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Copper(II) complex with (4*Z*,4*Z*′)-1,1′-[disulfanediylbis(ethane-2,1-diyl)]-bis[2-methylthio-4-(pyridin-2-ylmethylidene)-1*H*-imidazol-5(4*H*)-one] onto a gold electrode surface – a catalyst of electrochemical reduction of nitrite in water solution

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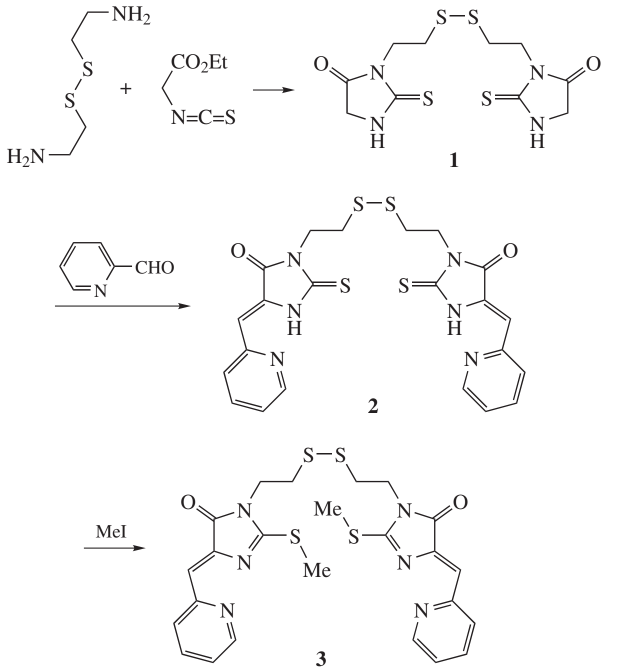
A new organic ligand (4*Z*,4*Z*′)-1,1′-[disulfanediylbis(ethane-2,1-diyl)]bis[2-methylthio-4-(pyridin-2-ylmethylidene)-1*H*-imidazol-5(4*H*)-one] chemisorbed on gold electrode surface forms coordination compound with copper(II), which catalyzes the electrochemical reduction of nitrite in water solution.

The reduction of nitrite is one of the steps of the denitrification process (2NO$_3^-$ → 2NO$_2^-$ → 2NO → N$_2$O → N$_2$) in the global nitrogen cycle. In nature, the reduction of NO$_2^-$ to NO and water is catalyzed under ambient conditions during microbial denitrification by the copper- or iron-containing metalloenzymes, nitrite reductases (NiRs).[1,2] Several Cu^{II} complexes have been so far reported as models of the Cu–NiR active site.[3–13] The problems in their using as electrocatalytic systems are due to the fact that many Cu^{II} complexes exhibit irreversible electrochemistry leading to unstable Cu^{I} or directly to Cu^{0} complexes. These features of the electroreduction process are connected with the difference in the coordination geometry preferred by the Cu^{II} and Cu^{I} ions, so that large inner-coordination sphere rearrangements are required during the redox process in order to produce a stable Cu^{I} form of the complex. We have recently demonstrated that metal complexes of 3-phenyl-2-alkylthio-5-(2-pyridylmethylene)-3,5-dihydro-4*H*-imidazol-4-ones[14,15] or *N*-(2-phenylselenocyclohexyl)-*N*-(pyridin-2-ylmethylidene)amine[16] can be reversibly reduced on glass carbon or noble metal electrodes, and the reduced forms of these complexes are capable of catalyzing the reduction of nitrous oxide to N$_2$ under mild conditions at moderate potential ($E_{\text{pc}} < -1.0$ V). In this study, we prepared a gold electrode modified with Cu^{II}–3-phenyl-2-alkylthio-5-(pyridin-2-ylmethylidene)-3,5-dihydro-4*H*-imidazol-4-one complex and investigated the electrochemical reduction of nitrite on it.

Ligand **3** was synthesized in three steps from cystamine and ethyl isothiocyanatoacetate (Scheme 1).† Both products **2** and **3** were formed as single geometric isomers, which were identified as the *Z* isomers based on the chemical shifts of the vinylic protons in the ^{1}H NMR spectra.[17–19]



Scheme 1

Ligand **3** was chemisorbed on gold electrode surface by means of immersion of electrode in a solution of disulfide-derivatized compound **3**. Self-assembly of dialkyl disulfides on gold usually results in monolayers of thiolates.[20–22] The insertion of copper

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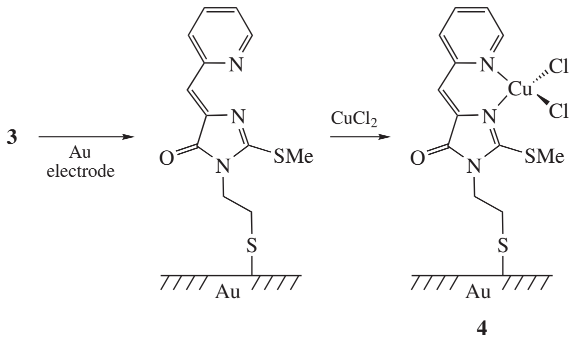
† *3,3′-[Disulfanediylbis(ethane-2,1-diyl)]bis(2-thioxoimidazolidin-4-one)* **1**. A mixture of cystamine (1.12 g, 7.36 mmol) and ethyl isothiocyanatoacetate (2.13 g, 14.7 mmol) in 20 ml of Et$_2$O was stirred at room temperature for 14 h. When the reaction was completed (monitoring by TLC), Et$_2$O was decanted, then 30 ml of EtOH and 10 ml of 10% aqueous HCl were added, and the resulting mixture was boiled for 2 h. The precipitate that formed under cooling was filtered off and dried in air to obtain compound **1** (1.85 g, 5.29 mmol, 72%), mp 264–266 °C. ^{1}H NMR (DMSO-d_6) δ: 2.98 (t, 2H, J 7.09 Hz), 3.96 (t, 2H, J 7.09 Hz), 4.11 (s, 2H), 10.20 (s, 1H). IR (ν/cm^{-1}): 3220, 1750, 1745, 1705, 1535, 1460, 1345. Found (%): C, 34.10; H, 4.29; N, 15.75; S, 36.98. Calc. for C$_{10}$H$_{14}$N$_4$O$_2$S$_4$ (%): C, 34.27; H, 4.03; N, 15.98; S, 36.64.

(5Z,5Z′)-3,3′-[Disulfanediylbis(ethane-2,1-diyl)]bis[5-(pyridin-2-ylmethylidene)-2-thioxoimidazolidin-4-one] **2**. Compound **1** (0.5 g, 1.43 mmol) was added to a solution of 0.2 g KOH in 10 ml of MeOH and the mixture was stirred at room temperature to complete dissolution of a solid. Then 2-pyridinecarbaldehyde (0.3 g, 2.86 mmol) was added, and the mixture was stirred for 12 h. Glacial AcOH (3 ml) was added under stirring, then the reaction mixture was poured into 20 ml of water. The formed light-yellow precipitate was filtered off and dried in air to obtain compound **2** (0.66 g, 1.25 mmol, 86%), mp > 300 °C. ^{1}H NMR (DMSO-d_6) δ: 3.07 (t, 2H, J 6.94 Hz), 4.10 (t, 2H, J 6.85 Hz), 6.61–6.71 (m, 1H), 7.30–7.39 (m, 1H), 7.83–7.95 (m, 2H), 8.67–8.74 (m, 1H). IR (ν/cm^{-1}): 1730, 1660, 1462, 1435, 1383. Found (%): C, 48.22; H, 3.99; N, 14.92; S, 24.03. Calc. for C$_{22}$H$_{22}$N$_6$O$_3$S$_4$ (**2**·H$_2$O) (%): C, 48.33; H, 4.06; N, 15.37; S, 23.46.



Scheme 2

ion was performed by soaking the ligand monolayer on the gold surface in $CuCl_2 \cdot 6H_2O$ solution in DMF.‡ The structure of the forming coordination compounds proposed according to previously established structures of copper complexes with analogous ligands[14,15,18,23] is shown in Scheme 2.

Compound **3** was studied by cyclic voltammetry (CV) in the solution using glass carbon (GC) electrode and as the adsorbed form on Au electrode.§ The electrochemical oxidation and reduction potentials are given in Table 1. Ligand **3** undergoes a three-step reduction on GC electrode [Figure 1(*a*)] at –1.32, –1.81 and –2.17 V; it oxidizes in one irreversible step at 1.49 V. Apparently, the ligand oxidation occurs at the sulfur-containing fragment, and the first and second steps of the reduction occur at O=C–C=C system, similarly to earlier studied 3-substituted 2-alkylthio-5-(pyridin-2-ylmethylidene)-3,5-dihydro-4*H*-imidazol-4-ones.[14,15,18–21] The adsorption of ligand **3** on gold electrode [Figure 1(*b*)] results in slight shift of first and second reduction peaks; at the same time two additional peaks at –0.52 and –0.83 V corresponding to the reduction of adsorbed compound **3** appear on CV curve. An interaction of disulfide **3** with Au electrode surface proceeds with the breaking of S–S bond and the formation of gold thiolate

Table 1 Electrochemical oxidation (E_p^Ox) and reduction ($E_\mathrm{p}^\mathrm{Red}$) potentials for compounds **3**, **4** measured by CV technique using GC or Au electrodes in DMF in the presence of 0.1 M Bu_4NClO_4. The potential scan rate was 200 mV s^{-1}. The values after the slash marks represent the peak potentials for the reverse CV scans.

Compound (electrode)	$E_\mathrm{pc}^\mathrm{Red}$/V	$E_\mathrm{pa}^\mathrm{Ox}$/V
3 (GC)	–1.32/–1.25, –1.81/–1.67, –2.17/–1.90	+1.49
3 (Au)	–0.52, –0.83, –1.34, –1.88	+1.25
4 (Au)	+0.28/+0.34, –0.12 (the desorption peak of Cu^0 is observed on reverse scan of CV curve), –0.92, –1.32, –1.84	

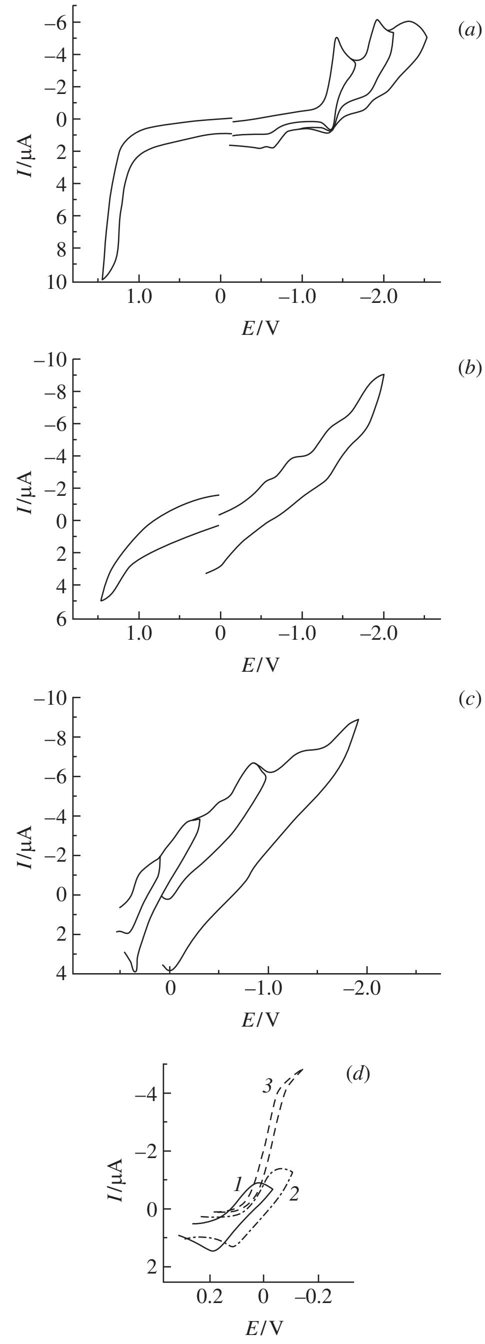


Figure 1 Cyclic voltammograms: (*a*) ligand **3** (10^{-3} M, DMF, GC electrode, Bu_4NClO_4, scan rate 200 mV s^{-1}); (*b*) ligand **3** on gold electrode surface (DMF, Bu_4NClO_4, scan rate 200 mV s^{-1}); (*c*) complex **4** on gold electrode surface (DMF, Bu_4NClO_4, scan rate 200 mV s^{-1}); (*d*) complex **4** on gold electrode surface (H_2O, 0.1 M $LiClO_4$, scan rate 10 mV s^{-1}): (*1*) in the absence of $NaNO_2$, (*2*) in the presence of 0.5 M $NaNO_2$ and (*3*) in the presence of 0.5 M $NaNO_2$ after addition of $HClO_4$ to pH 5.3.

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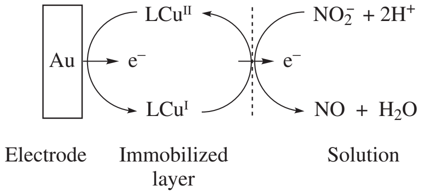
*(4Z,4Z')-1,1'-[Disulfanediylbis(ethane-2,1-diyl)]bis[2-methylthio-4-(pyridin-2-ylmethylidene)-1*H*-imidazol-5(4*H*)-one]* **3**. Solution of KOH (15%, 1.4 ml) was added to a suspension of thiohydantoin **2** (0.5 g, 0.95 mmol) in the mixture of 10 ml of MeOH and 10 ml of H_2O. After a complete dissolution of the solid, MeI (0.53 g, 3.8 mmol) was added and the mixture was stirred at room temperature for 1 h. The precipitate that formed was filtered off, washed with diethyl ether and dried in air to obtain compound **3** (0.42 g, 0.76 mmol, 79%), mp > 300 °C. ^{1}H NMR (DMSO-d_6) δ: 2.74 (s, 3H), 3.03 (t, 2H, *J* 6.48 Hz), 3.88 (t, 2H, *J* 6.42 Hz), 6.77 (s, 1H), 7.31–7.41 (m, 1H), 7.85–7.96 (m, 1H), 8.65 (d, 1H, *J* 3.18 Hz), 8.78 (d, 1H, *J* 8.19 Hz). IR (ν/cm^{-1}): 3430, 1720, 1645, 1495, 1470, 1350. Found (%): C, 49.07; H, 4.51; N, 13.35; S, 21.48. Calc. for $C_{24}H_{28}N_6O_4S_4$ (**3**·$2H_2O$) (%): C, 48.63; H, 4.76; N, 14.18; S, 21.63.

‡ To prepare the monolayer of organic ligand on the gold surface, a well-polished and ultrasonically cleaned Au electrode was immersed in a 50 mM solution of ligand **3** in DMF at room temperature for 16 h, and then the electrode was sufficiently rinsed with DMF and supporting electrolyte to remove the unbound ligand molecules. The insertion of copper ion was performed by soaking the ligand monolayer on the gold surface in 10 mM $CuCl_2 \cdot 6H_2O$ solution in DMF at room temperature for 5 h. An electrode was thoroughly washed with DMF to remove excess of free Cu ions, giving the Cu complex on Au surface (**4** in Scheme 2).

§ Electrochemical studies were performed at 25 °C using a IPC-2000 potentiostat with the refinement program complex (developed in A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, RAS; author V. E. Kasatkin, vadim_kasatkin@mail.ru; see, for example http://www.expo.ras.ru/base/prod_data.asp?prod_id=4687). Glass carbon and Au disks (both 2 mm in diameter) polished with Al_2O_3 (< 10 μm) were used as the working electrodes, and a 0.1 M Bu_4NClO_4 solution in DMF or 0.1 M $LiClO_4$ aqueous solution served as the supporting electrolyte. Ag/AgCl/KCl(sat.) was used as the reference electrode. The potentials are given with allowance for *iR* compensation. All measurements were carried out under argon. The samples were dissolved in pre-deoxygenated solvent.

(chemical adsorption), which is proved by the presence of the Au–S reduction peak in accordance with the reaction $\mathrm{Au{-}SR + 1e \rightarrow Au^0 + RS^-}$ on CV curve [–0.83 V; Figure 1(*b*)]; a peak at –0.52 V corresponds to the reduction of disulfide **3** adsorbed on electrode surface without S–S bond breaking (physical adsorption).[22–24] After the complexation of adsorbed ligand **3** with $\mathrm{CuCl_2}$, two additional peaks at E_{pc} = +0.28/+0.34 and –0.12 V appear on CV curve, indicating of complex **4** formation [Figure 1(*c*)]. For complex **4** the intensity of peaks corresponding to copper ions reductions is practically equivalent to the intensity of the reduction peaks of organic ligand fragments [Figure 1(*c*); the peak intensities were determined by integrating the CVA curves using the program, which is part of the potentiostatic complex IPC-2000]. This leads to the conclusion that nearly 100% of immobilized ligand **3** molecules take part in coordination with copper ions.

Under the reduction of complex **4** in the presence of $\mathrm{NaNO_2}$ at the slow scan rates (10 mV s^{-1}) the first reduction half-peak potential was shifted from +0.28 to +0.14 V [Figure 1(*d*), curve *2*]. The effect of nitrite addition on redox potentials of immobilized copper complex implies that the coordination environment of copper atom was changed, probably due to nitrite binding to Cu as an additional ligand.[21,24] The further addition of acid ($\mathrm{HClO_4}$) to the nitrite-containing electrolyte dramatically changes the shape of the voltammogram, and an enhanced sigmoidal cathodic current–potential curve (catalytic current) is observed [in Figure 1(*d*), curve *3*]. The oxidation counterpart of the voltammetric reduction peak of the $\mathrm{Cu^{II}}$ complex disappears indicating that the electrochemically generated reduced form of the complex is required for the catalytic reduction of nitrite. These facts are consistent with an electrocatalytic process at the formal potential of the $\mathrm{Cu^{II}/Cu^{I}}$ redox couple. The appearance of the catalytic current indicates the regeneration of the initial $\mathrm{Cu^{II}}$ complex on the gold surface by the reduction of nitrite ligand.[26,27] The presumably working principle of gold electrode immobilized complex **4** is given in Scheme 3. The appearance of the reduction peak at –0.45 V on CV curve in the presence of $\mathrm{NaNO_2}$ indicates that NO is a nitrite reduction product.[17,28] $\mathrm{NH_3}$ clearly does not form under catalytical reduction, because the $\mathrm{NH_3}$ re-oxidation peak under $E_{\mathrm{pa}} \sim 1.0$ V is not observed at CV reverse scan in anodic region after the carrying of cathodic potential $E_{\mathrm{pc}} = -1.0$ V.



Scheme 3

In conclusion, the electroreduction of nitrite on the gold electrode modified by $\mathrm{Cu^{II}}$ complex with (4*Z*,4*Z*′)-1,1′-[disulfanediylbis(ethane-2,1-diyl)]bis[2-methylthio-4-(pyridin-2-ylmethylidene)-1*H*-imidazol-5(4*H*)-one] was observed under moderate potential. In comparison with the data presented in the literature on the use of copper complexes for the catalytic redox reaction of nitrite in the solution,[3–13] the modification of electrode surface by copper chelate has some advantages, consisting in the simplicity of complex preparation, stability, and the possibility of multiple use. We also note that the majority of the biological reactions occur at the interface (aqueous/lipid), and the incorporation of copper redox centers into the monolayers leads to the formation of the structure modeling the natural metalloenzymes, built in the biological membranes.

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References

1 S. Suzuki, K. Kataoka, K. Yamaguchi, T. Inoue and Y. Kai, *Coord. Chem. Rev.*, 1999, **190–192**, 245.
2 S. Suzuki, K. Kataoka and K. Yamaguchi, *Acc. Chem. Res.*, 2000, **33**, 728.
3 W. B. Tolman, *Inorg. Chem.*, 1991, **30**, 4880.
4 P. P. Paul and K. D. Karlin, *J. Am. Chem. Soc.*, 1991, **113**, 6331.
5 J. A. Halfen, S. Mahapatra, M. M. Olmstead and W. B. Tolman, *J. Am. Chem. Soc.*, 1994, **116**, 2173.
6 N. Komeda, H. Nagao, Y. Kushi, G. Adachi, M. Suzuki, A. Uehara and K. Tanaka, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 581.
7 L. Casella, O. Carugo, M. Gullotti, S. Doldi and M. Frassoni, *Inorg. Chem.*, 1996, **35**, 1101.
8 E. Monzani, G. J. Anthony, A. Koolhaas, A. Spandre, E. Leggieri, L. Casella, M. Gullotti, G. Nardin, L. Randaccio, M. Fontani, P. Zanello and J. Reedijk, *J. Biol. Inorg. Chem.*, 2000, **5**, 251.
9 R. L. Richards and M. C. Durrant, *J. Chem. Res.*, 2002 (S), 95.
10 H. Yokoyama, K. Yamaguchi, M. Sugimoto and S. Suzuki, *Eur. J. Inorg. Chem.*, 2005, 1435.
11 J. A. Halfen, S. Mahapatra, E. C.Wilkinson, A. J. Gengenbach, V. G. Young, Jr., L. Que, Jr. and W. B. Tolman, *J. Am. Chem. Soc.*, 1996, **118**, 763.
12 M. Sundararajan, I. H. Hillier and N. A. Burton, *J. Phys. Chem. B*, 2007, **111**, 5511.
13 A. C. Merkle and N. Lehnert, *Dalton Trans.*, 2012, **41**, 3355.
14 A. G. Majouga, E. K. Beloglazkina, O. V. Shilova, A. A. Moiseeva and N. V. Zyk, *Russ. Chem. Bull., Int. Ed.*, 2009, **58**, 1392 (*Izv. Akad. Nauk, Ser. Khim.*, 2009, 1353).
15 A. G. Majouga, E. K. Beloglazkina, S. Z. Vatsadze, A. A. Moiseeva, K. P. Butin and N. V. Zyk, *Mendeleev Commun.*, 2004, 115.
16 A. N. Chernysheva, E. K. Beloglazkina, A. A. Moiseeva, R. L. Antipin, N. V. Zyk and N. S. Zefirov, *Mendeleev Commun.*, 2012, **22**, 70.
17 A. Kudo and A. Mino, *J. Electroanal. Chem. Interfacial Electrochem.*, 1996, **408**, 267.
18 E. K. Beloglazkina, S. Z. Vatsadze, A. G. Majouga, N. A. Frolova, R. B. Romashkina, N. V. Zyk, A. A. Moiseeva and K. P. Butin, *Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 2771 (*Izv. Akad. Nauk, Ser. Khim.*, 2005, 2679).
19 A. G. Majouga, E. K. Beloglazkina, S. Z. Vatsadze, N. A. Frolova and N. V. Zyk, *Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 2850 (*Izv. Akad. Nauk, Ser. Khim.*, 2004, 2734).
20 E. K. Beloglazkina, A. G. Majouga, I. V. Yudin, N. A. Frolova, N. V. Zyk, V. D. Dolzhikova, A. A. Moiseeva, R. D. Rakhimov and K. P. Butin, *Russ. Chem. Bull., Int. Ed.*, 2006, **55**, 1015 (*Izv. Akad. Nauk, Ser. Khim.*, 2006, 978).
21 E. K. Beloglazkina, A. G. Majouga, I. V. Yudin, N. V. Zyk, A. A. Moiseeva and K. P. Butin, *Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 2163 (*Izv. Akad. Nauk, Ser. Khim.*, 2005, 2099).
22 H. Yokoyama, K. Yamaguchi, M. Sugimoto and S. Suzuki, *Eur. J. Inorg. Chem.*, 2005, 1435.
23 M. D. Bartberger, W. L., E. Ford, K. M. Miranda, C. Switzer, J. M. Fukuto, P. J. Farmer, D. A. Wink and K. N. Houk, *Proc. Natl. Acad. Sci. USA*, 2002, **99**, 10958.
24 A. Ulman, *Chem. Rev.*, 1996, **96**, 1533.
25 Y. Migita, H. Yokoyama, A. Minami, T. Mori, M. Nojiri, S. Suzuki and K. Yamaguchi, *Electroanalysis*, 2009, **21**, 2441.
26 H. Hagenström, M. A. Schneeweiss and D. M. Kolb, *Langmuir*, 1999, **15**, 2435.
27 J. Zhang, Q. Chi, J. U. Nielsen, E. P. Friis, J. E. T.Andersen and J. Ulstrup, *Langmuir*, 2000, **16**, 7229.
28 D. M. Stanbury, *Adv. Inorg. Chem.*, 1989, **33**, 69.

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