DOI: 10.1002/anie.200906358

Chemical Polishing

Hydroxyl Radicals Attack Metallic Gold**

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Gold is used for various purposes because of its resistance to oxidation and its electrical, magnetic, optical, and other physical properties. Gold is one of the most important materials in the electronics industry, for optics, and in electrochemistry as an electrode material.[1–3] The surface smoothness and cleanness of gold is of utmost importance, in particular for optical and electrochemical applications. For surface cleaning and smoothing of gold, a number of physical, chemical, and electrochemical methods have been reported;[3–10] however, a tool for dissolving only the asperities on a gold surface has not been reported to date. Metallic gold is widely used in medicine as implant material.[11,12] Such gold implants release gold into the adjacent tissue and it was hypothesized that the release occurs by an immune reaction by oxidation.[13]

Herein, we report unexpected experimental results showing that $OH^{\bullet}$ radicals in Fenton's reagent quickly dissolve gold from a mechanically polished gold surface to lead to a much smoother, that is, chemically polished, surface. The $OH^{\bullet}$ radicals preferentially dissolve the gold atoms that are part of small asperities present on the surface, even after careful mechanical polishing. The reaction terminates after dissolution of the asperities. The reported effect can explain the release of gold from medical implants, and it may be used for polishing gold for various applications. Although it is well known that the $OH^{\bullet}$ radicals of Fenton's reagent rapidly dissolve the rather stable self-assembled monolayers of alkyl sulfides on Au electrodes,[14] attack on a bare Au surface was unexpected because gold is known for its stability towards oxidation unless the gold ions are strongly complexed, as, for example, in cyanide solutions.

Figure 1 a shows an AFM image of the Au surface after mechanical polishing and before attack by $OH^{\bullet}$ radicals. Figure 1 b is the seventh AFM image recorded following seven periods of $OH^{\bullet}$ generation in an electrochemical Fenton reaction for 10 seconds between each image recording. Figure 1 c shows the 32nd image after a sequence of 25 $OH^{\bullet}$ generations each of 10 seconds duration (see the Experimental Section). Figure 1 a–c clearly indicates that the electrode surface is smoothed considerably. The decrease of real surface area was also studied with two independent electrochemical methods, namely a) evaluation of the "gold oxide system", and b) underpotential deposition (upd) of Pb. The decrease in real surface area of the gold was quantified by CV (−0.3 V to 1. 5 V (vs. Ag/AgCl)) in 0.1 M H_2SO_4 solution. The "gold oxide system" (method a) was recorded and evaluated with respect to the charge underneath the oxidation and reduction peaks. That charge (and also the peak currents) depends on the real electrode surface and strongly decreased after a series of attacks by Fenton's reagent (see Figure 2). Control experiments have shown that the "gold oxide system" is neither affected by hydrogen peroxide, nor by Fe^{II} or Fe^{III} ions. The decrease of the oxidation charge is due to the diminished real electrode surface, as is clear from the AFM images. The final real surface area was 37 % of the initial surface area. The real surface area of gold (method b) was also determined by upd of Pb on Au (according to reference [15]). The obtained results show that the anodic and cathodic peak charge of underpotential-deposited Pb decreased to 30.4 % after $OH^{\bullet}$ attack for 70 minutes, that is, the final real surface area was 30.4 % of the initial area. The strongest surface area decrease happened during the first 20 minutes. The electrode was always mechanically polished before attack by Fenton's reagent, that is, the polishing was essentially a roughening compared to the smoothing from Fenton's reagent. To be sure that the surface area decrease was really due to dissolution of Au, the concentration of Au was determined in the Fenton solution as a function of attack time. Figure 3 shows that the attack rate was high at the beginning and very small at the end of the reaction. The reduction in Au dissolution rate does not mean that Au is not further oxidized, as could be proved by the following experiment: the Au electrode was mechanically polished, then electrochemically reduced at 0.2 V for 5 s, then attacked by $OH^{\bullet}$, and finally a voltammogram was recorded from 1.0 to 0.2 V (the starting potential was chosen so that no gold oxide could be formed electrochemically, and indeed without $OH^{\bullet}$ exposure the Au did not show any reduction peak). After $OH^{\bullet}$ exposure the reduction peak of gold oxide was present, and the peak decreased after subsequent $OH^{\bullet}$ exposure and finally became constant (because of smoothing). The final roughness factor was 1.04, and from the reduction charge it was calculated that 1.08 monolayers of Au were oxidized. This experiment proves that the surface of Au is always oxidized by $OH^{\bullet}$, but a measurable dissolution takes place only as long as the surface has certain asperities.

Our results show that $OH^{\bullet}$ oxidizes the surface of gold, preferentially dissolves the asperities on the metal surface, and thus accomplishes a very effective smoothing of the surface. Since the smooth parts of the gold surface are not measurably dissolved, it is inferred that the reaction of $OH^{\bullet}$ with the more ordered gold atoms leads to a stable gold oxide layer that can be reduced back to gold without any significant

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[**] AMN acknowledges kind support by DAAD, Bonn.

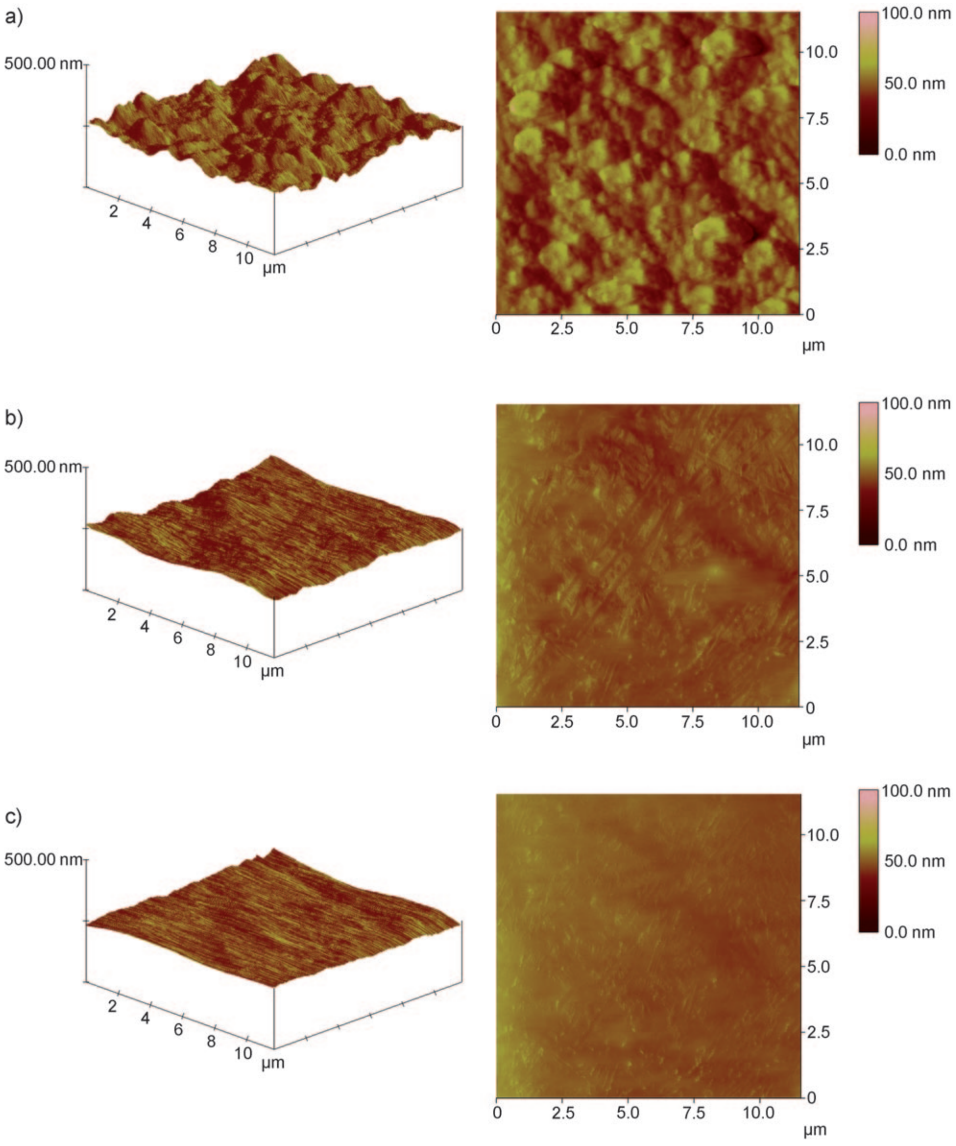

Figure 1. In situ atomic force micrographs of a polished gold surface a) before exposure to OH$^•$ radicals, b) after 7 cycles of 10 s OH$^•$ generation/6 min image recording, and c) after 32 cycles of 10 s OH$^•$ generation/6 min image recording.

loss of material. The dissolution of asperities and the formation of stable gold oxide layers on the smooth gold surface must be a kinetic effect as the very positive standard potential of OH$^•$/H$_2$O (2.38 V)[16] is sufficient also for the oxidation of bulk Au (Au$^+$/Au: 1.83 V; Au^{3+}/Au: 1.52 V).[17] The described experimental results are in complete agreement with these data.

The observed dissolution of Au by OH$^•$ sheds new light on the release of gold from gold implants, which is most likely the result of an immune reaction in which either OH$^•$ or superoxide radicals are formed. Since we have observed a strongly preferential dissolution of the rough parts of the gold surface, the release of gold from implants may be reduced by a preliminary chemical polishing of Au implants by OH$^•$. It is also likely that polishing of gold surfaces with Fenton's reagent may find wide applications in other fields in which gold is used.

Experimental Section

Cyclic voltammetry (CV) was performed with an Autolab, PGSTAT 20 potentiostat (Eco-Chemie, Utrecht). All CV experiments were carried out in the three-electrode system. An Au disc electrode (1 mm radius; Metrohm) was used as working electrode, a KCl saturated Ag/AgCl electrode served as reference

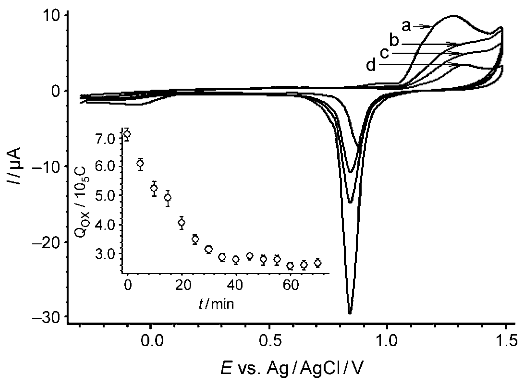

Figure 2. Cyclic voltammograms (50 mV s^{-1}) of Au recorded in 0.1 M H$_2$SO$_4$ after exposure to OH$^•$ for a) 0, b) 10, c) 15, and d) 70 min. Inset: Charge of the oxidation peak versus time of reaction with OH$^•$.

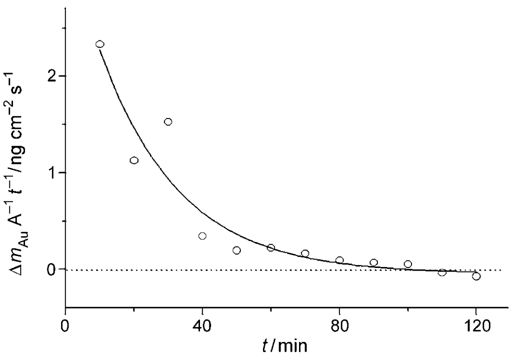

Figure 3. Rate of Au dissolution as function of time. A gold plate with 4.2 cm^2 overall geometric surface area was exposed to 2 mL of Fenton's reagent. Every 10 min, 300 µL solution was removed for analysis and replaced by 300 µL 1 M H$_2$O$_2$ solution.

electrode, and a platinum wire was used as auxiliary electrode. Fenton's reagent (1 mM Fe^{2+}) was always freshly prepared from $(NH_4)_2Fe(SO_4)_2\cdot 6(H_2O)$ (Merck), ethylenediaminetetraacetic acid (EDTA; Merck), acetate buffer (pH 4.7; 0.01M), and H_2O_2. The molar ratio of Fe^{2+}/H_2O_2 was 1:10, and the ratio of Fe^{2+}/EDTA was 1:1. Before the measurements, the surface of the working electrode was polished with 1 μm and 0.3 μm Al_2O_3 on a wet pad, then rinsed with water (Sartorius, Millipore), and dried. Then the electrode was cycled between 0.3 V and 1.5 V (vs. Ag/AgCl) in 0.1M H_2SO_4 solution until a stable voltammmogram typical of a clean gold electrode was obtained.[18] The electrode was washed with water and exposed to freshly prepared Fenton solutions for 5 min in every procedure, and this exposure was repeated so that the overall exposure time ranged from 5 to 70 min. The reaction of the Fenton's reagent with Au was terminated by removing the Au from the Fenton's reagent and washing it with water. The result of the attack by Fenton's reagent was probed by measuring CVs in 0.1M H_2SO_4 or upd of Pb on Au.[19] AFM images were recorded with a "NanoScope I" (Digital Instruments) using the software "NanoScope E 4.23r3". To minimize the catalytic decomposition of H_2O_2 at the gold surface and at the cantilever during AFM imaging, the $OH^{\bullet}$ radicals were generated electrochemically. The gold surface was fixed in a self designed cell with a three-electrode assembly under pure O_2 atmosphere. The reference electrode was an Ag/AgCl (3M KCl) electrode, the working and counterelectrode were both platinum electrodes. The electrolyte was Na_2SO_4 (0.05 mol L^{-1}), $(NH_4)_2Fe(SO_4)_2$ (0.2 or 10^{-4} mol L^{-1}) in H_2SO_4 (0.1M). The H_2O_2 was galvanostatically generated with 0.01 mA for 10 s. After this procedure an AFM image was recorded and $OH^{\bullet}$ was generated again. This procedure was repeated until no further changing of the Au surface was detectable. By doing so, the H_2O_2 concentration was small enough to avoid the generation of oxygen bubbles on the gold surface and the platinum-coated cantilever.

Received: November 11, 2009

Keywords: electrochemistry · Fenton's reagent · gold · radicals · voltammetry

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