Asian Journal of Chemistry Vol. 22, No. 10 (2010), 8167-8173

Layer-by-Layer of Thin Films of Nickel Hexacyanoferrate Multilayer Anchored to Self-Assembled of Mercaptoacetic Acid

JIANYING QU*, SHUMIN WANG and WENJING CHEN
Institute of Environmental and Analytical Science, College of Chemistry and Chemical Engineering, Henan University, Kaifeng, Henan 475001, P.R. China
E-mail: lilyqujy@yahoo.com.cn

A general methodology to prepare redox active inorganic mutilayers consisting of nickel hexacyanoferrate layers formed by layer-by-layer assembly was constructed. The layers were anchored through mercaptoacetic acid on gold electrode. The electrochemical characteristics of nickel hexacyanoferrate modified electrode in the presence of different ions (K^+, Na^+, Cl^-, Br^- and F^-) were investigated by cyclic voltammetry and exhibited a near-Nernstian with a slope of 54 mV/decade to potassium ions in the range from 1×10^{-2}-1 mol/L, which can be use as potential sensor to determine concentration of potassium ion. The modified electrodes showed good stability.

Key Words: Nickel hexacyanoferrate, Modified electrode, Layer-by-layer.

INTRODUCTION

Recently, a layer-by-layer (LBL) assembly technique based on electrostatic interaction between oppositely charged species has been used to build a variety of multilayer assemblies[1]. This technique can obtain high uniformity and stability films with accurately controlled layer thickness and amount of the components, which has being attracted more and more attentions.

Prussian blue (PB) and its analogues constitute an interesting group of polymer inorganic compounds that can be adsorbed on charged self-assembles and among them. Prussian blue type hexacyanoferrate of different metals attract more concentrations due to their attractive physicochemical characteristics, such as electrochromism, ion exchange and molecular magnetism besides electrocatalytic properties[2-7].

Based on this, a new prussian blue analogues film on gold electrode was constructed. First, mercaptoacetic acid (MA) modified gold electrode (MA/Au) was prepared through self-assembly technique. Then, using adsorption between MA and hexacyanoferratte, we proposed a simple approach for construction of nickel hexacyanoferrate (NiHCF) film through layer-by-layer technique. The fabrication strategy of nickel hexacyanoferrate multilayer on the MA/Au is based on complexation between metal ion and with hexacyanoferrate and covalent bonding on gold surface. At the same time, the electrochemical behaviours of the resulting NiHCF/MA/Au modified electrode were studied. Experiments showed this modified electrode exhibited different response to different ions, particularly, showed Nernstian to potassium ion in the range of 1 × 10^{-2}-1 mol/L, which can be used a potential sensor. And these modified electrodes exhibited with high stability.

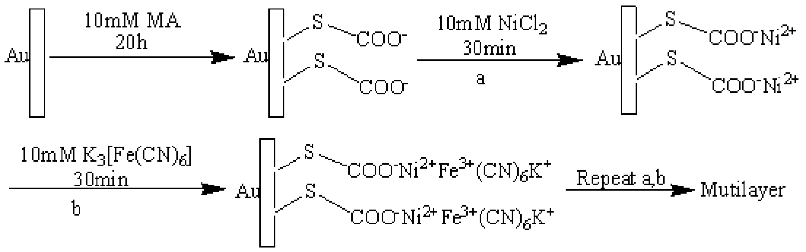
EXPERIMENTAL

Mercaptoacetic acid (MA, $HSCH_2COOH$) was purchased from Tianjin Kermal chemical reagent Co., Ltd, $NiCl_2$, $K_3[Fe(CN)_6]$ and other chemicals were analytical grade and used as received without further purification. All aqueous solutions were prepared using doubly distilled water.

Cyclic voltammetry was performed with a CHI 650 electrochemical workstation (USA) in a conventional three-electrode electrochemical cell using gold (disc diameter = 1 mm) as the working electrode, twisted Pt wire as the counter electrode and Ag/AgCl (*versus* saturated KCl) as the reference electrode.

Preparation of nickel hexacyanoferrate multilayers on gold electrode: Before each experiment was carried out, the gold electrode was carefully cleaned and polished according to the methodology presented elsewhere[8]. Self-assembled monolayer of mercaptoacetic acid on the gold surface was obtained by dipping the gold electrode in an aqueous solution of mercaptoacetic acid (0.01 mol/L) for 20 h followed by thorough rinsing with water. The mercaptoacetic acid modified gold (referred to as MA/Au) were ready for characterization or further modification.

As shown in **Scheme-I**, after being immersed in a 10 mmol/L $NiCl_2$ aqueous solution for 0.5 h, the MA/Au electrode was removed and rinsed, then dipped in a 10 mmol/L of $[Fe(CN)_6]^{3-}$ aqueous solution for 0.5 h, resulting in a monolayer of nickel hexacyanoferrate on MA/Au to give NiHCF/MA/Au electrode.



Scheme-I: An ideal assembly model of nickel hexacyanoferrate multilayer films on the gold electrode

Repetition of the above steps on the monolayer of nickel hexacyanoferrate leads to a of a nickel hexacyanoferrate film multilayer on gold surface to obtain $[(NiHCF)_n/MA/Au]$ electrode. Formation of nickel hexacyanoferrate is verified by checking the cyclic voltammogram of the film in 0.1 mol/L KCl solution.

Electrochemical measurements: All electrochemical experiments were carried out in 0.1 mol/L KCl solutions unless otherwise specified with a three-electrode system. The twisted Pt wire, Ag/AgCl and gold electrodes (bare and modified electrode) served as the reference, counter and working electrode, respectively.

RESULTS AND DISCUSSION

Characterization of MA/Au electrode: In 0.1 mol/L KCl solution, comparison of the cyclic voltammetry (CV) response of MA/Au and an Au electrode (Fig. 1) was done. Experiments showed the significant decrease of the background current with MA/Au modified electrode[9,10], which indicated that the mercaptoacetic acid monolayer is permeable to the electrolyte[11] and the monolayer formation reduces the electron transfer rate between the electrode surface and the solution.

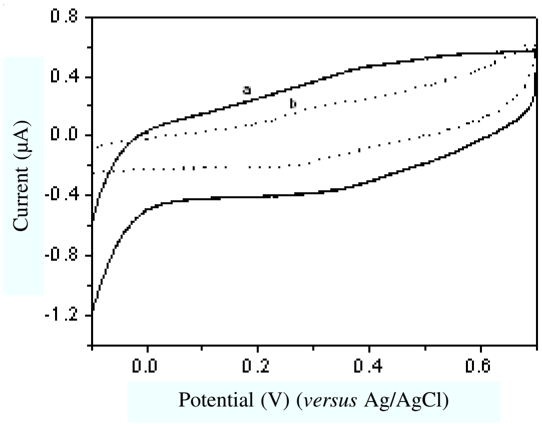


Fig. 1. Cyclic voltammetry response of Au (a, solid line) and MA/Au (b, dot line) electrode in 0.1 mol/L KCl solution. Scan rate: 100 mV s^{-1}

Then, $[Fe(CN)_6]^{3-/4-}$ redox couple was used as the electrochemical probe to study the electrochemical characterization of the self-assembled modified gold electrode. Fig. 2 showed that the existence of mercaptoacetic acid membranes on gold surface hindered the electron transfer, which testified the formation of mercaptoacetic acid film on gold electrode surface.

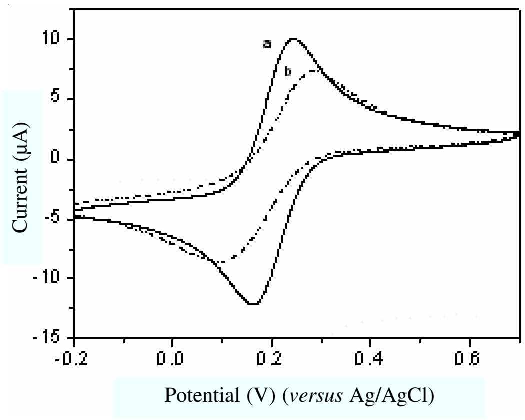


Fig. 2. Cyclic voltammetry response of Au (a, solid line) and MA/Au (b, dot line) electrode in 0.1 mol/L KCl solution containing 5 mmol/L $K_3[Fe(CN)]_6$. Scan rate: 100 mV s^{-1}

Cyclic voltammetry of nickel hexacyanoferrate multilayer film on MA/Au electrode: Cyclic voltammetry was employed to monitor the deposition processes of the nickel hexacyanoferrate multilayers and to characterize their electrochemical behaviour. Fig. 3 shows the cyclic voltammetry curves of the as-prepared multilayers (nickel hexacyanoferrate as the outermost layers) with different number of nickel hexacyanoferrate layers in 0.1 mol/L KCl aqueous solution. A pair of obvious redox peaks with formal potential of about 0.6 V is assigned to the expected surface redox process of nickel hexacyanoferrate[12], which attached to the gold surface through mercaptoacetic acid moieties. The redox reaction of nickel hexacyanoferrate is proposed as follows:

$$KNi^{2+}[Fe^{3+}(CN)_6] + e + K^+ \rightarrow K_2Ni^{2+}[Fe^{2+}(CN)_6] \qquad (1)$$

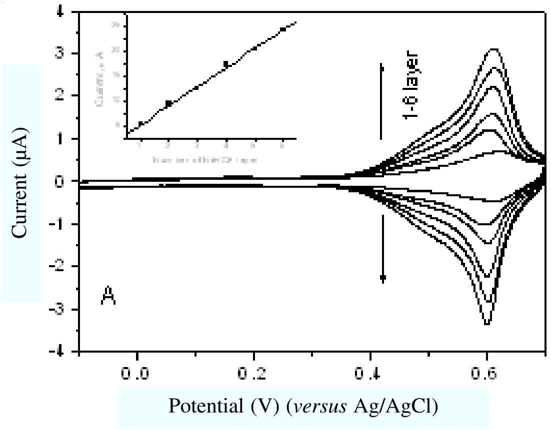


Fig. 3. Cyclic voltammetry of one to six nickel hexacyanoferrate layers on MA/Au electrode in 0.1 mol/L KCl solution. The inset shows the relationship between the oxidation peak current and the number of layers. Scan rate: 100 mV s^{-1}

With the number of nickel hexacyanoferrate multilayer increasing, the redox peak currents increase gradually. And the growth of nickel hexacyanoferrate multilayer is demonstrated by linearly increasing of peak current with the layer number, as shown in the inset of Fig. 3. It indicated that uniform and homogeneous multilayer films have been fabricated on the MA/Au substrate.

Fig. 4 presents cyclic voltammetry of the nickel hexacyanoferrate multilayer film modified electrode in 0.1 mol/L KCl solutions with different scan rates. As shown in the inset of Fig. 4, the peak current of the nickel hexacyanoferrate is increases linearly with increasing of scan rate (between 10-100 mVs^{-1}), which demonstrates that the multilayer films corresponds to a surfaced-confined process.

Identification to different ions

Response to halide anions: The nickel hexacyanoferrate modified electrode with five-layers was studied by cyclic voltammetry in 0.1 mol/L of KF, KCl and KBr aqueous solutions, respectively and the results are showed in Fig. 5. From the

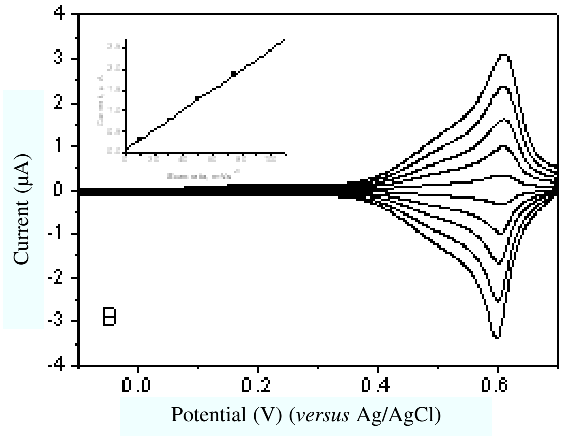


Fig. 4. Cyclic voltammetry of six-layers of nickel hexacyanoferrate on MA/Au electrode in 0.1 mol/L KCl solution with different rates: 10, 30, 50, 75 and 100 mV s^{-1}. The inset shows the relationship between the oxidation peak current and the rates. Scan rate: 100 mV s^{-1}

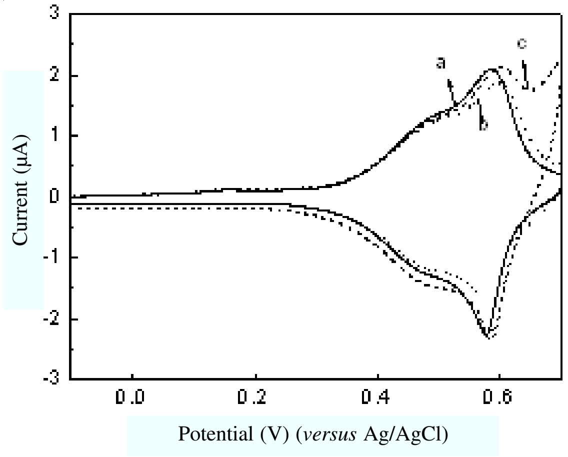


Fig. 5. Cyclic voltammetry of five-layers of nickel hexacyanoferrate on MA/Au electrode in 0.1 mol/L KF (a, solid line), 0.1 mol/L KCl (b, dot line) and 0.1 mol/L KBr (c, dash line) solutions. Scan rate: 100 mV s^{-1}

figure, it is observed that the peak heights and peak potentials are close to each other for the three different potassium halide. However, it is noticeably that the response current in KBr solutions increase considerably with an increase of the potential. The large current may be caused by lower electronic bridge energy of Br^-[13].

Response to K^+ and Na^+ cations: Bocarsly *et al.*[14,15] have reported that the aqueous electrolytes of all the alkali metals support appreciable rates of charge transfer for nickel hexacyanoferrate films. They find that the redox potential of the surface-confined film varies with the alkali-metal cation present in the solution.

So, the cyclic voltammetry of nickel hexacyanoferrate modified electrode with five-layers in 0.1 mol/L aqueous KCl and NaCl solutions are compared. As seen in Fig. 6, a pair of well-defined redox peak near to 0.6 V can be observed in KCl solution (the solid line). However, a pair of round and broad peak was observed, in NaCl solution (the dotted line). Compared with the redox of nickel hexacyanoferrate in KCl solution, it shifted negative direction in NaCl. Furthermore, the peak currents in NaCl solution decreased drastically than that in KCl solution. These phenomena are similar to the previous report[16]. The above results indicate that the nickel hexacyanoferrate film on MA/Au electrode surface possess greater selectivity for K^+ as a counter cation, which might be used as potential sensor of K^+.

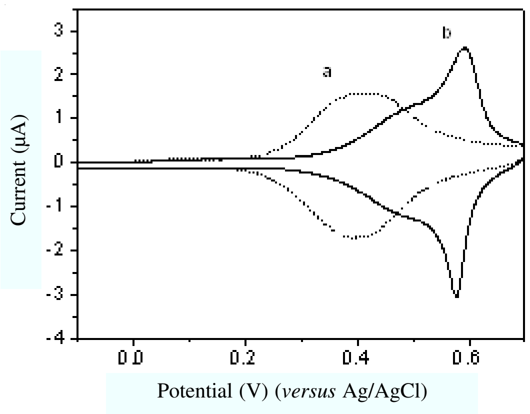


Fig. 6. Cyclic voltammetry of five-layers of nickel hexacyanoferrate on MA/Au electrode in 0.1 mol/L NaCl (a, dot line) and 0.1 mol/L KCl (b, solid line) solutions. Scan rate: 100 mV s^{-1}

The response of the nickel hexacyanoferrate film to different K^+ concentration has been studied, which is showed in Fig. 7. The results show that the peak potentials shift anodically with increasing K^+ concentration and agreement with the involvement of K^+ in the redox reactions as reported[17]. The potential shift is almost Nernstian with a slope of 54 mV/decade. It is somewhat lower than the theoretical valve of 59 mV/decade (Nernstian behaviour), which would be expected for the involvement of solely a cation in the reaction mechanism. So anion has an effect on the redox reaction of nickel hexacyanoferrate films. A similar conclusion was obtained in the reference[16]. Further, K^+ concentration exhibits near-Nernstion response to K^+ potential in the range of 1×10^{-2}-1 mol/L, as shown on the top inset of Fig. 6.

Stability of the nickel hexacyanoferrate modified electrode: The stability of the nickel hexacyanoferrate film immobilized on MA/Au electrode surface was studied during potential scanning in 0.1 mol/L KCl aqueous solution for 100 successive cycles between -0.1 and 0.7 V at a scan rate of 100 mV s^{-1}, the redox currents had no obvious changes. The results demonstrated that nickel hexacyanoferrate film modified electrode possess good stability.

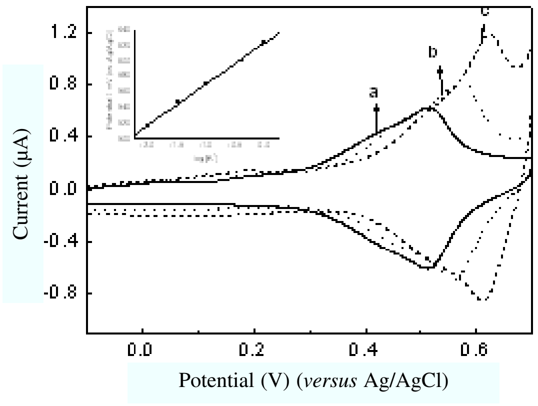


Fig. 7. Cyclic voltammetry of two-layers of nickel hexacyanoferrate on MA/Au electrode in 0.01 mol/L KCl (a, solid line), 0.1 mol/L KCl (b, dot line) and 1 mol/L KCl (c, dash line) solutions. Scan rate: 100 mV s^{-1}. The inset shows the relationship between Ep, c and logarithms of K^+ concentrations

Conclusion

In conclusion, we have demonstrated the feasibility of building a multilayer of nickel hexacyanoferrate on a gold substrate by layer-by-layer technique. The cyclic voltammetry results show that the electrochemical properties of NiHCF films depended on anions such as F^-, Br^-, Cl^- and cations K^+, Na^+. What's more, it exhibits near-Nernstion response to potassium ion in the range of 1×10^{-2}-1 mol/L, which can be use as potential sensor to determine concentration of K^+. The modified electrodes showed good stability.

REFERENCES

1. G.J. Decher, *Science*, **277**, 1232 (1997).
2. P.J. Kulesza, M.A. Malik, M. Berrettoni, S. Giorgetti, R. Zamponi, R. Schmidt, R.J. Marassi, *J. Phys. Chem. B.*, **102**, 1870 (1998).
3. M.A. Malik, K. Miecznikowski, A. Wolkiewicz, S. Zamponi, M. Barrettoni and R. Marassi, *J. Electrochem. Soc.*, **143**, L10 (1996).
4. O. Kahn, *Nature*, **378**, 667 (1995).
5. C. Lin and A.B. Bocarsly, *J. Electroanal. Chem.*, **300**, 325 (1991).
6. M. Sadakane and E. Steckham, *Chem. Rev.*, **98**, 219 (1998).
7. C.X. Cai, H.X. Ju and H.Y. Chen, *Anal. Chim. Acta*, **310**, 145 (1995).
8. J. Manríquez, E. Juaristi, O. Muñoz-Muñiz and L.A. Godínez, *Langmuir*, **19**, 7315 (2003).
9. E. Sabatani and I. Rubinstein, *J. Phys. Chem.*, **91**, 6663 (1987).
10. C. Miller, P. Cuendet and M. Cratzel, *J. Phys. Chem.*, **95**, 877 (1991).
11. Q. Cheng and A.B. Toth, *Anal. Chem.*, **64**, 1998 (1992).
12. J. Joseph, H. Gomathi and G.P. Rao, *Electrochim. Acta*, **36**, 1537 (1991).
13. W. Tao, D. Pan, Y. Liu, L. Nie and S. Yao, *J. Electroanal. Chem.*, **572**, 109 (2004).
14. A.B. Bocarsly and S. Sinha, *J. Electroanal. Chem.*, **140**, 167 (1982).
15. S. Sinha, B.D. Humphrey and A.B. Bocarsly, *Inorg. Chem.*, **23**, 203 (1984).
16. S. Bharathi, V. Yegnaraman and G.P. Rao, *Langmuir*, **11**, 666 (1996).
17. A. Salimi and K. Abdi, *Talanta*, **63**, 475 (2004).

(*Received*: 21 April 2010; *Accepted*: 5 August 2010) AJC-8952