



Editorial Nanoporous Gold and Other Related Materials

Keith J. Stine

Department of Chemistry and Biochemistry, University of Missouri, Saint Louis, MO 63121, USA; kstine@umsl.edu; Tel.: +1-314-516-5346

Received: 17 July 2019; Accepted: 24 July 2019; Published: 27 July 2019



The field of nanomaterials continues to expand with the discovery of new nanostructures opening up new possibilities for both the study of unique physical properties and new applications. Over the past 15 years, the study of nanoporous gold (np-Au) has accelerated rapidly, with the material initially referred to as porous gold. In 2004, there were 13 papers published in this area, while in 2018, the number was 119 with the total number of papers well over 1000. Some of the early work on porous gold has been reviewed [1,2]. It was quickly realized that np-Au posed high interest as a support material that could be modified with biological molecules and had the prospects for many applications in life science in biosensor development, drug release, and as a surface for controlled interactions with living cells. The material has many special properties that have spawned entire avenues of investigation, including novel plasmonic optical properties, catalytic properties, and mechanical properties. The study of nanoporous forms of other metals has also been stimulated by these discoveries, with gold having the special properties of its environmental and chemical stability. The entire field of nanostructured forms of gold and other metals or alloys continues to rapidly advance [3]. The modification of these nanomaterials has also stimulated a continuing development of many novel and more complex modified nanoparticles, especially for biological applications. This special issue covers a wide range of aspects of np-Au and closely related materials including biosensing, cellular interactions, and mechanical properties. Some aspects of novel developments of nanoparticles are also presented in this issue.

One of the most widely explored applications of np-Au has been to the field of biosensor development, as reviewed in this issue by Bhattarai et al. [4]. This nanoporous metal offers advantages of providing an inert gold surface that is readily surface modified using self-assembled monolayer technology or by the direct adsorption of biomolecules. The adjustable pore size can fall in a range that is especially suitable for the incorporation of proteins, oligonucleotides, antibodies, and enzymes within the structure. The applications of these np-Au based biosensors are very broad and cover the detection of DNA, cancer biomarker proteins, and many applications for sensing glucose. The development of biosensors based on np-Au continues to be an active and growing field [5–7]. In this issue, the exciting field of DNA detection based on np-Au is explored in the paper by Seker and coworkers [8]. The use of np-Au for electrochemical detection of DNA hybridization is shown to overcome some of the limitations in sensitivity, selectivity, and detection limits that are found when flat gold surfaces are used. Electrochemical biosensors built on np-Au for specific oligonucleotides that are biomarkers for breast cancer genes are demonstrated in a microfluidic format. The rising interest in biomarker detection based on DNA and for example on circulating DNA indicates that there is great potential for electrochemical biosensors based on np-Au in the rapidly growing field of precision medicine that is on the cusp of broad commercialization [9–11]. There is a need for nanostructured electrodes for use in electrophysiology studies and especially for the study of neural behavior and neurotransmitter levels in the brain [12]. The article in this issue by Seker and coworkers demonstrates that use of np-Au as an electrode material can reduce the problem of astrocyte adhesion to the gold surface through the change in morphology from that of a flat gold surface [13]. In this study, the new concept of a morphology library is introduced so that the variation of cellular adhesion with np-Au morphological features such

as ligament dimensions and pore size can be studied. This paper also demonstrates the integration of np-Au, microfluidics, and cellular adhesion studies. Additional aspects of the applications of np-Au in life sciences, including promising applications such as controlled drug release [14,15], have recently been reviewed [16]. The basic mechanical properties of np-Au continue to be improved and the paper by Leitner and coworkers [17] presents a novel strategy to improve the yield strength of np-Au by plastic deformation of an AuFe nanocomposite followed by the etching of iron. There are many aspects of interest for np-Au, which is why it is a material of such high interest, and novel mechanical properties have been a major research direction [18,19]. The ability to form macroscopic size samples of np-Au enables their study by special nanoidentation methods, as are described in the paper. The interconnected morphology of ligaments and pores that is seen in np-Au is also found in other nanostructured metals, such as nanoporous copper (NPC) formed on the surface of the bulk metallic glasses (BMG) of the alloy $Cu_{50}Zr_{45}A_{15}$ by HF treatment, as studied in the paper by Wang and coworkers [20]. These rod like structures with a BMG interior and NPC shell are shown to exhibit superior energy absorption properties.

In addition to np-Au, there are other nanostructures of gold that can be made such as dendritic gold nano-forests, whose novel optical properties are used in the paper by Shiao and coworkers [21]. Gold nanostructures exhibit localized surface plasmon resonance behavior that can be tuned by varying the morphology [22]. Using the plasmon absorbance of these dendritic nano-forests, this study demonstrates their application as a photocatalyst for the degradation of pollutants.

Two of the papers in this Special issue focus on nanoparticle structures targeted at biological applications. In the paper by Li and coworkers [23], a new approach to the preparation of polyion complex vesicles using gold nanoparticles as templates. Using block copolymers of opposite charge, vesicles are produced that could have applications in drug delivery and other areas and have tunable features that make them attractive alternatives to the traditional lipid based vesicles. The paper by Bigi and coworkers [24] describes the production of nanocrystals of hydroxyapatite that, when functionalized with hydroxystearate, show enhanced binding of silver nanoparticles that are widely under investigation for their antimicrobial properties [25].

I would like to thank all authors of this Special Issue of *Nanomaterials* for their contributions and the prompt and constructive comments from the referees, and also the consistently outstanding and efficient support from the editorial office.

Funding: The author acknowledges support from the National Institutes of Health (NIGMS R01-GM111835).

Acknowledgments: In this section you can acknowledge any support given which is not covered by the author contribution or funding sections. This may include administrative and technical support, or donations in kind (e.g., materials used for experiments).

Conflicts of Interest: The author declares no conflict of interest.

References

- Ding, Y.; Kim, Y.J.; Erlebacher, J. Nanoporous Gold Leaf? Ancient Technology? Advanced Material. Adv. Mater. 2004, 16, 1897–1900. [CrossRef]
- Newman, R.C.; Corcoran, S.G.; Erlebacher, J.; Aziz, M.; Sieradski, K. Alloy Corrosion. *Mater. Res. Soc. Bull.* 1999, 24, 24–28. [CrossRef]
- 3. Stine, K.J. Biosensor Applications of Electrodeposited Nanostructures. Appl. Sci. 2019, 9, 797. [CrossRef]
- Bhattarai, J.K.; Neupane, D.; Nepal, B.; Mikhaylov, V.; Demchenko, A.V.; Stine, K.J. Preparation, Modification, Characterization, and Biosensing Application of Nanoporous Gold Using Electrochemical Techniques. *Nanomaterials* 2018, *8*, 171. [CrossRef] [PubMed]
- Stine, K.J. Enzyme Immobilization on Nanoporous Gold: A Review. *Biochem. Insights* 2017, 10, 1–12. [CrossRef] [PubMed]
- 6. Xiao, X.; Si, P.; Magner, E. An Overview of Dealloyed Nanoporous Gold in Bioelectrochemistry. *Bioelectrochemistry* **2016**, *109*, 117–126. [CrossRef]

- Matharu, Z.; Daggumati, P.; Wang, L.; Dorofeeva, T.S.; Li, Z.; Seker, E. Nanoporous-Gold-Based Electrode Morphology Libraries for Investigating Structure–Property Relationships in Nucleic Acid Based Electrochemical Biosensors. ACS Appl. Mater. Interfaces 2017, 9, 12959–12966. [CrossRef] [PubMed]
- 8. Veselinovic, J.; Li, Z.; Daggumati, P.; Seker, E. Electrically Guided DNA Immobilization and Multiplexed DNA Detection with Nanoporous Gold Electrodes. *Nanomaterials* **2018**, *8*, 351. [CrossRef]
- 9. Wang, Y.; Sun, S.; Zhang, Z.; Shi, D. Nanomaterials for Cancer Precision Medicine. *Adv. Mater.* **2018**, *30*, 1705660. [CrossRef]
- 10. Ahmed, M.U.; Saaem, I.; Wu, P.C.; Brown, A.S. Personalized Diagnostics and Biosensors: A Review of the Biology and Technology Needed for Personalized Medicine. *Crit. Rev. Biotech.* **2014**, *34*, 180–196. [CrossRef]
- 11. Yoon, H.J.; Kozminsky, M.; Nagrath, S. Emerging Role of Nanomaterials in Circulating Tumor Cell Isolation and Analysis. *ACS Nano* 2014, *8*, 1995–2017. [CrossRef] [PubMed]
- 12. Chapman, C.A.R.; Wang, L.; Chen, H.; Garrison, J.; Lein, P.J.; Seker, E. Nanoporous Gold Biointerfaces: Modifying Nanostructure to Control Neural Cell Coverage and Enhance Electrophysiological Recording Performance. *Adv. Funct. Mater.* **2017**, *27*, 1604631. [CrossRef] [PubMed]
- 13. Hampe, A.E.; Li, Z.; Sethi, S.; Lein, P.J.; Seker, E. A Microfluidic Platform to Study Astrocyte Adhesion on Nanoporous Gold Thin Films. *Nanomaterials* **2018**, *8*, 452. [CrossRef] [PubMed]
- 14. Seker, E.; Berdichevsky, Y.; Staley, K.J.; Yarmush, M.L. Microfabrication-Compatible Nanoporous Gold Foams as Biomaterials for Drug Delivery. *Adv. Healthc. Mater.* **2012**, *1*, 172–176. [CrossRef] [PubMed]
- 15. Santos, G.M.; Zhao, F.; Zeng, J.; Shih, W.C. Characterization of Nanoporous Gold Disks for Photothermal Light Harvesting and Light-Gated Molecular Release. *Nanoscale* **2014**, *6*, 5718–5724. [CrossRef] [PubMed]
- 16. Seker, E.; Shih, W.-C.; Stine, K.J. Nanoporous Metals by Alloy Corrosion: Bioanalytical and Biomedical Applications. *MRS Bull.* **2018**, *43*, 49–56. [CrossRef]
- 17. Leitner, A.; Maier-Kiener, V.; Kiener, D. High Temperature Flow Behavior of Ultra-Strong Nanoporous Au Assessed by Spherical Nanoindentation. *Nanomaterials* **2018**, *8*, 366. [CrossRef]
- Şeker, E.; Reed, M.L.; Begley, M.R. Nanoporous Gold: Fabrication, Characterization, and Applications. *Materials* 2009, 2, 2188–2215. [CrossRef]
- 19. Sun, X.Y.; Xu, G.K.; Li, X.; Feng, X.Q.; Gao, H. Mechanical Properties and Scaling laws of nanoporous gold. *J. Appl. Phys.* **2013**, *113*, 023505. [CrossRef]
- 20. Wang, C.; Li, M.; Zhu, M.; Wang, H.; Qin, C.; Zhao, W.; Wang, Z. Controlling the Mechanical Properties of Bulk Metallic Glasses by Superficial Dealloyed Layer. *Nanomaterials* **2017**, *7*, 352. [CrossRef]
- 21. Shiao, M.H.; Lin, C.T.; Zeng, J.J.; Lin, Y.S. Novel Gold Dendritic Nanoforests Combined with Titanium Nitride for Visible-Light-Enhanced Chemical Degradation. *Nanomaterials* **2018**, *8*, 282. [CrossRef] [PubMed]
- 22. Jin, Y. Engineering Plasmonic Gold Nanostructures and Metamaterials for Biosensing and Nanomedicine. *Adv. Mater.* **2012**, *24*, 5153–5165. [CrossRef] [PubMed]
- Li, J.; Liang, L.; Liang, J.; Wu, W.; Zhou, H.; Guo, J. Constructing Asymmetric Polyion Complex Vesicles via Template Assembling Strategy: Formulation Control and Tunable Permeability. *Nanomaterials* 2017, 7, 387. [CrossRef] [PubMed]
- 24. Boanini, E.; Cassani, M.C.; Rubini, K.; Boga, C.; Bigi, A. (9*R*)-9-Hydroxystearate-Functionalized Anticancer Ceramics Promote Loading of Silver Nanoparticles. *Nanomaterials* **2018**, *8*, 390. [CrossRef] [PubMed]
- 25. Prabhu, S.; Poulose, E.K. Silver Nanoparticles: Mechanism of Antimicrobial Action, Synthesis, Medical Applications, and Toxicity Effects. *Int. Nano Lett.* **2012**, *2*, 32. [CrossRef]



© 2019 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).