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Article

Oxidation of Elemental Gold in Alcohol Solutions

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Gold is designated as the noblest metal because of its chemical inertness. It is known to dissolve in cyanide solutions in the presence of air or H_2O_2 or in halogen-containing solutions, aqua regia being the most famous example. Herein, we report a unique thiol, especially 4-pyridinethiol (4-PS), assisted dissolution of Au in alcohol solutions. Although dissolution was found to be very selective for pyridinethiols, such a phenomenon is astonishing since thiols are commonly used as etch resists for Au and even 4-PS is extensively used as a surface modifier for Au. To gain further understanding of the dissolution process, the influence of the reaction conditions was extensively studied. On the basis of the obtained results, a mechanism for the dissolution reaction is proposed. Fascinatingly, by tuning of the reaction conditions, this phenomenon can be applied in selective preparation of self-supporting nanometer-thick Au foils.

Introduction

Besides the conventional uses of Au in electronics, gold has lately gained new interesting applications[1] and is now widely used as a substrate for self-assembled monolayers (SAMs) of organothiols because of the facile Au−S bond formation.[2,3] Surfaces modified with thiols have been used as resists for electron beam lithography and etching (e.g., protection against cyanide solutions).[4] Especially, surfaces modified with aromatic thiols have attractive electronic properties.[5] They have recently received interest as templates for chromophores, molecular devices, and nanoscale surface patterning.[6]

Organothiols and disulfides are suggested to adsorb on an Au surface as thiolates by the cleavage of the S−H or S−S bond, respectively, thus oxidizing the surface atoms to Au^I. The proposed reaction mechanism involves loss of hydrogen by the elimination of H_2 or, in the presence of an oxidant, by the elimination of water.[2,3b,c,7] It has been suggested that the formed strong Au^I−S bonds loosen the adhesion within the top two atomic layers and increase the mobility of surface Au atoms.[3a,b] As a result, Au vacancy islands of typically one atom deep or protruding Au islands are observed on surfaces after the organothiol adsorption.[3a,b,5b,8] Although the choices of solvent and O_2 concentration have no significant effects on the size or number of the vacancy islands, the surface coverage of the islands increases with extended immersion time and elevated temperatures.[5b,9a−c]

Due to their high surface area, Au nanoparticles (Ag as well) are even more vulnerable to surface modifiers than bulk

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Au surfaces.[10] This property can be also beneficial and, for example, polyhedral particles of 10−100 nm can be modified to smaller, relatively monodisperse spherical particles (average sizes ca. 5−9 nm). In these processes, the right combination of a cationic surfactant and a soft base such as alkanethiol, alkylamine, or alkylsilane is essential. Although the mechanism for this reversible modification is not fully understood, it has been proposed that the process involves etching of the nanoparticles.[10]

Despite its inherent inertness, metallic gold is well-known to be oxidized in electrochemical reactions[11] and in cyanide- or halogen-containing solutions,[12] with recent examples being the dissolution of Au with different dihalogen adducts[13] or cetyltrimethylammonium bromide/$CHCl_3$ solution by using O_2 as an oxidant.[14] Although chemisorption of 4-pyridinethiol (4-PS) on Au has been widely studied as it is a common surface modifier,[9b,15] its potential to dissolve gold had remained undiscovered. As shown here, in the presence of 4-PS, thin films on thermally oxidized Si or on glass, nanopowder, and bulk Au can indeed be dissolved in MeOH and EtOH solutions. To gain further understanding about the dissolution reaction, effects of solvent, temperature, O_2 pressure, 4-PS concentration, and immersion time on the process were thoroughly studied.

Experimental Section

General Procedures. Atomic absorption spectroscopy measurements were performed with a Perkin-Elmer 3030 atomic absorption spectrophotometer, ^1H and ^{13}C NMR with a Varian Gemini 200 apparatus, and electrospray ionization time-of-flight mass spectrometry (ESI-TOF MS) with a Bruker micrOTOF mass spectrometer. IR spectra were run with a Perkin-Elmer Spectrum One. All chemicals were purchased from Aldrich and were used as received. Gold nanopowder (+99.9%) has a particle size of 30−130 nm.

The Si/SiO_2/Au, glass/Ti/Au, Si/Ti/Ag, and Si/Ti/Cu/Au structures were prepared at room temperature by electron beam evaporation. For Si/SiO_2/Au, an n-type Si(100) wafer was first oxidized thermally at 1000 °C to form an approximately 150 nm thick SiO_2 layer on its surface. After evaporation of a ca. 30 nm thick Au layer on the wafer, it was annealed in air at 250 °C for 3 h.[16] For all other structures, a thin Ti film was used as the adhesion layer. The glass/Ti/Au structure was prepared by evaporating on borosilicate glass ca. 35 nm of Ti followed by ca. 100 nm of Au. The Si/Ti/Ag and Si/Ti/Cu/Au structures were prepared by first evaporating ca. 10 nm of Ti on an untreated Si(100) wafer, followed by ca. 50 nm of Ag or ca. 40 nm of both Cu and Au, respectively. The preparation procedures for Pt and Pd thin films are described elsewhere.[17,18]

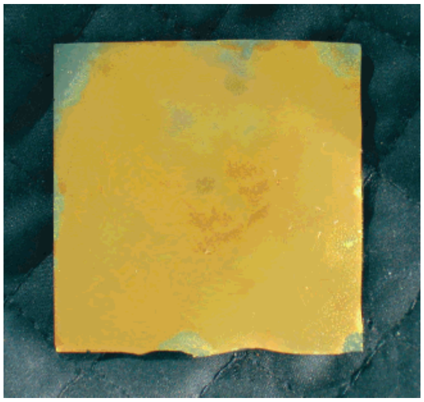

Figure 1. Photograph of the supported Au thin film which has been briefly immersed into alcohol solution of 4-PS. Dissolution of Au begins from the corners and edges of the film.

Experiments with Au^0. The etching (Figure 1) and dissolution studies of Au^0 were carried out at 22 °C in 8 mM EtOH, MeOH, and water solutions of 4-PS. When Au thin films were treated in air, the substrates were immersed in beakers covered with Parafilm. For the experiments carried out under an argon atmosphere, standard Schlenk techniques were used. After immersion, the substrates were washed with the pure solvent and dried in air flow.

Possible impurities on the Au surface that might have an influence in the dissolution of Au were excluded by treating thin films (30 nm thick, area ca. 1.4 cm^2, deposited on glass with Ti as an adhesion layer) for 15 min in Piranha solution (3:1 v/v H_2SO_4/H_2O_2). ***Caution!*** *This solution reacts violently with organic materials and should be handled with great care*. Then the supported Au films were washed with ion-exchanged water and immersed in freshly prepared 8 mM EtOH and H_2O solutions of 4-PS for 72 h. Dissolution of the Au film occurred only in alcohol solutions.

Au nanopowder (0.278 g) and pieces of bulk Au (1.288 g, pieces ca. 2 × 5 mm^2) were immersed in a MeOH solution (85 mL) of 4-PS (9.279 g, 0.98 mol). The suspension formed was stirred in a beaker at room temperature with a magnetic stirring bar for several weeks, during which time a greenish-brown powder precipitated.[19] The powder was washed with diethyl ether to remove elemental sulfur, unreacted 4-PS, and side products. Results of analysis for cationic $C_{10}H_{10}N_2S_2Au_1^+$ follow. ^1H NMR (200 MHz, DMSO-*d*): 7.61 (d, $^3J_{HH} = 6.0$ Hz, 4H, CH), 8.12 (d, $^3J_{HH} = 6.0$ Hz, 4H, CH) ppm. ^{13}C NMR (50 MHz, DMSO-*d*): 126.85, 142.86, 165.69 ppm. HRMS ESI-TOF *m*/*z* (%): $[C_{10}H_{10}N_2S_2Au_1]^+$ 419 (100, calcd 418.99454, found 418.99448, error 0.4 ppm).

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[19] It should be noted that elemental sulfur formed from the decomposition of 4-PS forms a passivating coverage on Au which considerably retards the dissolution of Au.

Table 1. Dissolution of Au Thin Films at Ambient Conditions[a]

entry	thiol	substrate	immersion time	solvent	effect
1	4-PS	$Si/SiO_2/Au$	1 h	EtOH	etch pits
2	4-PS	glass/Ti/Au	2 d	EtOH	dissolution
3	4-PS	$Si/SiO_2/Au$	2 d	MeOH	dissolution
4	4-PS	glass/Ti/Au	several weeks	H_2O	etch pits
5[b]	4-PS	glass/Ti/Au	several months	EtOH	etch pits
6	4,4′-PSSP	$Si/SiO_2/Au$	several months	EtOH	etch pits
7	2-PS	glass/Ti/Au	several weeks	EtOH	etch pits

[a] Film area ca. 1 cm^2, thickness 30 nm, thiol concentration 8 mM. [b] Reaction performed under argon.

The suspension, on the other hand, was filtered, and after solvent removal, a brownish-yellow oil was obtained. The oil was extracted with diethyl ether to remove unreacted 4-PS, side products, and impurities. When the oil was dissolved in MeOH and diethyl ether was added to the solution, a Au^I complex precipitated (60 mg, 0.14 mmol). HRMS ESI-TOF *m/z* (%): $[C_{10}H_{10}N_2S_2Au_1]^+$ 419 (100, calcd 418.9945, found 418.9932, error 3.31 ppm). These results underscore that a part of the Au^I complex precipitates during the oxidation reaction.

Kinetics of the Dissolution. A series of experiments were conducted with MeOH solutions of 4-PS (concentration 8, 16, or 40 mM) in steel autoclaves at 22 and 80 °C with O_2 pressure of 3 or 10 bar. In a typical experiment, a test tube equipped with a magnetic stirring bar was charged with MeOH (15 mL), 4-PS (13.6 mg, 122 μmol; 27.0 mg, 243 μmol; or 66.7 mg, 609 μmol), and Au nanopowder (1 mg, 5 μmol). The test tube was then closed and placed into an autoclave, and the O_2 pressure and temperature selected were applied.

Preparation of Self-Supporting Au and Ag Thin Foils. Self-supporting Au foils were prepared by detaching Au films from Si/SiO_2 substrates (ca. 1 cm^2). In the treatment, supported Au films were immersed in an 8 mM EtOH solution of 2-pyridinethiol (2-PS) or in a MeOH solution of 4-PS (c = 9 mM, 0.18 mmol) and 2,2,6,6-tetramethylpiperidine *N*-oxyl (TEMPO; c = 5 mM, 0.10 mmol). Ag foil was detached from the $Si/SiO_2/Ti$ substrate (ca. 1 cm^2) by immersing a supported Ag film into an 8 mM MeOH solution of 2-PS.

Results and Discussion

A series of dissolution experiments were conducted with different reaction parameters, and the Au concentration in the reaction solutions was monitored as a function of time. When two similar Au thin films prepared with electron beam evaporation were treated in argon and air atmospheres, the latter film fully dissolved in 2 days whereas the former one did not dissolve during the monitored period of several months. Evidently, the dissolution of gold with 4-PS into alcohol solutions requires O_2 as the oxidant (Table 1). However, O_2 overpressure seems to have only a marginal effect; the higher pressure employed resulted in only a slightly enhanced dissolution rate (Figure 2, curves 1 and 4).

As demonstrated here with gold nanoparticles, the thiol concentration is the most important parameter for the dissolution of Au. The dissolution rate increases noticeably with increasing 4-PS concentration (Figure 2, curves 1−3). To further understand the influence of the 4-PS concentration, a second portion of 4-PS was introduced into the reaction after approximately 90 h, which is the time required to stabilize the Au concentration. As a result, the theoretical concentration of 4-PS increased from 8 to 16 mM and the Au concentration in the solution began to rise again (Figure 3, curve 6). By this approach, the amount of dissolved Au was actually higher in the end than was achieved by using the same 16 mM concentration of 4-PS from the beginning of the reaction (Figure 3, curves 2 and 6). These results suggest that 4-PS can be partially decomposed under reaction conditions. It has been previously concluded that O_2 has no role in the decomposition of 4-PS.[15b]

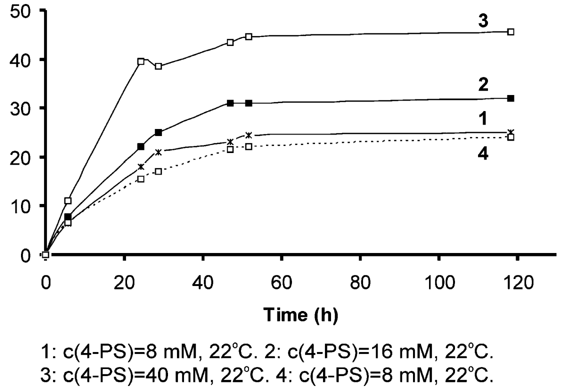

Figure 2. Effect of 4-PS concentration and O_2 pressure on the dissolution rate. Reaction conditions: Au nanopowder (1 mg, particle size 30−130 nm), MeOH solution of 4-PS (15 mL), O_2 pressure 10 bar (3 bar in entry 4), temperature 22 °C. Concentration of Au was determined by AAS.

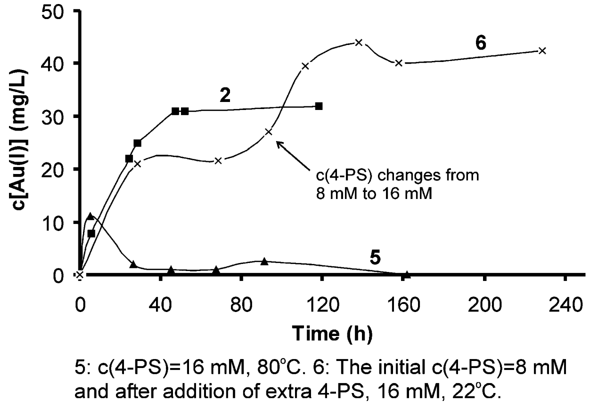

Figure 3. Effect of high temperature (curve 5, 80 °C) and increase in 4-PS concentration on the dissolution rate (curve 6). Reaction conditions are otherwise the same as for curve 2 (see above).

Increased reaction temperature has a clear effect on the rate of dissolution. Compared with the rates achieved in the analogous reactions carried out at room temperature, at 80 °C the dissolution rates accelerated in the beginning of the reaction (Figure 3). However, when the reaction is kept at this temperature, the Au concentration in the solution decreases rapidly and reaches finally zero. This decrease is due to the thermal instability of the soluble Au^I complex resulting in ligand coupling and desulfurization; i.e., formation of 4,4′-dipyridyl sulfide, elemental S, and Au^0 was detected. The extensive decomposition of 4-PS at elevated temperature appears to be a dominating side reaction and can be a reason for the measured low Au concentrations (see above).

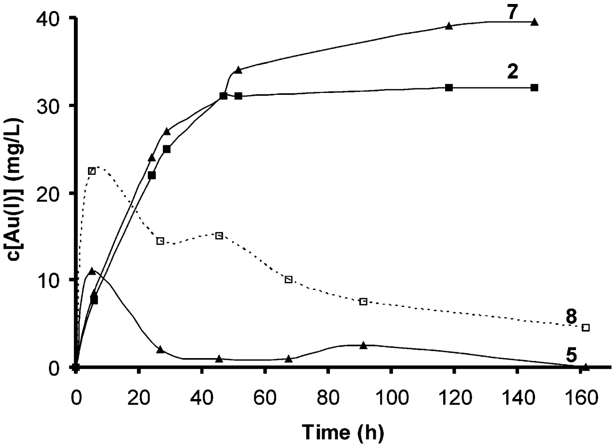

Figure 4. Enhancing effect of Cu^{II} on the dissolution rate. In curves 7 and 8, the molar ratio of Au/Cu is 10:1. Otherwise, reaction conditions for curve 7 were the same as for curve 2 and those for curve 8 were the same as for curve 5 (see above).

Since it has been reported that Cu^{II} ion accelerates the oxidation of Pd,[20] its effect on the oxidation of Au was studied as well.[21] The experimental data (Figure 4) show that Cu^{II} accelerates the dissolution of Au at 80 °C, but at 20 °C the effect is diminished. Nevertheless, at both temperatures the dissolution of Au is enhanced when compared with analogous reactions without Cu^{II}. It is important to note that in all experiments the dissolution reaction proceeds steadily, although the Au concentration in solutions remains low and reaches a steady state after a certain time. This is related to the low solubility of the formed Au^{I} complex rather than to the oxidation reaction itself (Figure 5).

Further studies affirm the unique and apparently structure-related oxidation properties of 4-PS. As commonly known, pyridine and thiophenol cannot dissolve Au in EtOH solutions. Even 4,4′-pyridyl disulfide (4,4′-PSSP), which adsorbs effectively on Au surfaces via the cleavage of the S−S bond,[15a] turned out to be inactive. This underlines the fact that thiolate-type coordination of 4-PS is not a prerequisite for the dissolution. Another structure isomer of 4-PS, 2-PS, can also dissolve gold but with a significantly reduced rate (Table 1). Whereas with 4-PS the dissolution is completed in less than 2 days, with 2-PS the dissolution occurs over several weeks. Therefore, pyridinethiol structure is, in general, needed for the dissolution while relative positions of the N and S atoms affect the efficiency of the dissolution. Presumably, due to the vicinity of the S and N atoms, 2-PS forms a more strongly adsorbed chelate on a metal surface whereas 4-PS can coordinate only via the S atom, thus providing a faster dissolution (see below).[15b,c,e,22] In addition, this dissolution reaction is feasible also for Ag and Cu, whereas Pd and Pt as well as Ti remained untouched (see the Supporting Information). This selectivity might be related to an oxidation state 1+ which is common for group 11 elements. In general, these monocations prefer a coordination number of 2 and a linear geometry.[23]

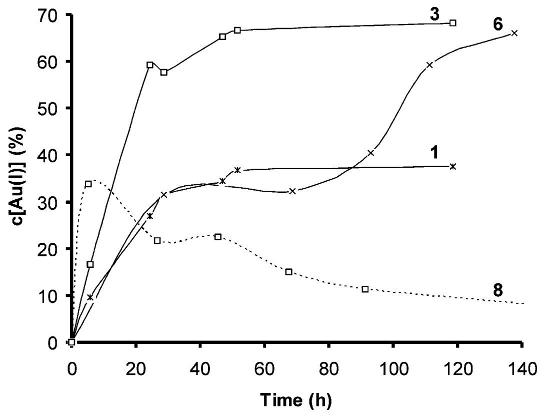

Figure 5. Percentages of Au in solution as a function of time for the curves 1, 3, 6, and 8 shown in Figures 2−4. Due to the low solubility of the Au^{I} complex, a part of the dissolved gold precipitates during the reactions.

In solutions, pyridinethiols prefer to exist as the thione isomer.[24] The possibility for the thiol−thione tautomerization via the zwitterionic isomer distinguishes pyridinethiols from other thiols or disulfides and seems essential when their ability to dissolve Au is considered. On the basis of ^{13}C NMR measurements, only the 4-pyridinethione and 2-pyridinethione isomers are present in alcohol solutions under applied reaction conditions (Scheme 1, first step). According to ESI-MS studies, the Au^{I} complex formed in the dissolution reaction has two pyridinethiol ligands. Unexpectedly, on the basis of ^{1}H and ^{13}C NMR studies, in the Au^{I} complex both ligands are in their zwitterionic form. This observation provides an insight into the pyridinethiol-assisted redox reaction.

Although 4-PS has been previously reported to adsorb on Au surfaces as the thiolates[15a−c], it is reasonable to assume that under the conditions applied in this work, 4-PS coordinates in the beginning in its zwitterionic form and forms a SAM on Au (Scheme 1). As dissolution starts from the corners of Au thin films, simultaneous coordination of two ligands on one Au atom seems beneficial for the dissolution. This bonding model also explains the need for high initial pyridinethiol concentration and the observed slower kinetics with 2-PS rather than with 4-PS. As a chelating ligand, 2-PS will inhibit the coordination of the

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(21) When Cu^{II} and 4-PS are reacted, desulfurization and ligand-coupling reactions are possible. Furthermore, Cu^{II} can be reduced to Cu^{I}. For details, for example, see: (a) Wen, Y.-H.; Cheng, J.-K.; Zhang, J.; Li, Z.-J.; Yao, Y.-G. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2004**, *C60*, m618−m619. (b) Downes, J. M.; Whelan, J.; Bosnich, B. *Inorg. Chem.* **1981**, *20*, 1081−1086. (c) Cheng, J.-K.; Chen, Y.-B.; Wu, L.; Zhang, J.; Wen, Y.-H.; Li, Z.-J.; Yao, Y.-G. *Inorg. Chem.* **2005**, *44*, 3386−3388. (d) Cheng, J.-K.; Yao, Y.-G.; Zhang, J.; Li, Z.-J.; Cai, Z.-W.; Zhang, X.-Y.; Chen, Z.-N.; Chen, Y.-B.; Kang, Y.; Qin, Y.-Y.; Wen, Y.-H. *J. Am. Chem. Soc.* **2004**, *126*, 7796−7797. To the best of our knowledge, O_2 does not react with 4-PS (see reference 15b).

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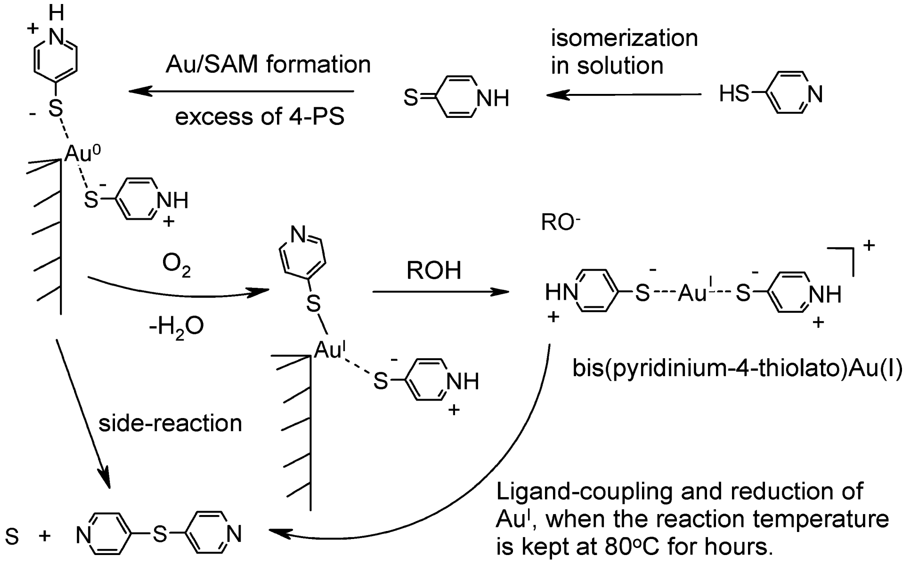
Scheme 1. Proposed Reaction Mechanism for the Oxidation of Au^0



second pyridinethiol. Afterward, pyridinethiol-assisted oxidation of Au can take place by loss of H from one of the coordinated thiols. Apparently, O_2, which was proven to be essential for the dissolution reaction, works here as an end oxidant. As a result, the gold(I) thiolato species is formed on the surface and water is released.

As the structure of the isolated complex indicates (see the Supporting Information for MS and NMR data), the detachment of the Au^I species from the surface requires a further protonation of the pyridinethiolato nitrogen. It is reasonable to assume that alcohols, although weak Brønsted acids, provide a suitable proton source and a negatively charged alkoxy moiety balances the charge. As Au^I prefers a linear structure,[25] completed here with two zwitterionic pyridinethiols, the anion will stay at the outer sphere. Despite our efforts, the unambiguous structure for the labile counterion remained unresolved. Although similar protonation of pyridinethiolato nitrogen is possible in water, low solubility of the Au^I complex might be a reason why the dissolution reaction does not take place in aqueous media (Table 1).

Interestingly, when the above-described reaction conditions or the substrate structure of the Au thin films is modified, the use of both 2- and 4-PS in alcohol solutions resulted in selective detachment of deposited Au thin films. Previously, nanometer-thick Au foils have been prepared by predepositing an unreactive parting agent, such as NaCl, on the substrate prior to Au deposition. Afterward, dissolution of the parting agent releases the self-supporting Au foil.[26]

The detachment of Au thin films with pyridinethiols is dependent on the substrate structure. The pyridinethiol treatment does not demount Au films from glass/Ti/Au structures under any applied conditions, whereas Si/SiO_2/Au structures turned out to be favorable. As an example of the method, thin (30 nm) self-supporting Au foils were prepared by detaching films from Si/SiO_2 substrates with pyridinethiols. 2-PS, which dissolves gold very slowly, separates Au films efficiently from their substrates. The films, the largest examples being 1 cm × 3 cm in dimension, were fully detached in a period of 2 days when treated in an EtOH solution of 2-PS (Figure 6). The process was even faster when a mixture of 4-PS and TEMPO as a mediator[27] was applied. In a MeOH solution, the films were fully detached after approximately 14 h. Thin film detachment was also successful with Ag films when treated in a MeOH solution of 2-PS. As the demounting method is gentle and selective with 2-PS, the foils are perfect replicas of their substrate. In addition, because the thickness and the area of the film are tuneable, the method provides an interesting concept for the selective preparation of various large-area self-supporting nanometer-thick Au foils as well as other gold nanostructures.

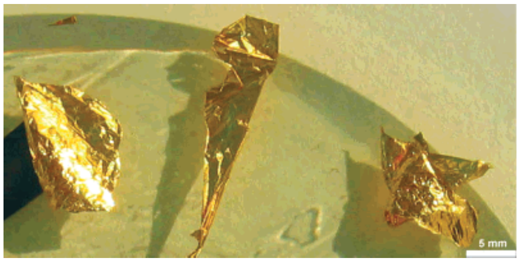


Figure 6. Thirty nanometer thick self-supporting Au foils.

Conclusions

To summarize, the dissolution of solid Au with pyridinethiols provides a new and important extension to the

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(25) Pyykkö, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 4412−4456.

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(27) TEMPO is generally used as a mediator in transition-metal-catalyzed oxidation reactions using molecular oxygen or hydrogen peroxides as end oxidant. Unexpectedly, the detachment of the Au thin film rather than changes in the dissolution rate was observed. For TEMPO reviews, see: (a) Sheldon, R. A.; Arends, I. W. C. E. *J. Mol. Catal. A: Chem.* **2006**, *251*, 200−214. (b) Sheldon, R. A.; Arends, I. W. C. E. *Adv. Synth. Catal.* **2004**, *346*, 1051−1071. (c) Ishii, Y.; Sakaguchi, S.; Iwahama, T. *Adv. Synth. Catal.* **2001**, *343*, 393−427. (d) Adam, W.; Möller, C. R.; Ganeshpure, D. A. *Chem. Rev.* **2001**, *101*, 3499−3548.

chemistry of gold and is of special interest for scientists working with Au and aromatic thiols having thione−thiol tautomery. As no parting agent is used, the pyridinethiol concept to produce various self-supporting and nanometer-thick Au foils clearly differs from traditional approaches. Because of the method, Au surfaces are covered with the thiol SAM and the shape of the substrate is replicated to the Au foil, thus providing a very exciting concept for future construction of gold nanostructures and objects.

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Supporting Information Available: Experimental data for the Au^I complex and additional results from experiments with Pd, Pt, Ag, and Cu thin films. This material is available free of charge via the Internet at http://pubs.acs.org.

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