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First example of the ring-opening transformation of thiazolidines to iminothiols on gold surface

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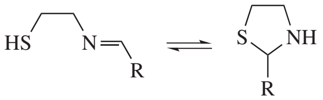
A new way to construction of the self-assembling monolayers on gold surfaces based on ring opening reactions of thiazolidines to iminothiols followed by Au–S bond formation has been proposed.

The formation of the self-assembling monolayer (SAM) of sulfur-containing compounds on metal surfaces (such as gold and silver) has been a topic of great interest during the past decade. The majority of these investigations have been focused on the self-assembly of various alkanethiols and dialkyl disulfides.[1] It has been demonstrated that sulfides,[2] thiophenols,[3] xantogenates,[4] thioureas[5] and other sulfur-containing molecules form monolayers on gold surface. The SAMs on the solid surface are of interest for application ranging from molecular sensing devices to molecular electronics and nonlinear optical materials.[6] It is generally accepted that the thiolate monolayers resulting from the self-assembly of thiols and disulfides are indistinguishable.[7] One factor that has led to the predominant use of thiols as the reagent of choice for the formation of SAMs is that thiols have much higher solubilities than disulfides. The low solubility of disulfides makes them difficult to use in solution, and their precipitation has been noted as a marked source of multilayer contamination of the substrate if the conditions of the sample preparation are not controlled carefully.[8]

Here we describe a new method for the preparation of self-assembling monolayers on gold surface based on chemisorption of iminothiols. Iminothiols are non-cyclic form of the thiazolidines (Scheme 1).

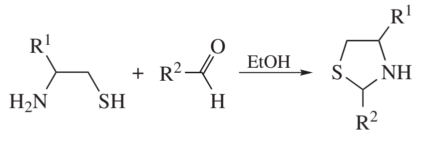


Scheme 1

The synthetic route to the thiazolidines is summarized in Scheme 2. The ligands were prepared in one step from the corresponding aromatic or heterocyclic aldehyde and aminoethane thiol.[9] Obtained compounds **1**–**3** are stable at storage and soluble in most of the common solvents.

We studied the effectiveness of adsorption of compounds **1**–**3** from solutions on the surface of a gold electrode. It is expected that the cyclic form, which prevalently exists in solution, presumably transforms into an acyclic iminothiol form during the adsorption of molecules **1**–**3** on the gold surface, forming the covalent S–Au bond. Electrochemical (Figure 1, Table 1) and FT-IR spectroscopic measurements confirm this transformation.

The IR spectra of compounds **1**–**3** in KBr exhibit NH-adsorption bonds at ~3230 cm^{-1}. For the same compounds on the gold surface the adsorption bands of NH are disappeared and C=N adsorption bands at ~1620 cm^{-1} are observed.



1 R^1 = H, R^2 = Ph
2 R^1 = H, R^2 = 4-MeOC$_6$H$_4$
3 R^1 = COOMe, R^2 = α-Py

Scheme 2 Synthetic route to the thiazolidines.

Compounds **1**–**3** were studied by cyclic voltammetry (CV) and rotating disk electrode (RDE) techniques on gold electrode in anhydrous MeCN with 0.05 M Bu$_4$NBF$_4$ as the supporting electrolyte.[†] The electrochemical oxidation and reduction potentials are given in Table 1.

The first reduction step of **1**–**3** takes place at potentials between –0.14 and –1.47 V and presumably involves the sulfur

Table 1 Electrochemical oxidation and reduction potentials for compounds **1**–**3**, as measured by Au (SAM) or Pt (solution) electrode. The values after slash marks refer to peak potentials relevant to reverse scans of CV curves.

Compound	E^{Ox}/V (Au electrode – for SAM; Pt electrode – for 10^{-3} M MeCN solution)	E^{Red}/V (Au electrode – for SAM; Pt electrode – for 10^{-3} M MeCN solution)
1 (solution)	0.99/ 0.77; 1.83	–1.47; 1.73
1 (SAM)	1.84	–1.03/ –0.67
2 (solution)	1.20/ 0.76; 1.86/ 1.50; 2.60	–1.14; –2.14
2 (SAM)	1.74/ 1.28; 2.46	–0.82/ –0.74
3 (solution)	0.56/ 0.30; 1.56/ 0.86	–1.36; –1.74/ 1.60
3 (SAM)	1.65/ 0.97	–0.70/ –0.64; –1.74/ 1.52

[†] Electrochemical studies were performed using a PI-50-1.1 potentiostat on Pt (d = 2 mm) or Au (d = 1 mm) electrode. Polycrystalline Au electrode was polished with a diamond slurry and sonicated for 10 min in water. The supporting electrolyte was an 0.05 M Bu$_4$NBF$_4$ solution, and the reference electrode was an Ag | AgCl | KCl (sat.) electrode. A potential scan rate was 200 (CV) or 20 mV s^{-1} (RDE), 2800 rpm. All measurements were made under argon; samples were dissolved in a preliminarily deaerated solvent. The SAMs of **1**–**3** were fabricated by immersing the Au electrode in a 10^{-3} M acetonitrile solution of a test compound for at least 24 h. Then, the electrode was rinsed several times with MeCN, dried in air, and transferred into the pure supporting electrolyte; after that, CV curves were recorded.

atom, yielding in the electrochemically stable radical anion, a result that is consistent with previously reported electrochemical reduction of sulfides.[10]

The first oxidation step of **1**–**3** in the solution takes place at potentials between 0.56 and –1.20 V and presumably involves the NH group.[11] Compound **3′**, which has no NH group, oxidized at higher anodic potential. The potential of the second oxidation peak lies in the region of oxidation potentials of organic sulfides.[10]

As we can see in Table 1, the oxidation of **1** adsorbed on the gold electrode surface is retarded and the reduction is facilitated. This data indicates that compounds **1**–**3** adsorbed on the electrode surface may have a structure different from that in solution. It is evident that both oxidation and reduction of the adsorbed forms of **1**–**3** involve the imine fragment. Based on the electrochemical data obtained for **1**–**3**, we can propose a scheme of processes occurring at the surface of the gold electrode, assuming that these compounds are adsorbed in the open iminothiol form rather than the cyclic thiazolidine form. The driving force of this process may be the formation of a thiol self-assembled monolayer during the adsorption of **1**–**3** in their open forms **1′**–**3′**.

During the reverse of potential after +1.5 V, the corresponding oxidation anodic peak at a potential of $E_\mathrm{p}^\mathrm{Red}$ ~ –0.6 V displaying the anion RS$^-$ is observed (Figure 1).[12]

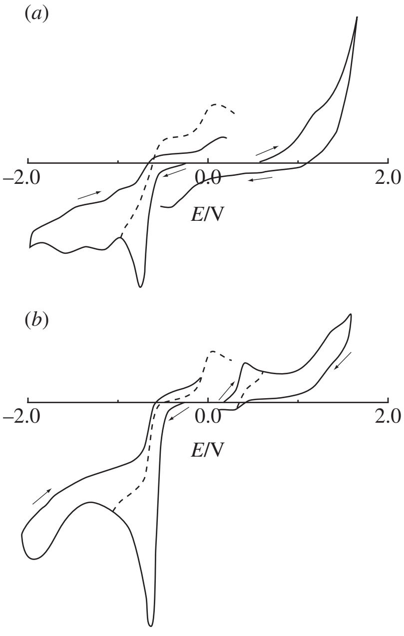
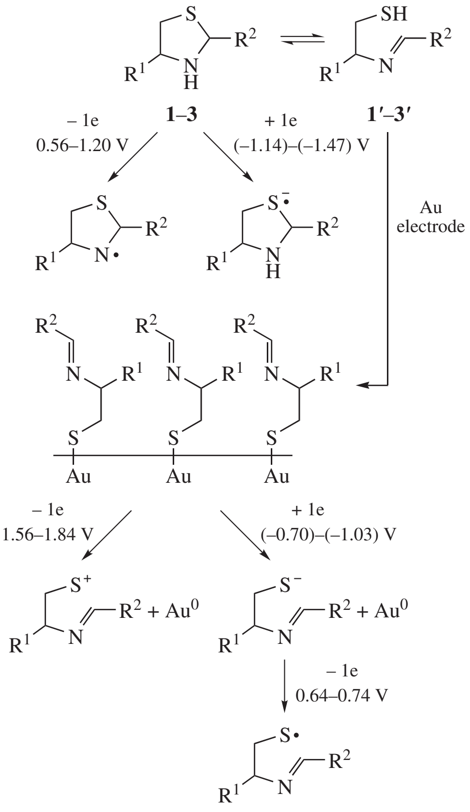


Figure 1 Cyclic voltammograms (0.05 M Bu_4NBF_4, 20 °C) of (*a*) compound **1** in MeCN solution (Pt electrode, concentration 10^{-3} mol dm^{-3}) and (*b*) compound **1** adsorbed on Au electrode.

Summarizing, the following scheme of the processes taking place under oxidation and reduction of compounds **1**–**3** in the solution and on the Au electrode surface may be proposed (Scheme 3).

Generalizing the results, we can conclude that we found a new way to construction of the self-assembling monolayers on gold surfaces based on ring opening reaction of thiazolidines to iminothiols followed by Au–S bond formation. This conclusion has been made on the basis of electrochemical and IR spectroscopy data.



Scheme 3

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References

1 J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo and G. M. Whitesides, *Chem. Rev.*, 2005, **105**, 1103, and references therein.
2 E. Katz, N. Itzhak and I. Willner, *J. Electroanal. Chem.*, 1992, **336**, 357.
3 E. Sabatani, J. Cohen-Boulakia, M. Bruening and I. Rubinstein, *Langmuir*, 1993, **9**, 2974.
4 A. Ihs, K. Uvdal and B. Liedberg, *Langmuir*, 1993, **9**, 733.
5 T. R. G. Edwards, V. J. Cunnane, R. Parsons ans D. Gani, *J. Chem. Soc., Chem. Commun.*, 1989, 1041.
6 C. A. Mirkin, *Inorg. Chem.*, 2000, **39**, 2258.
7 (*a*) C. D. Bain, H. A. Biebuyck and G. M. Whitesides, *Langmuir*, 1989, **5**, 723; (*b*) H. A. Biebuyck, C. D. Bain and G. M. Whitesides, *Langmuir*, 1994, **10**, 1825.
8 J. C. Love, D. B. Wolfe, R. Haasch, M. L. Chabinyc, K. E. Paul, G. M. Whitesides and R. G. Nuzzo, *J. Am. Chem. Soc.*, 2003, **125**, 2597.
9 Z. Zhang, A. E. Martell, R. J. Motekaitis and L. Fu, *Tetrahedron Lett.*, 1999, **40**, 4615.
10 A. P. Tomilov, Yu. M. Kargin and I. N. Chernykh, *Elektrokhimiya organicheskikh soedinenii: elementy IV, V i VI grupp* (*Electrochemistry of Organic Compounds: Group IV, V, and VI Elements*), Nauka, Moscow, 1986, pp. 212–235 (in Russian).
11 C. K. Mann and K. K. Barnes. *Electrochemical Reactions in Non-aqueous Systems*, Marcel Dekker, New York, 1970, ch. 9.
12 J. Simonet, M. Carriou and H. Lund, *Liebigs Ann. Chem.*, 1981, 1665.

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