Gold Electrodes Modified with Multilayers of M–TTF–Tetrathiolate ($M = Ni^{II}$ and Cu^{II}, TTF = Tetrathiafulvalene)

Yu Liu,[1] Qin-Yu Zhu,*[1] Guo-Qing Bian,[1] Wen-Juan Guo,[1] Wen Lu,[1] and Jie Dai*[1,2]
[1]*Key Laboratory of Organic Synthesis of Jiangsu Province, Suzhou University, Suzhou 215006, P. R. China*
[2]*State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P. R. China*

(Received December 12, 2006; CL-061453; E-mail: daijie@suda.edu.cn)

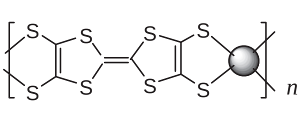
Gold electrodes, on which multilayered metal–TTF derivatives (M–$TTFS_4$) were assembled, exhibit a redox activity, and the redox potentials are sensitive to the metal ions being coordinated. The M–$TTFS_4$ showed broad and very strong absorbance in the range of near IR, attributed to the charge-transfer band between the metal ions and the ligand.

Tetrathiafulvalene (TTF) and its derivatives, as the famous functional compounds, have been widely investigated.[1] The LB films of charge-transfer TTFs[2] or self-assembled monolayers (SAMs) of TTFs[3] have received considerable attention for the studies of redox-active sensors. However, the chemical assembly of redox-active TTF multilayers onto surface of a bulky material or an electrode is rarely explored. Tieke et al. have reported the layer-by-layer modification of [Ni(TTO)] (TTO = tetrathiooxalate, $C_2S_4{}^{2-}$) on surface of bulky materials and measured their conductivity.[4] We have also prepared nanoparticles assembled with multilayers of [Ni(TTO)], using this method.[5a]

As an extended study of our group on the coordination assembly of dithiolate derivatives,[5] the present work is devoted to a new gold electrode on which multilayered metal–TTF derivatives $\{M_m[M(TTFS_4)]\}_x$, abbreviated as M–$TTFS_4$, were assembled (Chart 1). The $(TTFS_4)^{n-}$ anion is a tetrathiolate ion fused with a tetrathiafulvalene (TTF) moiety, and the m and n are variable.[6] Through the layer-by-layer modification of M–$TTFS_4$, the surface composition (metal ion) and the modified layers (x) become controllable.

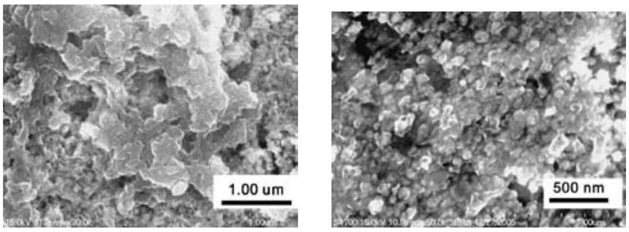
The precursor tetra(2-cyanoethylthio)tetrathiafulvalene (TCETTF) was synthesized by a previously reported method.[7] The preparation method for the electrode is based on the sequential alternating adsorption of $(TTFS_4)^{n-}$ anions and metal cations on a carefully polished Au electrode[8] in analogy to the recently reported method for organic–inorganic hybrid materials.[4,9] The studies about the polymers, $\{M_m[M(TTFS_4)]\}_x$, can be traced to last century.[6] Because the polymeric compounds are amorphous and the anion usually exhibit variable charges, only proposed structures, 1D ribbon and 2D coordinated layer, were described.[6a,10] The most possible structure of the modified layer on Au electrode should be the 2D coordinated layers.

The SEM micrographs of the modified electrodes are shown in Figure 1. The surface of the modified electrode is not a uniformly layered structure in micro view. The layered structure for Cu–$TTFS_4$ is a terrace-like structure with many hollows, while the appearance of Ni–$TTFS_4$ shows to some extent grainy structure. The size of these microstructures is about 100 nm–1 μm scale.



M-$TTFS_4$

Chart 1.



(a) (b)

Figure 1. SEM micrographs of the electrodes with Cu–$TTFS_4$ (a) and Ni–$TTFS_4$ (b) multilayers.

The M–$TTFS_4$-modified electrodes were studied by cyclic voltammatry (CV), and they showed two pairs of redox peaks in CH_3CN–Bu_4NClO_4 (0.1 mol·dm^{-3}) medium and the data are listed in Table 1. Figure 2 gives the CV graph of the Cu–$TTFS_4$-modified Au electrode. The two pair of peaks, $E_{1/2}(1)$ and $E_{1/2}(2)$ correspond to TTF/TTF$^{\bullet+}$ and TTF$^{\bullet+}$/TTF^{2+} redox couples, respectively.[1] Because of the direct charge transfer or charge disperse from the M–$TTFS_4$ to bulky body of the gold electrode, the redox peaks shift to more positive potentials (0.62 and 0.94 V for precursor TCETTF). The shift of $E_{1/2}(1)$ is large enough, so that the two waves are overlapped to some extent with ΔE ($E_{1/2}(2) - E_{1/2}(1)$) about 0.2 V. The phenomena of the positive shift of the $E_{1/2}$(TTF) have been found in other TTF-modified systems.[5b]

Table 1 summarizes the CV data of the M–$TTFS_4$-modified Au electrode (vs. SCE). To further compare the redox potentials of the electrodes with different metal center, Fe–$TTFS_4$-modified electrode was prepared using the method as that for Cu/Ni–$TTFS_4$, and the data are also reported in the Table 1

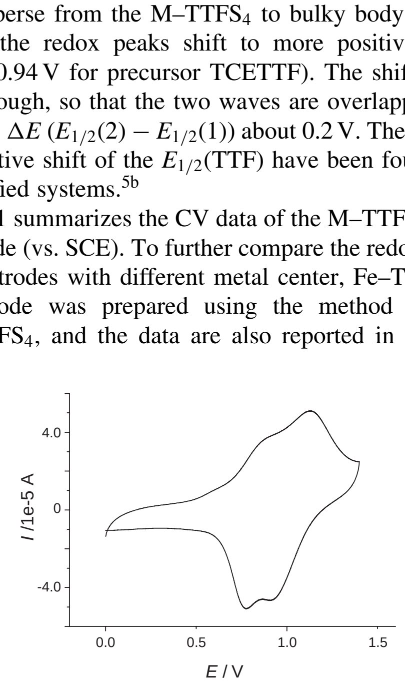


Figure 2. Cyclic voltammogram of the Cu–$TTFS_4$-modified Au electrode in CH_3CN (V vs SCE).

Table 1. CV data of the modified electrodes in CH_3CN (V vs. SCE)

		$E_{1/2}^{(1)}$	$E_{1/2}^{(2)}$	$\Delta E_{1/2}$
Cu–$TTFS_4$	$E_{1/2}$	0.82	1.03	0.21
Ni–$TTFS_4$	$E_{1/2}$	0.81	0.98	0.17
Fe–$TTFS_4$	$E_{1/2}$	0.63	0.93	0.30

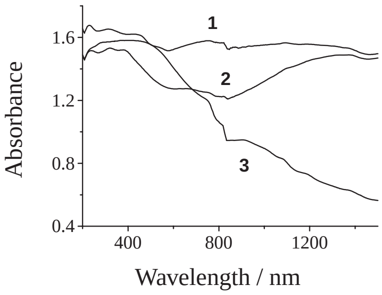


Figure 3. The UV–vis–NIR spectra of the M–$TTFS_4$ samples (line 1, Cu; line 2, Ni; line 3, Fe).

(see SI materials). Comparing these data, both the $E_{1/2}(1)$ and $E_{1/2}(2)$ are in the order of $E_{1/2}(\mathrm{Cu}) \geq E_{1/2}(\mathrm{Ni}) \gg E_{1/2}(\mathrm{Fe})$. The reported crystal structures have showed that most of the Ni/Cu tetrathiolate compounds take the square coordination geometry,[11] although tetrahedral distortion are found for some Cu compounds. The larger positive shift for Cu/Ni–$TTFS_4$ is attributed to their square or quasi-square coordination structure, which allows the π electron conjugated with the metal center. The calculations have indicated that distortion from the planar geometry will decrease the electron transfer.[12] The coordination geometry for Fe ion is octahedral or tetrahedral, and thus the conjugated system is interrupted to some extent, which causes no significant shift of the potentials and the larger ΔE (0.30 V).

In order to study the charge transition of these surface materials, powder samples were prepared by mixing directly the solutions of the metal cations and the $TTFS_4^{4-}$ anion, and solid-state UV–vis–NIR spectra of them were measured. The results of the diffuse reflection measurements are shown in Figure 3. The difference between Cu/Ni and Fe samples is obvious. In the range of the NIR, the square coordinated Cu/Ni samples show broad and very strong absorbance, which is attributed to the charge-transfer band between metal ion and ligand.[13] The result is in accordance with that found in CV measurement, namely that the electron density of the TTF moiety is significantly affected by the square coordinated Ni^{II} and Cu^{II} ions. The conductivity of the samples has been estimated by two electrode method (about 1×10^{-4} and $1 \times 10^{-5}\,\mathrm{S{\cdot}cm^{-1}}$ for Cu/Ni–$TTFS_4$ and Fe–$TTFS_4$, respectively).

In conclusion, the M–$TTFS_4$-modified gold electrodes exhibit redox activity with two pairs of quasi-reversible peaks of the TTF moiety, which are sensible to the metal ions being coordinated. The results reveal that square-coordinated metal ions are the best candidate for linkers of functional TTF moieties, which can improve the electron transition between the electrode and the multilayers.

This work was supported by the National Natural Science Foundation (No. 20371033).

References and Notes

1 a) J. M. Williams, M. A. Beno, H. H. Wang, P. C. W. Leung, T. J. Emge, U. Geiser, K. D. Carlson, *Acc. Chem. Res.* **1985**, *18*, 261. b) E. Coronado, C. J. Gómez-García, *Chem. Rev.* **1998**, *98*, 273. c) M. B. Nielsen, C. Lomholt, J. Becher, *Chem. Soc. Rev.* **2000**, *29*, 153.

2 a) Y. Urai, C. Ohe, K. Itoh, *Langmuir* **1998**, *14*, 4873. b) L. M. Goldenberg, V. Yu. Khodorkovsky, J. Y. Becker, P. J. Lukes, M. R. Bryce, M. C. Petty, J. Yarwood, *Chem. Mater.* **1994**, *6*, 1426. c) L. M. Goldenberg, J. Y. Becker, O. P. T. Levi, V. Yu. Khodorkovsky, M. R. Bryce, M. C. Petty, *J. Chem. Soc., Chem. Commun.* **1995**, 475.

3 a) A. J. Moore, L. M. Goldenberg, M. R. Bryce, M. C. Petty, A. P. Morikman, C. Marenco, J. Yarwood, M. J. Joyce, S. N. Port, *Adv. Mater.* **1998**, *10*, 395. b) S.-G. Liu, H. Liu, K. Bandyopadhyay, Z. Gao, L. Echegoyen, *J. Org. Chem.* **2000**, *65*, 3292. c) A. J. Moore, L. M. Goldenberg, M. R. Bryce, M. C. Petty, J. Moloney, J. A. K. Howard, M. J. Joyce, S. N. Port, *J. Org. Chem.* **2000**, *65*, 8269.

4 a) M. Pyrasch, D. Amirbeyki, B. Tieke, *Adv. Mater.* **2001**, *13*, 1188. b) M. Pyrasch, D. Amirbeyki, B. Tieke, *Colloids Surf., A* **2002**, *198–200*, 425.

5 a) L. Guo, J. Dai, G.-Q. Bian, D.-X Jia, Q.-Y. Zhu, J.-S. Zhang, *Inorg. Chem. Commun.* **2003**, *6*, 1323. b) J. Dai, L. Guo, Y. Jiang, R. A. Gu, Q. Y. Zhu, D. X. Jia, W. J. Guo, *J. Nanosci. Nanotechnol.* **2005**, *5*, 474.

6 a) R. D. McCullough, J. A. Belot, *Chem. Mater.* **1994**, *6*, 1396. b) N. M. Rivera, E. M. Engler, R. R. Schumaker, *J. Chem. Soc., Chem. Commun.* **1979**, 184. c) N. Yoshioka, H. Nishide, K. Inagaki, E. Tsuchida, *Polym. Bull.* **1990**, *23*, 631.

7 a) N. Svenstrup, K. M. Rasmussen, T. K. Hansen, J. Becher, *Synthesis* **1994**, 809. b) L. Binet, J. M. Fabre, C. Montginoul, K. B. Simonsen, J. Becher, *J. Chem. Soc., Perkin Trans. 1* **1996**, 783.

8 The gold electrode was polished first with emery paper, aluminium oxide–water slurry on cotton cloth and then treated in an ultrasonic pool for 10–15 min in order to remove any adsorbate. The cleared gold electrode was electrochemically pretreated in 0.5 M H_2SO_4 solution by repeating the potential scan in the range of 0–1.4 V for 30 times and pre-treated by electrochemical scanning in 0.10 M KCl solution for 30 times. As a typical procedure, small quantity of 25% Me_4NOH in MeOH was added to a THF solution (1 mL) of TCETTF (11.1 mg, 0.02 mmol) to remove the 4-cyanoethyl group under an argon atmosphere and then add 10 mL of ultra-purified water. A solution with $(TTFS_4)^{4-}$ ion was obtained. A carefully polished dish-shaped gold electrode in 3 mm diameter was first dipped into the solution for 10 min, and then was dipped into a 0.1 mM aqueous solution of M ion for 2 min and then rinsed by ultrapurified water, M = Cu^{II}, Ni^{II}, and Fe^{II}. Thus, the processes were carried out alternately for appropriate times under an argon atmosphere.

9 a) A. Mamedov, J. Ostrander, F. Aliev, N. A. Kotov, *Langmuir* **2000**, *16*, 3941. b) T. Cassagneau, F. Guerin. J. H. Fendleer, *Langmuir* **2000**, *16*, 7318. c) M. Schütte, D. G. Kurth, M. R. Lindford, H. Colfen, H. Mohwald, *Angew. Chem., Int. Ed.* **1998**, *37*, 2891.

10 S. Alvarez, R. Vicente, R. Hoffman, *J. Am. Chem. Soc.* **1985**, *107*, 6253.

11 a) A. E. Pullen, S. Zeltner, R. M. Olk, E. Hoyer, K. A. Abboud, J. R. Reynold, *Inorg. Chem.* **1997**, *36*, 4163. b) A. E. Pullen, S. Zeltner, R. M. Olk, E. Hoyer, K. A. Abboud, J. R. Reynold, *Inorg. Chem.* **1996**, *35*, 4420. c) J. Piotraschke, A. E. Pullen, K. A. Abboud, J. R. Reynold, *Inorg. Chem.* **1995**, *34*, 4011.

12 a) H. Tanaka, H. Kobayashi, A. Kobayashi, *J. Am. Chem. Soc.* **2002**, *124*, 10002. b) K. Ueda, M. Goto, M. Iwamatsu, T. Sugimoto, S. Endo, N. Toyota, K. Yamamoto, H. Fujita, *J. Mater. Chem.* **1998**, *8*, 2195.

13 a) G. Matsubayashi, M. Nakano, H. Tamura, *Coord. Chem. Rev.* **2002**, *226*, 143. b) K. Natsuaki, M. Nakano, G. Matsubayashi, R. Arakawa, *Inorg. Chim. Acta* **2000**, *299*, 112.