Fenton Polishing

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A Golden Episode Continues Fenton's Colorful Story**

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In 1900, Henry J. H. Fenton, then a Fellow of the Royal Society working in the Chemical Laboratory of the University of Cambridge, completed and published the first part (or episode) of an interesting and colorful story[1a] that started before 1876 with his curiosity during undergraduate studies.[1b] Fenton's story was often told with organic colors as he described with passion: "When tartaric acid in aqueous solution interacts with certain oxidizing agents in presence of a trace of a ferrous salt, a solution is obtained which gives a beautiful violet color on the addition of caustic alkali".[1c] Of various oxidizing agents tested, Fenton found that "hydrogen dioxide", or hydrogen peroxide, (H_2O_2) as it is now known, was particularly effective.[1c] The aqueous mixture of Fe^{2+} and H_2O_2 with or without other necessary additives has since been widely studied, and is nowadays called Fenton's reagent.

Interestingly, Fenton gave his 1900 paper the title, "The oxidation of organic acids in presence of ferrous iron. Part I", thus indicating his belief that there should be at least a Part II of the story, or even more. However, possibly owing to his interest being shifted to other reactions, such as CO_2 reduction to formaldehyde in water,[1d] Fenton neglected to publish Part II of his work, although he did tell his color story again later.[1e] Nevertheless, the past 110 years have seen many of Fenton's followers report new findings for various interests and purposes.[2–5] It is now generally accepted that the remarkable oxidizing activity of Fenton's reagent results from the hydroxyl radicals ($OH^{\bullet}$ and $OOH^{\bullet}$) produced through the following catalytic reactions in the mixture.

$$Fe^{2+} + H_2O_2 = Fe^{3+} + OH^- + OH^{\bullet} \quad (1)$$

$$Fe^{3+} + H_2O_2 = Fe^{2+} + H^+ + OOH^{\bullet} \quad (2)$$

More complicated or slightly modified mechanisms of the Fenton reaction are present in the literature, depending on the substrate and reaction conditions.[2] Further, the concept and technologies have evolved into, for example, electro-Fenton, photo-Fenton, and hetero-Fenton processes in which the oxidizing agent is regenerated or supported on a solid substrate.[3a–c] An important addition to Fenton's original work is the use of chelating agents, such as EDTA (ethylenediaminetetraacetic acid) and EDDS (ethylenediaminedisuccinic acid), to modulate the effectiveness of H_2O_2, or prevent Fe^{2+} from hydrolytic precipitation in near neutral or alkaline solutions ($pH > 5$).[3d–f] Of particular relevance to the environmental impact of industrial processes, Fenton's reagent and its derivatives have been investigated and applied for the removal of organic, often toxic, pollutants from various waste waters and soils.[3a–c]

Nonetheless, there is a common point in almost all past research on Fenton's reagent—the target to be oxidized is typically an organic or biological substrate. The effects of this extraordinary reagent on inorganic substrates, particularly metals, have been largely neglected until recently.[2d,4] One rare exception exploited the oxidizing power of Fenton's reagent, in line with expectation, to create a thin biocompatible TiO_2 coating on the surface of a shape memory alloy, NiTi.[2d] Now, as shown in Figure 1, a surprising new study has demonstrated that Fenton's reagent can attack gold, despite the fact that it is one of the most inert metals known.[4a] This intriguing finding was reported by Nowicka, Scholz, and coworkers. They discovered that the gold treated by Fenton's reagent had lost its surface roughness and presented a more polished appearance.

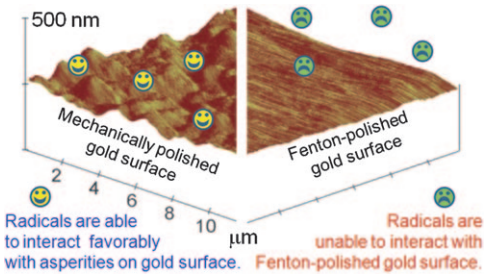

Figure 1. Comparison of the images obtained by atomic force microscopy (extracted from ref. [4a]) of mechanically and Fenton polished gold, and schematic illustration of radical species (happy faces) interacting favorably with the defect sites (asperities) on the gold surface, and of the same radical species (unhappy faces) finding difficulties to interact with the Fenton polished smoother gold surface.

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As Nowicka, Scholz, and co-workers recognized,[4a] ultra-smooth gold is needed in many practical applications such as electrochemistry, microelectronics, optics, and life-supporting medical implants, in addition to its well-known aesthetic appeal. In all these cases, the surface conditions of the metal are a vital factor. In comparison with other metals, pure gold is very soft and ductile. These characteristics make it easy to deform but tricky to polish the metal mechanically. Indeed, upon application of the standard polishing procedure with 1 μm and 0.3 μm alumina powders on a wet pad, micrometer and nanometer sized asperities were still observed on the metal's surface under examination with an atomic force microscope (AFM). After treatment with Fenton's reagent, however, these asperities were all removed, leaving a much smoother surface as shown in Figure 1. Nowicka and Scholz call such selective dissolution of asperities on the gold surface "Fenton polishing", and believe that local oxidation of gold by the hydroxyl radicals in Fenton's reagent is responsible.

In electrochemistry, a smoother electrode surface produces a smaller current than a rougher one, if all other conditions are the same. This outcome was readily confirmed by the team of Nowicka and Scholz. In addition, they found that Fenton's reagent was only effective for the first 30–40 minutes of the immersion experiment, which suggests that the attack is selective to the asperities, but not to the smooth gold surface. This feature is very useful in terms of manufacturing because the chemical polishing process terminates itself at the correct smoothness without incurring unnecessary loss of gold. In addition, such a polishing treatment can be applied to small gold artifacts with unusual shapes, such as jewelry. Further, unlike mechanical polishing in which the removed gold is lost with the polishing powder and fluids, the dissolved gold in Fenton's reagent is in fact easily recoverable by, for example, electrowinning.

In a further study,[4b] the team of Nowicka and Scholz investigate the effect of "Fenton polishing" on the electrocatalytic activity of gold. They started with a hypothesis that the catalytic activity of gold originates from those surface defects having partially filled *d* orbitals which are interactive with the free radical intermediates in some reactions (in a similar manner to platinum). As illustrated in Figure 1, the surface defects are more likely associated with the asperities, and removal of the latter by Fenton polishing should make the gold surface catalytically inactive. They then carried out various electrochemical experiments on gold electrodes that were Fenton polished to various degrees. The outcomes matched the hypothesis with high satisfaction.

The findings reported by Nowicka, Scholz, and co-workers are very stimulating in terms of thoughts and questions that could be raised. For example, why was this effect of Fenton's reagent not discovered before during the past 110 years? The word "serendipity" is often used in magazines to account for important breakthrough in a historical scientific area, but is this also the case for this team of researchers? On the other hand, metallic catalysts are often used in the form of a fine powder to increase contact with substrate species. Particularly, gold particles of various sizes (nm to μm) could be prepared in amorphous, single crystalline, and polycrystalline forms.[5a] Uses of gold nanoparticles as catalysts are common research and industrial practices for processing waste waters, sometimes in the presence of Fenton's reagent.[5b,c] Thus, it would be of fundamental relevance and practical importance to investigate the effects of Fenton polishing on small gold particles. Figure 2 illustrates

Figure 2. Schematic illustration of a hypothetical Fenton polishing of a gold micro- or nanoparticle exaggerated with surface asperities or surface defects. Is such a gold particle that is Fenton polished less or more active for the catalysis of reactions with free radical intermediates?

schematically a hypothetical example of transferring this work on the flat gold surfaces, as shown in Figure 1, to a gold micro- or nanoparticle with surface asperities. There are however questions in relation to Figure 2. Is this "knock-out mechanism" applicable to a powdery metallic catalyst? Would an appropriately controlled treatment in the Fenton solution enhance the catalytic activity of micro- or nanometer metal particles because of the "size reduction" effect caused by selective dissolution? What is the probability of using Fenton's reagent to achieve complete dissolution of a metal powder, or selective dissolution of a particular component in an alloy powder or bulk sample? Many more questions could be added to this list, but answers, more detailed theories and, most importantly, advancement of the relevant sciences and technologies require input and effort from the large community of existing and future followers of Fenton.

Last, but not least, have Nowicka, Scholz and co-workers opened a new golden episode in the colorful and long lasting story of Fenton's reagent? The answer is yes, obviously!

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