LLNL-BOOK-511653

Introduction to Nanoporous Gold

A. Wittstock, J. Biener, M. Baeumer

November 8, 2011

Nanoporous Gold: From an ancient technology to a high-tech material. A comprehensive introduction into fabrication, characterization, and applications

Disclaimer

CHAPTER 1

Introduction to Nanoporous Gold

Arne Wittstock,[1, 2*] *Jürgen Biener,*[1] *and Marcus Bäumer*[2]

[1] Lawrence Livermore National Laboratory, Nanoscale Synthesis and Characterization Laboratory, 7000 East Avenue, Livermore, 7000 East Avenue, Livermore, CA 94500, United States of America

[2] University of Bremen, Institute of Applied and Physical Chemistry, Leobener Strasse NW2, 28359 Bremen, Germany

*Corresponding author: wittstock1@llnl.gov and awittstock@uni-bremen.de

Abstract

Nanoporous gold – from an ancient technology to a high tech material. In this chapter we will give an introduction to nanoporous gold and explain the broader background and the origins of the material. In particular, we will elucidate the reasons which have made this material one of the prime examples of nanotechnology leading to a large number of various applications. We will first give a brief introduction to the material itself followed by a concise review on the element gold, its history and uses throughout the centuries. In the following, we will explain why being “nano” in combination with gold evokes novel material characteristics of this element. It is the combination of gold and feature sizes on the nanoscale which lead to the many exciting technological applications which are highlighted in the different chapters of this book.

Table of Content

1.1. Nanoporous gold

Nanoporous gold is a corrosion derived bulk nanostructured material. It is generated by the corrosion of an alloy of Au and a less noble metal, such as Ag or Cu. By electrochemical removal (dealloying) of the less noble constituent the remaining gold undergoes a self-organization process forming a three-dimensional bicontinuous porous network of interconnected ligaments (Figure 1.1). Depending on the preparation conditions, the resulting pores and ligaments can be as small as 5 nm, yet, are typically around 30 to 40 nm. By IUPAC definition, the as-prepared material is mesoporous. Due to its high porosity and small feature size, this material has a specific surface area in the range of 10 m^2g^{-1}. The void or pore volume in the resulting material mostly depends on the concentration of the less noble metal (e.g. Ag) in the starting compound. Due to fundamental limitations for bulk dealloying, such as the “parting limit” (see chapter 2) and the stability of the evolving porous network, alloys containing between 60 at% and 80 at% Ag are most viable. Processing (dealloying) of according alloys results in pore volumes between about 60 % and 80 %.

Early experimental work on corrosion derived nanoporous Au by Pickering and Swan in the 1960s[1] and by Forty in the 1970s[2, 3] focused on the corrosion aspect using this material and its starting alloys, respectively, as a model system for studies on the molecular mechanism of alloy corrosion. With the onset of nanotechnology in the late 1990s and the beginning 2000s, researchers revealed and developed the potential of this material for a variety of technological aspects. As a consequence, the number of publications dealing with nanoporous Au has steeply increased by about 40 percent per year, from about 11 publication in the year 2001 to more than 150 in the year 2010.[4] One of the reasons for the success of this material is the comparatively simple preparation of this nano-material using bench-top corrosion techniques to generate bulk samples in the sizes of millimeters and even larger. By avoiding financially demanding techniques, as for example electron beam lithography, this material became available to a variety of research groups working on the optical or mechanical properties, the catalysis or the electrochemistry of the material.

Besides the availability of the material for different research groups, another crucial factor fueling the interest in this material is its structural and chemical flexibility (see Figure 1.1). Microfabrication of the material using for example fast ion bombardment (FIB) was used to generate various micron sized patterns and structures being interesting (e.g.) for mechanical tests.[5, 6] Temperature activated ripening of the nanostructures opens the door to materials with pores and ligaments in the size regime between about 30 nm all the way up to micrometers, without losing the typical bicontinuous structure of the material.[5, 7, 8] By using templating techniques, such as slip casting of alloy coated poly styrene beads and subsequent removal of the template, hierarchical nanoporous Au can be generated as well with relative densities as low as 2 to 3 percent.[9] In addition to these structural variations, the materials surface can be chemically modified with metals, organic entities or metal oxides boosting its applications in electrochemistry (e.g. fuel cell applications), sensorics, and catalysis.[10-14]

Although the term “nanotechnology” is rather new, the use of nanomaterials can be dated back several hundreds or even thousand years. First reports on using means of corrosion to generate nanoporous gold can be related to pre-columbian civilizations, such as for example the Incans (see chapter 2). Here, the superficial dealloying and subsequent burnishing of a comparably cheaper Au-Cu alloy (removal of the Cu from the alloy surface) was used to generate a shiny gold surface, giving the work piece the allure of pure gold. Undoubtedly, this evoked severe frustration of the Spanish conquistadores when melting the looted apparently pure gold pieces back in Spain. However, artisans throughout the centuries used this superficial enrichment of Au alloys as a means of gilding. The technique was thus dubbed depletion gilding or “mis-en-colour”, accordingly. For above reasons, when dealing with nanoporous gold, we speak of an ancient material, yet with novel technological impact.

[Figure 1.1 near here]

1.2 Gold – Some Facts

Gold is an element which inspired mankind ever since. About 700 BC the famous Greek poet Hesiod described the five ages of mankind in his poem *Works and Days*.[15] The first age he calls the golden age of mankind, free of the later gradual deterioration of moral values. And indeed, gold was the first metal recognized from humans even before bronze and iron.[16] Traces of gold can be found in early human settlements (~ 8000 BC) in the Euphrat and Tigris river system, an area which is today part of the Iraq. Archeological findings of gold from later high civilizations like Egypt and Mesopotamia can be dated back as early as 4000 BC. Back in those days, gold was already used as a means of payment, in the form of rings (about 2,700 BC) and later in the form of coins (since 600 BC). Earliest craftsmanship, like the funeral mask of the Egyptian Pharaoh Tutankhamun (1223 BC) or Solomon's famous temple in Jerusalem (build around 950 BC), allegedly overlaid with gold bear testimony to this early and lasting fascination evoked by gold.

The believing in gold as the embodiment of value continued throughout the centuries. Today, the drastically increasing demand of gold as a safe investment very well reflects this fact. One reason for investing in gold as a safe-haven of treasure and investment is its nobleness and obvious inability to corrode like iron. Gold stays in its metallic form, apparently unaffected by dirt and corrosion. The other reason is that gold is rare. Elements heavier than Iron (^{56}Fe) cannot be generated by fusion reactions occurring in a sun but result from neutron capture reactions like in supernovae, a comparatively rare astrophysical event. In the galaxy, elements such as gold are inherently rare, accordingly.

The fact that we still have unexpected high amounts of gold in the earth crust might be one fortunate cosmic coincidence. In the process of the formation of the earth the iron segregated into the core and was surrounded by a silicate mantle. In this process so called "iron-loving" metals like gold and also other precious metals were buried in the deep interiors of our planet. The presence of unexpected large amounts of gold in the earth crust, though, is discussed to originate from meteoritic material deposited after the formation of the core mantle. Willbold and co-workers very recently provided experimental data that the presence of gold in the earth crust is due to a meteor bombardment about 3.9 billion years ago.[17] In a very literal way one could say that our gold fell from the sky.

Yet, the gold in the earth crust is not evenly distributed. About 40 % of all gold mined within the last 120 years came from just one area, the Witwatersrand Basin in South Africa (Transvaal and Orange Free State). Since the average concentration of gold in the earth crust is just about 2-5 parts per billion (ppb, weight)[16, 18], mining of traces in many areas of the world is not economically viable. Hence, gold like in the Witwatersrand Basin is mined from deposits were it is largely enriched. The average gold content of the ore in these so called *conglomerate deposits* is about 12 ppm.[16] Although these numbers sound still very little, the gold in those deposits is enriched by a factor of more than 1000 and mining becomes economically viable. The explanation of its enrichment is that hot fluids (~ 400 °C) in the earth crust are able to dissolve gold traces in the soil[19], yet at shear zone faults the pressure and temperature drops and gold precipitates forming veins (*primary deposits*).[18] Later sedimentation and compaction of sand and shingle deposits can lead to *conglomerate deposits*, i.e. gold deposits finely dispersed in rock.

The mining of gold strongly profits from the development of production processes to remove the gold from deposits and bringing it into a concentrated and pure form. The total production of gold until the end of the Roman Empire can be estimated to be about 10,000 t, slowing down in the medieval ages to a total of about 2000 to 3000 tons. With the advent of the Californian Gold Rush in 1848, the production of gold steeply increased to about 40 t per year.[16] Yet, these numbers are very small when compared to the current mining and production of gold. In 2010, the world-wide annual production (mining) of gold was 2,500 t, more than 20 times the annual production from 1848.[20] During the last years, the production of gold from South Africa, mainly from the above mentioned famous Witwatersrand Basin, is continuously declining from 464 t in 1998 to only 190 t in 2010, making it still the fourth largest producer of gold. Today, the largest producer of gold is China with an annual production of 345 t, followed by Australia (255 t) and the United States of America (230 t). Noteworthy, the recycling of gold becomes more and more relevant. In 2010, the U.S. Department of Geological Survey reported that in the U.S. 205 t of gold were generated from recycling of new and old scrap, a number which was even higher than the actual consumption.[21] This reflects that gold is a very sustainable resource.

The mining and production of gold is of considerable economic value. Already in 1997 worldwide about 500,000 people were employed in the mining and production of gold. The value associated to gold primary production at this time was already in the range of ~ $ 30 billion. Since then it has drastically increased to about $ 100 billion in 2010 (based on an average price of gold of 40 $/g). Most gold is used in the form of jewelry (50 %) or as means of exchange (coins and money) and monetary asset (40 %).[22] The remaining 10 % of the world's gold production goes into the field of industry and technology. Here, it is mostly used in the field of electronics were gold is mainly deployed because of its high electrical conductivity and corrosion resistivity. Another very typical application of gold is its use as an "inert" coating. For example, gold alloyed to silver and palladium (Pallacid) is a very resistant coating against mineral acids especially at higher temperatures.

Yet, gold – as a nanomaterial - also plays an emerging and fascinating role in modern technologies such as in biomedicine, water purification, fuel cells, exhaust gas purification, energy-efficient glazing coating, touch sensitive screens, even solar cells, just to name a few.[22] At first glance, some of these applications seem to contradict the apparent inertness of gold as they involve for example chemical activity of the gold surface. But it is the unique combination of gold and its nanostructure opening the door for these high-tech applications. With the anticipated ongoing increase in world-wide research funding on nanotechnology to over $ 12 billion per year in 2015 (Cientifica Ltd), gold as a nanomaterial certainly opens a variety of promising perspectives also in the applied and industrial sector.

1.3 What makes "nano" special

As mentioned above a crucial factor for various applications of nanoporous gold is its nanostructure. The term “nano” or “nanomaterial” implies that critical features and structures of the according material are in the size of several nanometers (10^{-9} m), typically below 100 nm. This is less than one hundredth of the diameter of a human hair. When dealing with “nano” sized materials new material properties and applications emerge.[23, 24] But why and to what extend should the properties of a material such as gold “change” when becoming nano-sized? One important factor is the reduced characteristic length and the increased surface to volume ratio of the materials. When moving from objects with characteristic length-scales (e.g. diameter, edge length) in the order of centimetres or millimetres to the nanometer scale, the surface to volume ratio is increased by a factor of more than one million. The proportion of surface atoms in ligaments (pillars) with diameters in the range of some tens of nanometers is in the order of several percent. They hence constitute a sizable amount of the total number of atoms in the material (Figure 1.2).

[Figure 1.2 near here]

Nanosized object are to a large extend determined by the physicochemical properties of their surface, being distinguished from the bulk properties. In a way, nanosized materials bridge the realm of isolated atoms on the subnanometer scale (Å = 10^{-10} m) and bulk materials. Atoms at the surface have a lower number of neighbouring atoms. Considering a cut through a bulk crystal, the atoms along this cut have fewer neighbours and accordingly a lower coordination number (CN). Since gold crystallizes in a face centred cubic lattice (fcc), the CN of an atom in the bulk is 12, meaning that every gold atom is surrounded by 12 next neighbours. An Au atom at the surface has a reduced coordination number; depending on whether it is located on a terrace, an edge or a kink site the CN is reduced to 9, 7, and 6, respectively (Figure 1.2). In the following, effects which are related to surfaces and low coordination of atoms are exemplarily discussed.

One effect is that charge redistribution due to low coordination of surface atoms gives rise to surface stress (see chapter 7).[25-29] The excess charge from unsaturated bonds is redistributed into in-plane bonds which are strengthened or weekend, depending on whether the additional charge is distributed into bonding or antibonding states. Compared to bond length of atoms within the bulk, the distance between surface atoms can thus be altered leading to surface stress. For compressive stress the surface tends to expand compared to the bulk whereas for tensile stress the surface tends to shrink.[27] A typical consequence of surface stress is a reconstruction of the surface. Giving an example, the Au(111) surface reconstructs in the commonly known Herringbone reconstruction.[30, 31] The tensile surface stress of the Au(111) surface is compensated by incorporation of about 4 % additional atoms into the surface as compared to the bulk. Recently, several investigations showed that in case of nanoporous metals (npAu, npPt) a change of surface stress can lead to macroscopically detectable strain of the entire material, an effect formerly known only for piezo ceramics.[25, 26, 32, 33]

An additional effect is exploited in catalysis (see chapters 8, 9, 10). The low coordination of surface atoms enhances the reactivity of (metal) surfaces. The desorption enthalpy of CO on gold surfaces is (amongst others) a function of the roughness that is the coordination number of surface atoms (Figure 1.2).[34] Theoretically, there are two ways in which the coordination of a surface atom and the geometry of the surface, respectively, can influence the interaction with molecules and the activation barrier for the reaction; one is electronic and the other one is geometric. The adsorption and bonding of a molecule on a metal surface is determined by the electronic structure of the substrate. A concept describing the interaction (adsorption) of various molecules with transition metals was introduced by Nørskov and co-workers.[35] In transition metals the so called d-bands determine the reactivity of the substrate as they are the highest lying electronic states. The d-band centre is defined as the first moment (“average”) of the density of d-states. The position of the d-band centre with respect to the Fermi level affects the ability of a metal surface atom to form a bond with an adsorbate. For example, transition metals tend to have higher d-states in case of low coordination numbers (kink-, edge-sites). Accordingly, these atoms interact more strongly with adsorbates than atoms in a closed packed surface.[36] Additionally, the geometry of the substrate provides specific adsorption sites which can be crucial for the activation and reaction of the adsorbed molecules.[37] The impact of the latter geometrical effect depends on the transition state, i.e., the optimal local geometry of atoms to form and break bonds. Certainly, the electronic and the geometrical effect are hardly distinguishable, as the local geometry of a surface atoms always affects its electronic structure. Yet, both effects contribute to the catalytic performance of a metal. In case of gold the role of low coordination even determines whether the surface shows any catalytic activity.[38]

A third effect is employed in optics (see chapter 6). This visual effect of the size of the gold structure can be demonstrated by colloidal solutions of (spherical) gold particles which vary between red/ruby for particles in the range of several nanometers and the typical gold-yellow for larger particles. Similar as in case of depletion-gilding (s.o.) this optical “nano-effect” of gold, albeit unwittingly, was used by artisans many centuries ago. Roman artisans mixed gold chloride into molten glass generating colloidal gold to evoke a ruby staining of the glass. The famous Lycurgus Cup manufactured about 300 AD by roman artisans testifies to this early use of nanotechnology: depending on whether the light passes through the glass from the back or illuminates the front, it changes its color from ruby (back) to green (front). Further examples for the staining of glass by gold particles are the colorful glass windows of cathedrals as used throughout the centuries in Europe. The origin of this effect is that electrons in metals occupy delocalized bands. Coherent oscillations of conducting electrons along the surface determine the optical properties of metals. These oscillations are dubbed surface plasmons (SP). One type of surface plasmon resonance (SPR), the so called localized SPR (LSPR), is very pronounced in nanomaterials. For when it is confined in small place as in the case of nanomaterials a strong electromagnetic field is associated. The LSPR can among others be used for surface enhanced RAMAN spectroscopy. The size, shape, and the orientation of the nanostructures are key factors which strongly affects the LSPR. This optical properties of gold nanostructures might even be used for novel optical data storage exceeding the limit of current storage media by several orders of magnitude.[39] By using gold nanorods with varying aspect ratio (ratio of length and diameter) and different orientation on a flat surface the LSPR of single rots can be addressed generating a bit density 1.1 Tbit cm^{-3}, which corresponds to a data capacity of 1.6 Tbyte for a typical DVD disk.

More details regarding the fascinating applications and the background of this exemplary gold nanomaterial will be covered in the various chapters. The topics will range from the fundamentals of the formation of nano-patterns on a theoretical (chapter 2) as well as on the experimental level (chapter 3) all the way to its mechanical characterization (chapter 4) and micro fabrication (chapter 5). The final 5 chapters will cover different arenas of applications of this material, from the optical applications (chapter 6) to the actuation (chapter 7), the catalysis (chapter 8), electro catalysis (chapter 9) and sensors (chapter 10). This book will combine various interdisciplinary topics describing this gold based nanomaterial in its various aspects. The attempt of this book is to provide a platform for an understanding of the interplay of various disciplines such as material science, physics, chemistry and more as a critical step for the development of novel nanomaterials for technical applications.

Acknowledgements

A portion of this work (AW and JB) was performed under the auspices of U.S. Department of Energy by LLNL under Contract DE-AC52-07NA27344.

References

1. H. W. Pickering and P. R. Swann, *Corr.*, 1963, **19**, 373t.
2. A. J. Forty and P. Durkin, *Philos. Mag. a*, 1980, **42**, 295-318.
3. A. J. Forty, *Nature*, 1979, **282**, 597-598.
4. ISIWeb of Knowledge as of June/2011, Keyword "nanoporous gold"
5. J. Biener, A. M. Hodge, J. R. Hayes, C. A. Volkert, L. A. Zepeda-Ruiz, A. V. Hamza and F. F. Abraham, *Nano Lett.*, 2006, **6**, 2379-2382.
6. D. Lee, X. Wei, X. Chen, M. Zhao, S. C. Jun, J. Hone, E. G. Herbert, W. C. Oliver and J. W. Kysar, *Scr. Mater.*, 2007, **56**, 437-440.

7. J. Biener, G. W. Nyce, A. M. Hodge, M. M. Biener, A. V. Hamza and S. A. Maier, *Adv. Mater.*, 2008, **20**, 1211-1217.
8. A. M. Hodge, J. Biener, J. R. Hayes, P. M. Bythrow, C. A. Volkert and A. V. Hamza, *Acta Mater.*, 2007, **55**, 1343-1349.
9. G. W. Nyce, J. R. Hayes, A. V. Hamza and J. H. Satcher, *Chem. Mat.*, 2007, **19**, 344-346.
10. Y. Ding and M. W. Chen, *MRS Bull.*, 2009, **34**, 569-576.
11. R. Zeis, A. Mathur, G. Fritz, J. Lee and J. Erlebacher, *J. Power Sources*, 2007, **165**, 65-72.
12. M. M. Biener, J. Biener, A. Wichmann, A. Wittstock, T. F. Baumann, M. Bäumer and A. V. Hamza, *Nano Lett.*, 2011, null-null.
13. A. Wittstock, A. Wichmann, J. Biener and M. Baumer, *Faraday Disc*, 2011, **152**, 87-98.
14. C. C. Jia, H. M. Yin, H. Y. Ma, R. Y. Wang, X. B. Ge, A. Q. Zhou, X. H. Xu and Y. Ding, *J Phys Chem C*, 2009, **113**, 16138-16143.
15. A. N. A. Hesiod, *Hesiod; Theogony ; Works and days ; Shield*, JHU Press, 2004.
16. H. Renner, G. Schlamp, D. Hollmann, H. M. Lüschow, P. Tews, J. Rothaut, K. Dermann, A. Knödler, C. Hecht, M. Schlott, R. Drieselmann, C. Peter and R. Schiele, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, 2000.
17. M. Willbold, T. Elliott and S. Moorbath, *Nature*, 2011, **477**, 195-198.
18. H. E. Frimmel, *Science*, 2002, **297**, 1815-1817.
19. R. R. Loucks and J. A. Mavrogenes, *Science*, 1999, **284**, 2159-2163.
20. data from Mineral Commodity Report of U.S. Department of the Interior and the U.S. Geological Survey (http://minerals.usgs.gov/minerals/pubs/mcs/)
21. K. Salazar and M. K. McNutt, eds. U. S. D. o. t. Interior and U. S. G. Survey, USGS, Washington, 2011, pp. 66-67.
22. T. W. G. Council, About Gold, http://www.gold.org/about_gold/.
23. J. Biener, A. Wittstock, T. Baumann, J. Weissmüller, M. Bäumer and A. Hamza, *Materials*, 2009, **2**, 2404-2428.
24. J. Erlebacher and R. Seshadri, *MRS Bull.*, 2009, **34**, 561-568.
25. J. Biener, A. Wittstock, L. A. Zepeda-Ruiz, M. M. Biener, V. Zielasek, D. Kramer, R. N. Viswanath, J. Weissmuller, M. Baumer and A. V. Hamza, *Nat. Mater.*, 2009, **8**, 47-51.
26. J. Weissmuller, R. N. Viswanath, D. Kramer, P. Zimmer, R. Wurschum and H. Gleiter, *Science*, 2003, **300**, 312-315.
27. W. Haiss, *Reports on Progress in Physics*, 2001, **64**, 591-648.
28. H. Ibach, *Surf. Sci. Rep.*, 1997, **29**, 195-263.
29. C. E. Bach, M. Giesen, H. Ibach and T. L. Einstein, *Phys. Rev. Lett.*, 1997, **78**, 4225-4228.
30. J. Biener, M. M. Biener, T. Nowitzki, A. V. Hamza, C. M. Friend, V. Zielasek and M. Baumer, *ChemPhysChem*, 2006, **7**, 1906-1908.
31. B. K. Min, A. R. Alemozafar, M. M. Biener, J. Biener and C. M. Friend, *Top. Catal.*, 2005, **36**, 77-90.
32. H. J. Jin, L. Kurmanaeva, J. Schmauch, H. Rosner, Y. Ivanisenko and J. Weissmuller, *Acta Mater.*, 2009, **57**, 2665-2672.
33. D. Kramer, R. N. Viswanath and J. Weissmuller, *Nano Lett.*, 2004, **4**, 793-796.
34. W. L. Yim, T. Nowitzki, M. Necke, H. Schnars, P. Nickut, J. Biener, M. M. Biener, V. Zielasek, K. Al-Shamery, T. Kluner and M. Baumer, *J. Phys. Chem. C*, 2007, **111**, 445-451.
35. J. Greeley, J. K. Norskov and M. Mavrikakis, *Annual Review of Physical Chemistry*, 2002, **53**, 319-348.
36. J. K. Norskov, T. Bligaard, B. Hvolbaek, F. Abild-Pedersen, I. Chorkendorff and C. H. Christensen, *Chem. Soc. Rev.*, 2008, **37**, 2163-2171.
37. J. K. Norskov, T. Bligaard, A. Logadottir, S. Bahn, L. B. Hansen, M. Bollinger, H. Bengaard, B. Hammer, Z. Sljivancanin, M. Mavrikakis, Y. Xu, S. Dahl and C. J. H. Jacobsen, *J. Catal.*, 2002, **209**, 275-278.

38. H. Falsig, B. Hvolbaek, I. S. Kristensen, T. Jiang, T. Bligaard, C. H. Christensen and J. K. Norskov, *Angewandte Chemie-International Edition*, 2008, **47**, 4835-4839.
39. P. Zijlstra, J. W. M. Chon and M. Gu, *Nature*, 2009, **459**, 410-413.