

Hydroxyl Radical-Induced Etching of Glutathione-Capped Gold Nanoparticles to Oligomeric Au^I-Thiolate Complexes

Tzu-Heng Chen, Chih-Chun Nieh, Wei-Lung Tseng

Department of Chemistry, National Sun Yat-sen University
70, Lien-hai Road, Kaohsiung, Taiwan
tsengwl@mail.nsysu.edu.tw

Extended Abstract

The Fenton reaction involves the production of strongly oxidizing hydroxyl radicals via Fe^{II}-mediated reduction of hydrogen peroxide. (Neyens and Baeyens 2003; Pignatello et al. 2006) The formed hydroxyl radicals, which are one of the most powerful oxidizing species, are effective for the degradation of organic pollutants in soils and waters. (Krystynik et al. 2014; Quan et al. 2003; Yang et al. 2014) Studies have reported that hydroxyl radical can react with lipids, amino acids, proteins, and DNA, resulting in cell death. (Cadet et al. 1999) Under UV irradiation, the reaction of the Fenton reagent and graphene oxide produced nanoporous graphene sheets and graphene quantum dots. (Zhou et al. 2012) Even though gold provides resistance to oxidation and hot corrosion, the Fenton reaction has been demonstrated to be capable of removing metastable surface gold atoms from a Au surface. (Karthik et al. 2014; Nowicka et al. 2010)

This study proposed that the hydroxyl radicals in Fenton's reagent quickly etch glutathione (GSH)-capped gold nanospheres (GSH-AuNSs) to form oligomeric Au^I-thiolate complexes. GSH-AuNSs were produced by reducing HAuCl₄ with NaBH₄ in the presence of GSH. The as-prepared solution exhibited a surface Plasmon resonance (SPR) at 525 nm, which is characteristic of AuNSs. The Fenton reaction of the GSH-AuNSs proceeded in an aqueous solution containing 100 mM H₂O₂ and 5 mM Fe^{II}. H₂O₂ can be dissociated into hydroxyl radicals *via* one-electron reduction by Fe^{II}. (Bossmann et al. 2004) The hydroxyl radical-induced etching of GSH-AuNSs was demonstrated using absorption spectroscopy, transmission electron microscopy, dynamic light scattering, and Raman spectroscopy. The formed products were suggested to be oligomeric Au^I-thiolate complexes through X-ray photoelectron spectroscopy and ESI-MS.

The successful etching of GSH-AuNSs by hydroxyl radicals suggests that the same strategy may be implemented to etch other gold-based nanomaterials. Short gold nanorods and octahedral gold nanocrystals, for example, were used to test this hypothesis. Compared to the treatment of GSH-AuNSs with hydroxyl radicals, a similar transition in the absorption spectra was observed in the treatment of short gold nanorods and octahedral nanocrystals with hydroxyl radicals. TEM images show that the size of short gold nanorods and octahedral nanocrystals became extremely small (~ 2 nm) after the addition of hydroxyl radicals, reflecting that hydroxyl radicals indeed etch gold nanorods and octahedral nanocrystals.

Encouraged by these results, we envisaged that hydroxyl radicals could be used in place of cyanide for the removal of a layer of gold from scrap electronics. Importantly, the use of cyanide as a stripping solution has negative environmental implications. The gold-plated scrap was immersed into a solution of 100 mM H₂O₂ and 5 mM Fe^{II} at ambient temperature. Inductively coupled plasma mass spectrometry (ICP-MS) was utilized to quantitatively determine the concentration of liberated gold ions in the solution after varied incubation times. The concentration of gold liberated from the scrap gradually increased over time, signifying that the hydroxyl radicals effectively remove gold from scrap electronics. We suggest that the efficiency of the hydroxyl radical-induced removal of gold from scrap electronics can be further improved by increasing the concentration of the Fenton's solution.

- Bossmann, S.H., Oliveros, E., Kantor, M., Niebler, S., Bonfill, A., Shahin, N., Worner, M., & Braun, A.M. (2004). New Insights Into The Mechanisms Of The Thermal Fenton Reactions Occurring Using Different Iron(II)-Complexes. *Water Sci Technol.*, 49, 75-80.
- Cadet, J., Delatour, T., Douki, T., Gasparutto, D., Pouget, J.P., Ravanat, J.L., & Sauvaigo, S. (1999). Hydroxyl Radicals And DNA Base Damage. *Mutat. Res-Fund. Mol. M.*, 424, 9-21.
- Karthik, P.E., Jeyabharathi, C., & Phani, K.L. (2014). Oxygen Evolution Reaction Electrocatalyzed On A Fenton-Treated Gold Surface. *Chem. Commun.*, 50, 2787-2790.
- Krystynik, P., Kluson, P., Hejda, S., Masin, P., & Tito, D.N. (2014). A Highly Effective Photochemical System For Complex Treatment Of Heavily Contaminated Wastewaters. *Water Environ Res.*, 86, 2212-2220.
- Neyens, E., & Baeyens, J. (2003). A Review Of Classic Fenton's Peroxidation As An Advanced Oxidation Technique. *J Hazard Mater.*, 98, 33-50.
- Nowicka, A.M., Hasse, U., Hermes, M., & Scholz, F. (2010). Hydroxyl Radicals Attack Metallic Gold. *Angew. Chem. Int. Edit.*, 49, 1061-1063.
- Pignatello, J.J., Oliveros, E., & MacKay, A. (2006). Advanced Oxidation Processes for Organic Contaminant Destruction Based on the Fenton Reaction and Related Chemistry. *Crit. Rev. Environ. Sci. Tech.*, 36, 1-84.
- Quan, H.N., Teel, A.L., & Watts, R.J. (2003). Effect Of Contaminant Hydrophobicity On Hydrogen Peroxide Dosage Requirements In The Fenton-Like Treatment Of Soils. *J Hazard Mater.*, 102, 277-289.
- Yang, J., Hong, L., Liu, Y.H., Guo, J.W., & Lin, L.F. (2014). Treatment Of Oilfield Fracturing Wastewater By A Sequential Combination Of Flocculation. *Fenton Oxidation And SBR Process. Environ. Technol.*, 35, 2878-2884.
- Zhou, X., Zhang, Y., Wang, C., Wu, X., Yang, Y., Zheng, B., Wu, H., Guo, S., & Zhang, J. (2012). Photo-Fenton Reaction Of Graphene Oxide: A New Strategy To Prepare Graphene Quantum Dots For DNA Cleavage. *ACS Nano* 6, 6592-6599.