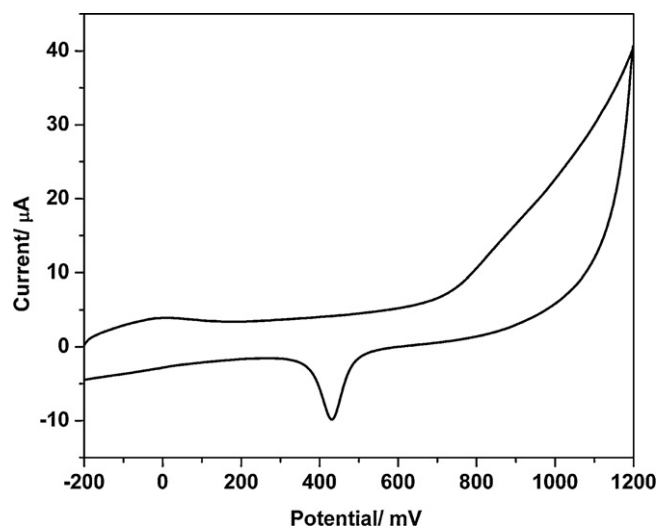


Fig. 6. Cyclic voltammogram of Au-Fe complex after reduction with NaBH_4 in 0.5 M H_2SO_4 at the scan rate of 50 mV s^{-1} .

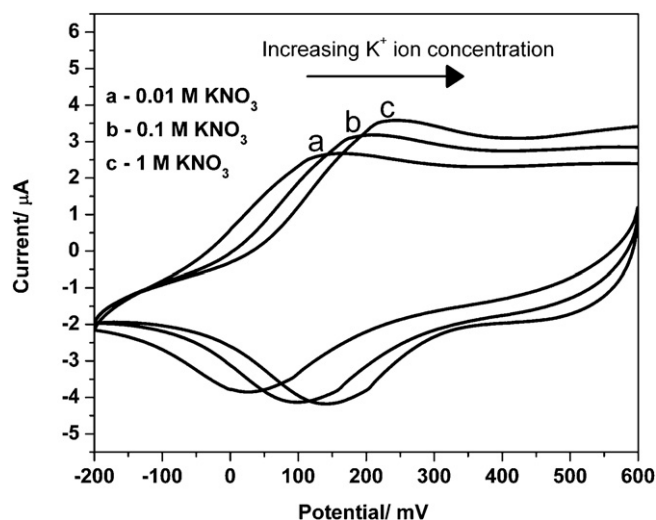


Fig. 8. Cyclic voltammogram shows the K^+ ion dependence of the Au-Fe complex at the scan rate of 10 mV s^{-1} .

mixtures of gold chloride with ferricyanide/ferrocyanide is discussed below.

4. Discussion

Various PB analogues can be electrochemically prepared as thin films on conducting substrates (like GC, indium tin oxide, Pt) by potential cycling the electrode in a medium containing the metal salt and potassium ferricyanide. However, there is no report on the formation of gold hexacyanoferrate by either electrochemical or chemical means. Electrochemical cycling of the GC surface in a mixture containing gold chloride and potassium ferricyanide was found to lead to the formation of Au_{nano} incorporated PB [9]. Our present experiments suggest that on similar cycling in a mixture of potassium ferrocyanide and gold chloride also resulted in the formation Au @ PB nanocomposite (figure not shown). The UV-Vis spectra [Fig. 1] do not present any features characteristic of a reaction between ferricyanide and gold chloride. However, when the same mixture is drop cast on GC and dried to form a film, the mod-

ified electrode showed two sets of redox peaks; one at 0.136 V and the other at 0.837 V typical of PB formation. It can now be stated that on mixing gold (III) chloride and potassium hexacyanoferrate (II/III) on GC, the following processes take place: step 1: increase in acidity due to an increase in $[\text{H}^+]$ during solvent evaporation (the initial pH of the mixture of 1 mM gold chloride and potassium ferricyanide or ferrocyanide is ~ 3.2); step 2: decomposition of potassium ferricyanide ion to free ferric ion under low pH conditions [5] [a similar decomposition of potassium ferricyanide to ferric ion during gold hydroxide formation caused by the interfacial acidity was reported by Senthil et al. [9]]; step 3: formation of PB takes place during electrochemical cycling through a complex formation between ferricyanide ion with free ferric ion. On the other hand, a redox reaction takes place when potassium ferrocyanide is mixed with gold chloride. The standard oxidation potential of potassium ferrocyanide is -0.37 V [25] and the reduction potential of $[\text{AuCl}_4]^-$ to $[\text{AuCl}_2]^-$ is 0.926 V [26]. Hence the reaction between the potassium ferrocyanide and gold chloride is *spontaneous* whereas this is not in the case of potassium ferricyanide. Spontaneous reaction between potassium ferrocyanide and gold chloride is observed in the UV-Vis spectra showing the conversion of ferrocyanide ion to ferricyanide ion and Au^0 , in turn undergoing reduction to either Au^+ or Au^0 . Although the oxidation potential of ferrocyanide is sufficient to reduce Au^{3+} to Au^0 ($E_{\text{Au}^{3+}/\text{Au}^0} = 1.002 \text{ V}$), we have not observed Au^0 formation from the UV-Vis spectra and XPS analyses. The difference between the reaction of gold chloride with potassium ferricyanide or ferrocyanide is due to the associated redox reaction in the later case. It may be summarized that the following steps are involved in the reaction between the potassium ferrocyanide and gold chloride, step 1: redox reaction between potassium ferrocyanide and gold chloride leading to the formation of ferricyanide ion and Au^+ . Step 2: concomitant decomposition of ferrocyanide/ferricyanide ion to free ferrous/ferric ion at high acidity conditions. The XPS spectra of the film prepared by drop casting the mixture on the plain glass plate indicate the formation of $[\text{Au}(\text{CN})_2]^-$. Au (I), Ag (I) and Cu (I) are known to form stable cyano-complexes [5] in which Au has more affinity towards CN^- ion and hence the extraction of Au was performed by cyanidation, known as 'MacArthur-Forrest process' [27]. In addition to this, the formation constant of $[\text{Au}(\text{CN})_2]^-$ in the cyanide medium is also very high ($\text{ca. } 10^{38}$) compared to other metals [5]. Hence, the gold ions might extract ligands from the potassium ferrocyanide forming the cyano-complex of gold. Similar ligand exchange isomerism between iron and chromium

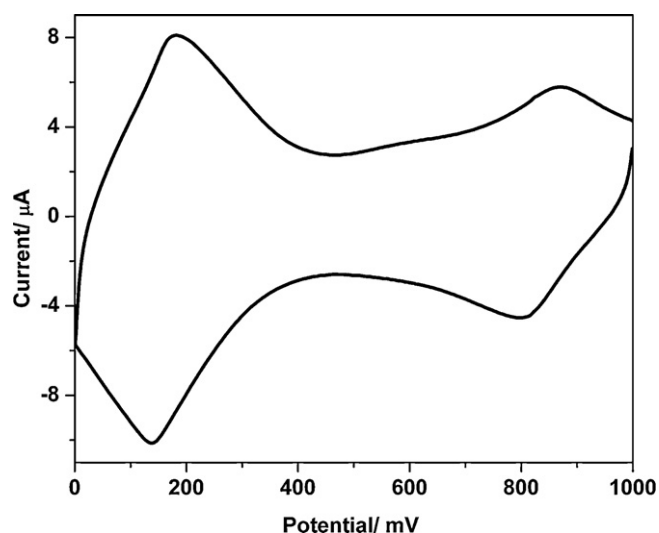


Fig. 7. Cyclic voltammogram of Prussian blue formed from ferricyanide and gold chloride in 0.1 M KNO_3 at the scan rate of 50 mV s^{-1} .

in chromium hexacyanoferrate during electrochemical cycling resulted in the formation of iron hexacyanochromate as reported by Dostal et al. [28]. To explain the stable voltammetric response shown in Fig. 5, we propose the formation of a complex between free $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $[\text{Au}(\text{CN})_2]^-$. Similar dicyanoaurate complex with metal ion/complexes were sparsely reported [29–32]. Dong et al. [33] synthesized $\{\text{Mn}[\text{Au}(\text{CN})_2]_2(\text{H}_2\text{O})_2\}_n$ and $\{\text{KFe}[\text{Au}(\text{CN})_2]_3\}_n$ from $[\text{Au}(\text{CN})_2]^-$. The voltammetric response of the GC modified with 1:1 molar ratio of gold chloride and potassium ferrocyanide showed a stable redox couple at 0.17 V. The redox peak potential matches with the high spin $\text{Fe}^{2+/3+}$ transitions in the complex. Based on our results and those of Dong et al. [33], we propose that the probable complex formed is of the general formula $\text{KFe}_x[\text{Au}(\text{CN})_2]_y$. As expected from this formula, the cyanide stretching vibration is comparable with that of Dong et al. [33], modified electrode is unstable when potential exceeds 0.6 V and the redox peak depends on K^+ ion concentration in the electrolyte. The cyanide stretching vibration observed from the FT-IR spectra is 2168 cm^{-1} and the reported value for the same type of complex is 2154 cm^{-1} [33]. This small variation observed in the wave number may be due to the difference in the stoichiometry of the complex. The instability of the cyclic voltammetric response when the potential cycling is extended beyond 0.6 V is probably due to the conversion of $[\text{Au}(\text{CN})_2]^-/[\text{Au}(\text{CN})_4]^-$ couple that occurs between 0.53 and 0.59 V [34], requiring additional cyanide ligands from the medium. The absence of the cyanide ligand in the supporting electrolyte 0.1 M KNO_3 might cause destabilization of the film during cycling. The K^+ ion dependence is known for various PB analogues and was found that the voltammetric mid-peak potential would decrease with decreasing potassium ion concentration for both the oxidation and reduction reactions [2]. The K^+ ion dependence of the formed complex is shown in Fig. 8 where redox peaks shifts in the positive direction when K^+ ion concentration increases from 0.01 M to 1 M and the mid-peak potential shows a near-Nernstian shift. These are the initial evidences in for supporting the proposed formula and further structural investigations of the complex are underway in our laboratory.

5. Conclusions

The interaction between gold chloride and potassium ferricyanide or ferrocyanide was studied using UV–Vis spectroscopy, FT-IR, XPS and cyclic voltammetric analysis. The studies showed no reaction between potassium ferricyanide and gold chloride but a redox reaction taking place when potassium ferrocyanide reacts with gold chloride. This redox reaction involves the conversion of ferrocyanide ion to ferricyanide ion and Au (III) to Au (I) resulting in the formation of $\text{KFe}_x[\text{Au}(\text{CN})_2]_y$, gold having more affinity to attract cyanide ligand. The Au (I) complex formation was confirmed from the XPS analysis and the presence of high spin iron in the outer sphere was also shown in cyclic voltammogram. The results show that the formation of “gold hexacyanoferrate” is not possible either by chemical or electrochemical reactions of gold (III)

chloride and potassium hexacyanoferrate (II/III) in contrast to other PB analogues.

Acknowledgements

We thank the Department of Science and Technology, India for financial assistance through a grant-in-aid programme [SR/S1/PC-22/2007]. S. Harish thanks Council of Scientific and Industrial Research, New Delhi for the award of a senior research fellowship. Authors also thank the Central Instrumentation Facility for using XPS and FT-IR analysis.

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