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Engineering Single Nanopore on Gold Nanoplate by Tuning Crystal Screw Dislocation

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Abstract

Compared with the large variety of solid gold nanostructures, synthetic approaches of their hollow counterparts are limited, largely confined to chemical and irradiation-based etching of preformed nanostructures. In particular, the preparation of through nanopore structure is extremely challenging. Here, we report a unique strategy for direct synthesis of gold nanopores in solution without the need of sacrificial templates and post-synthesis processing. By controlling the degree of crystal screw dislocation, a single through pore with diameter ranging from sub-nanometers to tens of nanometers in the center of large gold nanoplates can be engineered with precision. Ionic current rectification behaviors were observed using the gold nanopore, potentially enabling new capabilities in biosensing, sequencing, and imaging.

Graphical Abstract

High-throughput production of solid-state nanopores is a major challenge. Here, we report a novel methodology for solution-phase synthesis of Au nanoplates with a single through pore with diameters ranging from sub-nanometers to tens of nanometers in the center based on crystal screw dislocation.

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Supporting Information ((delete if not applicable))

Supporting Information is available from the Wiley Online Library or from the author.

Keywords

Nanopore; nanoplate; photo-synthesis; screw-dislocation; sensing; sequencing

The development of novel nanostructures and understanding of their formation mechanisms have captivated the field of nanoscience and nanotechnology for years. This is particularly true for metallic nanostructures such as gold (Au) and silver (Ag). A large number of fascinating shapes (*e.g.*, sphere, cube, rod, plate, pyramid, and tetrapod) and internal geometries (*e.g.*, core-shell) have been developed by controlling the reaction kinetics and introducing special capping reagents.^[1–15] Precisely controlled crystal synthesis offers enabling platforms for catalysis,^[16, 17] sensing,^[18, 19] and medicine.^[20] For bioapplications, Au nanoparticles can be tailored to desired sizes and conjugated to various functional compounds containing thiol and amine groups. As a result, they are widely used as artificial scaffolds for making biomimetic materials. For example, 5-nm-diameter Au nanoparticle has been used as a template for assembly of high-density lipoprotein, forming biomimetic spherical nanoparticles.^[21]

Besides the solid nanomaterials, nanopore is also a fascinating structure. Nanopores are extensively found in the biological systems, controlling the exchange of ions and molecules between subcellular compartments.^[22] To mimic these delicate biological functions, artificial nanopores have been engineered on polymer, Si₃N₄, SiO₂, and Graphene films, to detect biomolecules and control substance transport.^[23–29] To enhance their functionality, nanopores and nanochannels are often coated with a thin layer of Au, followed by adsorption of organic materials such as cysteine, phenylalanine-glycine-nucleoporins and polyethylene glycol-thiol.^[30–32] Direct synthesis of Au nanopores is desirable, but highly challenging. In contrast to the precise control of solid Au nanostructure formation, methods of synthesizing hollow structures are largely confined to chemical etching of sacrificial templates and irradiation of preformed nanostructures.^[1, 35–36] These approaches cannot drill single Au nanopores with precisely tuned sizes in monocrystalline nanocrystals.

Herein, we report a facile photo-driven solution-phase chemical method to directly fabricate ultrathin large Au nanoplates (submicron) with a single through pore in the center. Crystal screw dislocation is created on the Au nanoplate during growth, and a void defect forms in the center where the crystal stress is the highest. Manipulating the degree of screw dislocation simply by adjusting the pH value of the growth solution, the nanopore size can be tuned from subnanometer to tens of nanometer. The Au nanopore can be further combined with electrochemistry setups to fabricate functional devices.

The porous Au nanoplate was prepared through a photo-driven seed-mediated growth method in an aqueous solution containing HAuCl₄, polyvinylpyrrolidone (PVP), methanol, and Au nanoseeds (see details in the Supporting Information). Figure 1a shows a transmission electron microscopy (TEM) image of the obtained Au nanoplates after 7h of reaction. The thin nanoplates exhibit hexagonal shape with edge length of 189 ± 37 nm and thickness of 29.8 ± 3.9 nm (Figure S1a). The extinction spectrum for the Au nanoplates measured in solution shows a distinctive surface plasmon resonance dipole peak at 810 nm (Figure S1b). Strikingly, high-magnification TEM image (Figure 1b) reveals a very small

hole in the central region, with a unique boundary line (pointed by the white arrow) starting from the pore and radiating to the edge of the nanoplate. This line structure is different from other continuous and randomly oriented darker lines (pointed by the red arrows), which are commonly observed in thin Au nanoplates and have been attributed to bending.^[37, 38] By analyzing the central region via HRTEM (Figure 1c and Figure S2), the average diameter of the pores is only 0.85 ± 0.08 nm. The yield of the Au nanoplates with nanopores are generally greater than 90%, in which ~ 60% of the nanoplates contain a single pore, whereas the others have two or three pores. It has been previously reported that high-density crystallographic defects in the center of large semiconductor and metal nanoplates can lead to structural collapse and etching, forming ring- or frame-like structures.^[38–40] In contrast, the nanoplates (with a central pore) obtained here exhibit nearly perfect crystal lattices (Figure 1c). This is further demonstrated by the selected area electron diffraction (SAED) measurement taken from single Au nanoplate (Figure 1d) where the diffraction pattern can be attributed to single crystalline Au with parallel stacking faults.^[41, 42]

Based on above observations, we proceeded to investigate the nanopore formation mechanism. Intermediates obtained at various reaction times were inspected with TEM. Figure 2a(i) show a typical Au nanoseed of approximately 7 nm in diameter. After 1 h of reaction (Figure 2a(ii) and Figure S3a), the size of the Au seed becomes larger, and some of the edges grow faster than others, leading to formation of particles of irregular shapes. As the growth proceeds to 2h, a mixture consisting of spherical nanoparticles and Au nanoplates forms (Figure 2a(iii) and Figure S3b), suggesting asymmetrical two-dimensional growth on the planar twinned Au nanoseeds. This growth pattern becomes more notable after 3 h of reaction (Figure 2a(iv) and Figure S3c). At this stage, the Au nanoplates exhibit an asymmetric concave hexagon shape. As the reaction further prolongs to 4h (Figure 2a(v), (vi) and Figure S3d), the two edges of the Au concave hexagon nanoplate become close to each other and eventually coalesce into a hexagon nanoplate with a nanopore in the center. A boundary line is clearly visible along the coalescent area. Interestingly, the nanopore is highly stable and remains open even with further growth of the Au nanoplate reaching submicron size.

These detailed time-dependent studies on the structural evolution reveal a novel rolling growth process which can directly produce well-defined Au nanopores in the absence of sacrificial templates. The transformation from an asymmetric concave shape to a symmetric nanoplate follows coalescence of the two ends of the concave nanoplate. According to a recent report detailing the mechanism of light-driven Au nanoplate synthesis where methanol is used as a hole scavenger, net charges accumulate at the edge of Au nanoplate^[41] Under this condition, as depicted in Figure 2b, repulsion forces should exist between the two edges when they approach each other. As a result, the two edges of the thin plate are pushed out of the same plane, creating a screw dislocation (slight bending) after the edges coalesce. The screw dislocation causes a high stress field in the center,^[43] where Au atom cannot deposit stably, thus creating a nanopore. The screw dislocation of the nanoplate was further confirmed with atomic force microscopy (AFM). As shown in Figure S4a–d, crystalline dislocation is clearly visible for the porous Au nanoplate, which is consistent with the TEM characterization (Figure 1b). In contrast, the dislocation boundary line is not observed on conventional Au nanoplate (without a pore) obtained using previous reported methods

(Figure S4e and f).^[41] To rule out the possibility that the pore is created due to chemical etching of initially poreless nanoplates, Au nanoplates without the nanopore (Figure 2c) were prepared to replace the Au nanoseeds for further growth in the same chemical condition. As shown in Figure 2d and Figure S5, no nanopore was subsequently detected in the center of the enlarged Au nanoplates. Interestingly, however, several nanopores were formed close to the edges (shown in the red rectangle). Isolation of the intermediate structures during nanoplate growth clearly reveals that the pores are resulted from the same crystal growth process, coalescence between edges slightly off the same plane (Figure 2e).

During the 7h reaction, the pH value of the reaction solution gradually dropped from 4.5 to 3.2 caused by releasing of H^+ during methanol oxidation. At the beginning of the reaction where the pH value and the precursor concentration are relatively high, kinetics-controlled growth dominates, leading to formation of asymmetric two-dimensional small nanoplates of irregular shapes. As the reaction progresses, decreasing pH and Au precursor concentration slow down the reaction to a thermodynamics-controlled process, resulting in formation of hexagonal nanoplates. Methanol in the photo-driven Au precursor reduction system acts as a hole scavenger, rendering excited Au nanoplates rich in electrons.^[41] When the two edges of the negatively charged plates roll around and approach each other, they are pushed away from each other due to electrostatic repulsion and create variable degrees of defects depending on the repulsion force. Higher pH leads to faster reaction kinetics of methanol oxidation and electron buildup in the catalytic Au nanoplate.^[44] Therefore, the repulsion force and consequently the degree of edge dislocation and pore size can be adjusted by varying the pH of the reaction (Scheme 1). Indeed, slight increase of the initial growth solution pH (e.g., 4.8 and 5.2) results in significantly larger Au nanopores (Figure 3a–d and Figure S6). Further increasing the initial pH to 5.5 pushes the two edges away from each other and produce coils (Figure 3e, f, and Figure S7). In contrast, decreasing the initial pH to 3.5 leads to slow thermodynamically controlled symmetrical two dimensional growth of common poreless Au nanoplates (Figure S8).

The wet-chemistry approach discussed above not only produces a new type of nanostructure, but also enables a new platform for nanopore-based applications. The nanopore reported here is made of Au, avoiding the need of Au coating before additional surface functionalization as previously reported. Although the current work is focused on material synthesis (applications in sensing and sequencing is out of the scope), we explored the possibility of making an integrated nanopore device. This experiment will also unambiguously prove that the pore observed under TEM is indeed a through pore.

The device configuration is based on two chambers filled with ionic solutions separated by a membrane containing a single Au nanopore (Figure 4a). To immobilize the submicron nanoplate onto a larger surface for easy manipulation, the Au nanoplates are first immobilized on silicon TEM grids with a small Si_3N_4 window (0.25×0.25 mm, 15 nm thick). A hole was drilled in the thin Si_3N_4 layer with electron beam irradiation using the Au nanopore as a mask (Figure 4b). To test this simple nanopore device, the ionic current rectification (ICR) behaviors was investigated. As shown in Figure 4c, a nearly linear current-voltage response was observed, indicating ohmic behavior. Next, we change the solution to KCl and ran the same experiment. A negative current rectification was observed

(Figure 4d). This is because adsorption of the Cl^- ions onto the Au nanopore creates a net negative charge, blocking anions while facilitating cation transport. To demonstrate the versatility of Au surface in immobilizing thiolated molecules, the Au nanopore was modified with cystamine. When 100 mM KNO_3 solution (pH=7) was used for this nanopore, a positive current rectification was indeed observed (Figure 4e). These experiments prove the through pore feature of the Au nanoplates, and pave the road for future sensing and sequencing applications.

In conclusion, we have developed a novel wet-chemistry methodology to fabricate a nanopore in gold nanoplates. The pore size can be readily tuned from subnanometers to tens of nanometers simply by adjusting the pH value of the crystal growth solution. Different with previously reported chemical etching mechanisms, the pore formation is driven by a unique screw dislocation mechanism that can be precisely controlled. The gold nanopore was further inserted into an electrochemistry device to study the ionic current rectification behaviors. This simple setup by no means represent a functional device for real biological discoveries such as DNA sequencing, but it pave the way for future applications in bio-sensing, -imaging, and -sequencing based on electrochemistry. In addition, because of the unique plasmonic features of metallic nanostructures, we also envision that the nanopore may enable new mechanisms for detection such as Raman-based optical imaging and sensing.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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References

1. Sun Y, Xia Y. Science. 2002; 298:2176. [PubMed: 12481134]
2. Grzelczak M, Perez-Juste J, Mulvaney P, Liz-Marzan LM. Chem Soc Rev. 2008; 37:1783. [PubMed: 18762828]
3. Xia Y, Xiong Y, Lim B, Skrabalak SE. Angew Chem Int Ed. 2009; 48:60.
4. Wu H, Kuo C, Huang MH. Langmuir. 2010; 26:12307. [PubMed: 20557088]
5. Dreaden EC, Alkilany AM, Huang X, Murphy CJ, El-Sayed MA. Chem Soc Rev. 2012; 41:2740. [PubMed: 22109657]
6. Langille MR, Personick ML, Zhang J, Mirkin CA. J Am Chem Soc. 2012; 134:14542. [PubMed: 22920241]
7. Langille MR, Personick ML, Mirkin CA. Angew Chem Int Ed. 2013; 52:13910.
8. Jana NR, Gearheart L, Murphy CJ. J Phys Chem B. 2001; 105:4065.
9. Jin R, Cao Y, Mirkin CA, Kelly KL, Schatz GC, Zheng JG. Science. 2001; 294:1901. [PubMed: 11729310]
10. Kim F, Song JH, Yang P. J Am Chem Soc. 2002; 124:14316. [PubMed: 12452700]
11. Millstone JE, Hurst SJ, Métraux GS, Cutler JI, Mirkin CA. Small. 2009; 5:646. [PubMed: 19306458]

12. Niu W, Chua YAA, Zhang W, Huang H, Lu X. J Am Chem Soc. 2015; 137:10460. [PubMed: 26259023]
13. Weiner RG, Skrabalak SE. Angew Chem Int Ed. 2015; 127:1197.
14. Au L, Lim B, Colletti P, Jun Y, Xia Y. Chem Asian J. 2010; 5:123. [PubMed: 19967737]
15. Shankar SS, Rai A, Ankamwar B, Singh A, Ahmad A, Sastry M. Nat Mater. 2004; 3:482. [PubMed: 15208703]
16. Wang F, Li C, Chen H, Jiang R, Sun L, Li Q, Wang J, Yu J, Yan C. J Am Chem Soc. 2013; 135:5588. [PubMed: 23521598]
17. Shi Y, Wang J, Wang C, Zhai T, Bao W, Xu J, Xia X, Chen H. J Am Chem Soc. 2015; 137:7365. [PubMed: 26020144]
18. Liu K, Bai Y, Zhang L, Yang Z, Fan Q, Zheng H, Yin Y, Gao C. Nano Lett. 2016; 16:3675. [PubMed: 27192436]
19. Wang P, Lin Z, Su X, Tang Z. Nanotoday. 2017; 12:64.
20. Yang X, Yang M, Pang B, Vara M, Xia Y. Chem Rev. 2015; 115:10410. [PubMed: 26293344]
21. Thaxton CS, Daniel WL, Giljohann DA, Thomas AD, Mirkin CA. J Am Chem Soc. 2009; 131:1384. [PubMed: 19133723]
22. Kowalczyk SW, Blosser TR, Dekker C. Trends Biotechnol. 2011; 29:607. [PubMed: 21871679]
23. Dekker C. Nat Nano. 2007; 2:209.
24. Plesa C, Verschuere D, Pud S, van der Torre J, Ruitenberg JW, Witteveen MJ, Jonsson MP, Grosberg AY, Rabin Y, Dekker C. Nat Nano. 2016; 11:1093.
25. Venta K, Shemer G, Puster M, Rodríguez-Manzo JA, Balan A, Rosenstein JK, Shepard K, Drndić M. ACS Nano. 2013; 7:4629. [PubMed: 23621759]
26. Heerema SJ, Dekker C. Nat Nano. 2016; 11:127.
27. Miles BN, Ivanov AP, Wilson KA, Dogan F, Japrun D, Edel JB. Chem Soc Rev. 2013; 42:15. [PubMed: 22990878]
28. Zhang H, Tian Y, Jiang L. Nanotoday. 2016; 11:61.
29. Hou X, Guo W, Jiang L. Chem Soc Rev. 2011; 40:2385. [PubMed: 21308139]
30. Xu X, He H, Jin Y. Anal Chem. 2015; 87:3216. [PubMed: 25697179]
31. He H, Xu X, Jin Y. Anal Chem. 2014; 86:4815. [PubMed: 24745871]
32. Jovanovic-Talman T, Tetenbaum-Novatt J, McKenney AS, Zilman A, Peters R, Rout MP, Chait BT. Nature. 2009; 457:1023. [PubMed: 19098896]
33. Skrabalak SE, Chen J, Sun Y, Lu X, Au L, Cobley CM, Xia Y. Acc Chem Res. 2008; 41:1587. [PubMed: 18570442]
34. Wang X, Feng J, Bai Y, Zhang Q, Yin Y. Chem Rev. 2016; 116:10983. [PubMed: 27156483]
35. Genç A, Patarroyo J, Sancho-Parramon J, Bastús Neus G, Puntès V, Arbiol J. Nanophotonics. 2017; 6:1.
36. Ah CS, Yun YJ, Park HJ, Kim WJ, Ha DH, Yun WS. Chem Mater. 2005; 17:5558.
37. Shao Y, Jin Y, Dong S. Chem Commun. 2004; 9:1104.
38. Fang JX, Li J, Tian CF, Gao QQ, Wang XJ, Gao NY, Wen XL, Ma CS, You HJ, Yang ZL, Xu QH, Xiong QH, Li ZY. Npg Asia Mater. 2016; 8:e323.
39. Li F, Ding Y, Gao PX, Xin XXQ, Wang ZL. Angew Chem Int Ed. 2004; 43:5238.
40. Meldrum FC, Cölfen H. Chem Rev. 2008; 108:4332. [PubMed: 19006397]
41. Zhai Y, DuChene JS, Wang Y, Qiu J, Johnston-Peck AC, You B, Guo W, DiCiccio B, Qian K, Zhao EW, Ooi F, Hu D, Su D, Stach EA, Zhu Z, Wei WD. Nat Mater. 2016; 15:889. [PubMed: 27376686]
42. Xia Y, Gilroy KD, Peng H, Xia X. Angew Chem Int Ed. 2017; 56:60.
43. Jin S, Bierman MJ, Morin SA. J Phys Chem Lett. 2010; 1:1472.
44. Hidaka H, Honjo H, Horikoshi S, Serpone N. Sensors Actuat B: Chem. 2007; 123:822.

Figure 1. Characterization of Au nanoplate with a nanopore structure

a) TEM image of the Au nanoplates with a nanopore. **b)** Higher magnification TEM image of a single Au nanoplate with a nanopore. **c)** High resolution TEM (HRTEM) image of a Au nanopore. **d)** The SAED pattern of a Au nanoplate with a nanopore. The spots indicated by the circle, box, and triangle are correspond to the $\{220\}$, $\{422\}$, and $1/3\{422\}$ planes, respectively.

Figure 2. Time-dependent evolution of the Au nanopore

a) TEM images of the intermediate specimens taken over the course of reaction from 0h (i), 1h (ii), 2h (iii), 3h (iv), and 4h (v and vi), to monitor the formation of Au nanopore. **b)** Scheme of the formation mechanism of the Au nanopore. **c)** TEM image of a poreless Au nanoplate. **d)** TEM image of Au nanoplate with multiple nanopores near the edges obtained by replacing the Au particle with Au nanoplates as the crystal growth seeds under the same synthetic condition. **e)** TEM images of selected intermediate states during the pore formation process. Asymmetry growth of the Au nanoplates leads to formation of the concave shape (yellow arrows). When the two edges (yellow arrows) or three edges (green arrow) coalesce, nanopores form due to screw dislocation.

Figure 3. Influence of growth solution pH on Au nanopore synthesis

a and **b**) SEM and TEM images show the larger Au nanopore formed at a growth solution of pH 4.8. Insert: HRTEM of the Au nanopore. **c** and **d**) SEM and TEM images show the Au nanopore can be further enlarged at a growth solution of pH 5.2. **e** and **f**) SEM images of coiling Au nanoplates formed in a growth solution at pH 5.5.

Figure 4. Fabrication of Au nanopore junction for ions transportation

a) Schematic illustration of the fabrication of Au nanopore-based device. **b)** E-beam irradiation of Si_3N_4 membrane masked by the Au nanopore. **(i–iv)** TEM images showing the process of drilling a hole in the Si_3N_4 membrane. A relatively large Au nanopore (~10.2 nm) was used here for easy visualization of the Si_3N_4 hole evolvement. **c)** Current-voltage characteristics of a ~4.0 nm Au nanopore and poreless device measured in 100 mM KNO_3 solution. **d)** Current-voltage characteristics of Au nanopore measured in 100 mM KCl solution. **e)** Current-voltage characteristics of a cystamine modified Au nanopore measured in 100 mM KNO_3 solution.

Scheme 1.

Growth mechanisms of Au nanoplates with or without a nanopore in the center.