

# Formation Pathways of Porous Alloy Nanoparticles through Selective Chemical and Electrochemical Etching

Yingying Jiang, Lu Wang, Michel Meunier, and Utkur Mirsaidov\*

Porous alloy nanomaterials are important for applications in catalysis, sensing, and actuation. Chemical and electrochemical etching are two methods to form porous nanostructures by dealloying bimetallic nanoparticles (NPs). However, it is not clear how the NPs evolve during these etching processes. Insight into the morphological and compositional transformations of the NPs during the etching is critical to understanding the nanoscale details of the dealloying process. Here, using in situ liquid phase transmission electron microscopy, the structural evolution of individual AuAg alloy NPs is tracked during both chemical and electrochemical etching of their Ag component. The observations show that the electrochemical etching produces NPs with more uniform pore sizes than the chemical etching and enables tuning the NPs porosity by modulating the electrochemical potential. The results show that at the initial stages of both etching methods, Au-rich passivation layer forms on the surface of the NPs, which is critical in preserving the NP's porous shell as pores form underneath this layer during the etching. These findings describing the selective etching and dealloying of AuAg NPs provide a critical insight needed to control the morphology and composition of porous multimetallic NPs, and paves the way for synthesizing nanomaterials with tailored chemical and physical properties for various applications.

Dr. Y. Jiang, Prof. U. Mirsaidov Department of Physics National University of Singapore Singapore 117551, Singapore E-mail: mirsaidov@nus.edu.sg Dr. Y. Jiang, Prof. U. Mirsaidov Centre for Biolmaging Sciences Department of Biological Sciences National University of Singapore Singapore 117557, Singapore L. Wang, Prof. M. Meunier Laser Processing and Plasmonics Laboratory Department of Engineering Physics Polytechnique Montréal Montréal, QC H3C 3AT, Canada Prof. U. Mirsaidov Centre for Advanced 2D Materials and Graphene Research Centre National University of Singapore Singapore 117546, Singapore Prof. U. Mirsaidov Department of Materials Science and Engineering National University of Singapore Singapore 117575, Singapore

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/smll.202006953.

#### DOI: 10.1002/smll.202006953

Dealloying is a selective etching process of less noble components from an alloy metal, which typically results in the formation of porous structures composed of more noble components.<sup>[1]</sup> Over the years, the dealloyed porous structures, such as porous Au,<sup>[2]</sup> Pt,<sup>[3]</sup> Ag,<sup>[4]</sup> Ni,<sup>[5]</sup> Cu,<sup>[6]</sup> and Sn,[7] have gained significant attention due to their potential applications in catalysis,<sup>[2-4,8]</sup> sensing,<sup>[9]</sup> and actuation.<sup>[10]</sup> AuAg alloy is a model system for the fabrication of porous Au structures through chemical or electrochemical etching, where the etching process can be tuned by adjusting the type and concentration of acid/electrolyte, reaction temperature, etching time, and applied electrochemical potential.<sup>[11-13]</sup> Although these studies provide an important insight into the dealloying process, the nanoscale details of structural and compositional transformations that take place in metal alloys during selective etching is still missing.<sup>[14,15]</sup>

Recent experimental studies using in situ surface X-ray diffraction (XRD) and scanning tunnelling microscopy (STM)

revealed the structural changes on the surfaces (i.e., solidelectrolyte interfaces) of AuCu, PtCu, and AuAg crystals at the early stages of their electrochemical dealloying.<sup>[16-18]</sup> In the case of AuCu and PtCu alloys, these studies showed that respective Auand Pt-rich layers form on the surface during dealloying.<sup>[16,17]</sup> For AuAg, experimental and theoretical studies show that the surface topography is determined by the competing diffusion and dissolution rates of the surface atoms.<sup>[1,18,19]</sup> These studies established that when the less noble metal is etched away at a faster rate than the surface diffusion rate of the more noble element (e.g., Au diffusion and Ag removal during the dealloying of AuAg), the surface roughens as pits form on it. When the diffusion is faster than the etching rate, the reaction product has a much smoother surface profile. However, the approaches used in these studies have certain limitations: 1) in situ surface XRD lacks the spatial resolution and provides only averaged information about the surface structure;<sup>[16,17]</sup> 2) in situ STM can only probe the structural changes in the first few atomic surface layers and is blind to the rest of an AuAg alloy's volume;<sup>[18]</sup> 3) because of the computational challenges, theoretical simulations only account for Ag and Au diffusion and Ag dissolution, and they omit the effects of the associated liquid environment in which the etching takes place. Hence, these studies do not capture the full complexity of the dealloying process.

16136829.2021, 17. Downloaded from https://nlinelibrary.wiely.com/doi/10.1002/smll.020006935 by National Unversity Of Siggapore Nus Libraries, Wiley Online Library on [310/8/2024]. See the Terms and Conditions (https://onlinelibrary.wiely.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons





**Figure 1.** Structure of Au–AuAg core–shell NPs before and after selective chemical etching. Schematic, HAADF-STEM image, and EDX maps for A) a template Au–AuAg NP, B) intermediate NP obtained after 5 min of etching, and C) final NP obtained after 60 min of etching in a 0.3 M HNO<sub>3</sub> solution. D) Elemental line profiles (along the white dashed lines in the EDX maps) corresponding to the NPs in (A–C). The template NP in (A) comprises a 15-nm-diameter Au core (red shaded regions in (D)) and a 15-nm-thick AuAg alloy shell with the Au:Ag atomic ratio of ≈1:6. The boundary between the core and shell forms a diffuse interface (orange arrows in (A) and (D)). The intermediate NP in (B) is enclosed by Au-rich alloy surface layers (red arrows in (B) and (D)). In addition, the pore walls of the NP are enriched by Au (white arrows in (B)). The final NP in (C) comprises Au core and a porous Au-rich AuAg outer shell. The overall atomic percentages of Au and Ag for the template, intermediate, and final NPs are ≈30% and ≈70%, ≈45% and ≈55%, and ≈60% and ≈40%, respectively.

Owing to these limitations, some key details of the dealloying process remain unknown. For example, it is unclear how the pores form and the atomic species redistribute in an alloy? It is also not clear how the reaction parameters regulate the etching kinetics and the overall architecture of the nanostructures? To fully grasp the nanoscale details of dealloying process under relevant reaction conditions, it is important to capture the evolution of alloys in real-time with nanometer resolution.

To address these questions, we track the chemical and electrochemical selective Ag etching in AuAg alloy NPs using in situ liquid-phase transmission electron microscopy (TEM).<sup>[20–29]</sup> We chose these NPs because Au, Ag, and their alloys are among the best-characterized materials used for NP synthesis.<sup>[30–33]</sup> For example, a recent in situ liquid-phase TEM study by Liu et al.,<sup>[34]</sup> examining the transformation of solid AuAg alloy NPs to porous ones by chemical etching, found that the NPs shrink in size and their surfaces become denser as small pores form within the NPs.

To understand the effect of the composition on pore formation and overall structural evolution, we chose two types of AuAg NPs: i) Au-core and AuAg-alloy-shell (Au–AuAg)<sup>[35,36]</sup> and ii) uniform AuAg alloy NPs<sup>[37]</sup> (see Section S1 in the Supporting Information for the protocol of their synthesis). Furthermore, to test how the NP dealloying is impacted by the Ag dissolution rate, we extended our study to both selective chemical and electrochemical etching. In our in situ TEM experiments, the chemical etching is initiated by flowing an aqueous HNO<sub>3</sub> solution into our custom liquid cell, while the in situ electrochemical etching is induced by the electrochemical applied on the NPs inside an electrochemical cell.<sup>[28]</sup> Our observations reveal how these AuAg alloy NPs evolve into porous NPs with different architectures through dealloying induced by chemical and electrochemical etching.

Figure 1A shows the high-angle-annular-dark-field (HAADF)scanning TEM (STEM) image and energy-dispersive X-ray spectroscopy (EDX) elemental maps of a typical starting template Au–AuAg NP. These Au–AuAg NPs were fabricated by the co-deposition of Au and Ag onto 15-nm-diameter Au seeds, which resulted in the NPs with AuAg alloy shell encapsulating the Au core, where the core and shell are separated by a diffuse interface. The overall atomic percentages of Au and Ag in the NP were  $\approx$ 30% and  $\approx$ 70%, respectively. Moreover, because of the way we synthesize these NPs (Section S1, Supporting Information), Au in the alloy shell has a slightly higher concentration near the core–shell boundary than in the rest of the shell (Figure 1D; Section S2, Supporting Information). The overall atomic percentages of the Au and Ag in the shell are  $\approx$ 15% and  $\approx$ 85%, respectively.

During the chemical etching process, Ag is selectively removed from AuAg alloy due to the large difference in the reduction potentials of Au and Ag and can be described by the following reactions:<sup>[38]</sup>

$$Au^+ + e^- \rightleftharpoons Au \quad E_0 = 1.70 \text{ V versus SHE}$$
 (1)

$$Ag^+ + e^- \rightleftharpoons Ag \quad E_0 = 0.80 \text{ V versus SHE}$$
 (2)

We chose  $HNO_3$  solution as our chemical etchant because it is the most commonly used etchant when dealloying AuAg.<sup>[8]</sup>





**Figure 2.** Selective chemical etching of Au–AuAg NPs in HNO<sub>3</sub>. A) In situ HAADF-STEM images showing the structural evolution of an individual Au–AuAg NP in a  $3 \times 10^{-3}$  M HNO<sub>3</sub> aqueous solution (Video S1, Supporting Information). Two noticeable pores first form near the surface of the NP (red dashed circles) and grow larger inside the alloy shell. Meanwhile, the walls between two adjacent pores form ligaments (white arrows) that connect the NP core to the outermost part of the shell (i.e., the Au-rich passivation layer) as these pores enlarge in size. Here,  $t_0$  is the timepoint at which we start recording the reaction. B) The change in cumulative STEM intensity of individual NPs during in situ chemical etching. The blue, black, red, orange, and green curves represent the time-dependent intensity plots for the NP in(A) and Figure S4Ai–iv in the Supporting Information, respectively. C) Schematic showing how the morphology and elemental compositions of the NPs evolve during the selective chemical etching of Ag. Here, Au, Agrich, and Au-rich AuAg alloys are represented by red, yellow, and orange colors, respectively.

 $HNO_3$  oxidizes Ag atoms into Ag<sup>+</sup> ions, which then dissolve into the aqueous etchant solution, while Au atoms remain in the alloy:<sup>[38]</sup>

#### $NO_3^- + 3H^+ + 2e^- \rightleftharpoons HNO_2 + H_2O \quad E_0 = 0.93 \text{ V versus SHE}$ (3)

The products shown in Figure 1B reveal two large and few smaller pores that formed within the NP shell when etching in a 0.3  $\mbox{M}$  HNO<sub>3</sub> solution for 5 min. During this timespan, the overall Ag content of the NP dropped from  $\approx$ 70 to  $\approx$ 55% (at.). Moreover, EDX maps reveal that the shell is encapsulated by a thin ( $\approx$ 5 nm) Au-rich alloy layer (Figure 1B,D), and this layer is still present when the NP was etched further (60 min), and the overall Ag content of the NP dropped to  $\approx$ 40% (at.) (Figure 1C,D). The composition of the NPs before and after the etching is further confirmed by XRD and XPS (Section S4, Supporting Information), which are in line with the EDX results shown in Figure 1.

In order to understand how the NPs evolve during the chemical etching, we tracked their etching in a 0.3 м HNO<sub>3</sub> aqueous solution with HAADF-STEM in real-time (Figure 2A) (Section S3, Supporting Information). The reason that we used STEM imaging instead of TEM imaging is because the intensity of STEM signal is sensitive to the specimen thickness and the atomic number of the imaged materials; thus, STEM provides better contrast and unambiguous structural information of the evolving NPs than TEM imaging. Figure 2A shows the evolution of a Au-AuAg NP as it transforms from a solid sphere (Figure 2A:  $t - t_0 = 0$  s) into a NP with a solid Au core and porous Au-rich AuAg shell (Figure 2A:  $t - t_0 = 12-22$  s). Here, instead of uniform etching, two noticeable pores first formed near the surface of the NP (Figure 2A:  $t - t_0 = 12-14$  s) and propagated in the alloy shell (Figure 2A:  $t - t_0 = 16$  s). As the etching continues, surprisingly, the surface of the shell does not collapse but remains in place supported by AuAg ligaments (Figure 2A:  $t - t_0 = 16$  s) connected to the Au core. These ligaments form from the Au-rich network of the pore walls as pores enlarge in size (Figure 1B). Afterward, etching ceases and produces the final porous NP, and there is no further change to the NP inside the etchant (Video S1, Supporting Information).

By following how STEM intensity of each NP evolves (Figure 2B), we can pinpoint different stages of the etching and how these stages affect the morphology of the NPs. At the initial stage of the etching, the intensity doesn't change (Figure 2B:  $t - t_0 = 0$ –12 s, blue curve). Note that at this early stage of dealloying, the passivation layer starts to form. Next, Ag in the AuAg-shell undergoes a rapid dissolution, leading to the formation of the pores as marked by an abrupt change in the STEM intensity (Figure 2B:  $t - t_0 = 12$ –22 s, blue curve). At the last stage of the etching, the stable ligaments supporting the passivation layer form, and the dissolution slows down and eventually stops.

Based on these results, the dealloying pathway during selective chemical etching can be summarized as follows (Figure 2C). First, during the initial etching, most of the surface Ag atoms are removed, resulting in a Au-rich passivation layer surrounding the NP (step I). Next, several pores form near the NP surface and expand inward via Ag etching (step II), and Au remains at the etch front, which causes walls of the pores to be Au-rich. As the pores expand, more Au accumulates on the pore walls, and these walls transform into ligaments connecting Au core and Au-rich outer shell (i.e., Au-rich passivation layer) of the NP (step III). The final product of the etching is a NP with a solid Au-core and porous shell surrounded with Au-rich passivation layer (step IV).

As an alternative to the chemical etching, we next explored how NPs evolve during selective electrochemical etching because, in general, electrochemical etching is known to enable better and simpler control over the NP architecture.<sup>[28,39]</sup> We studied the selective electrochemical etching of the drop-casted NPs under the electrochemical potentials of +0.5 to +0.8 V inside the liquid cell with microfabricated working, reference,

NANO · MICRO

www.small-journal.com

www.advancedsciencenews.com



**Figure 3.** Selective electrochemical etching of Au–AuAg NPs in acetic acid. In situ HAADF-STEM images showing the structural evolutions of the Au–AuAg NPs under the electrochemical potentials of A) +0.8 V (Video S2, Supporting Information) and B) +0.5 V (Video S3, Supporting Information) in a 0.1% (v/v) aqueous acetic acid solution. Here,  $t_0$  is the timepoint at which we apply the electrochemical potential. STEM images and the corresponding EDX maps of the NPs after the in situ electrochemical etching with the applied potentials of C) +0.8 V and D) +0.5 V. The final NPs in both cases contain  $\approx$ 70 and  $\approx$ 30% (at.) of Au and Ag, respectively. E) Schematic showing how the morphology and elemental composition of the NPs evolve during the selective electrochemical etching at high and low voltages. Here, Au, Ag-rich and Au-rich AuAg alloys are represented by red, yellow, and orange colors, respectively.

and counter electrodes.<sup>[28]</sup> Here, we used an aqueous acetic acid (0.1% v/v) solution as the electrolyte because acetate ions (CH<sub>3</sub>COO<sup>-</sup>) and Ag<sup>+</sup> ions can form a soluble product (CH<sub>3</sub>COOAg), which lowers the oxidizing potential of Ag and further promotes the etching process.<sup>[38]</sup>

 $CH_3COOAg + e^- \rightleftharpoons Ag + CH_3COO^ E_0 = 0.64 \text{ V} \text{ versus SHE}$  (4)

In **Figure 3**, we compare the etching dynamics of the Au–AuAg NPs at the electrochemical potentials of +0.8 V (Figure 3A) and +0.5 V (Figure 3B). At +0.8 V, the NPs shrank distinctively in less than 2 s due to the fast stripping of Ag atoms, and a number of small pores formed within the alloy shell (Figure 3A:  $t - t_0 = 2$  s), after which we did not observe any further structural changes (Figure 3A:  $t - t_0 \ge 2$  s). STEM

NANO . MICRO

www.small-journal.com



images in Figure 3C show that the NPs have many small pores with an average size of ≈3 nm (Figure S12A and Section S5 in the Supporting Information). The walls of these pores within the NP shell form with Au-rich ligaments that support the outer Au-rich passivation layer (Figure 3C) as in the case of chemically etched NPs shown in Figure 1C. Here, however, pores are much smaller (~3 nm) than those obtained via chemical etching (7-12 nm) (Figures S5 and S6 and Section S3 in the Supporting Information). Moreover, the corresponding EDX map in Figure 3C shows that the atomic composition of the etched structures is ≈70% Au and ≈30% Ag, which points to slightly more removal of Ag during the electrochemical etching than the chemical etching (Figure 1C). Figure S13 in the Supporting Information shows the additional experiment of the electrochemical etching at +0.7 V, where the NPs evolved similarly to those shown in Figure 3A.

When we lower the electrochemical potential from +0.8 to +0.5 V (i.e., below the oxidizing potential of Ag in acetic acid: 0.64 V) (Figure 3B), we found that Ag still etches. We attribute this etching to the fact that the dissolved  $O_2$  in the acetic acid solution facilitates the oxidation of Ag, which in turn may induce the electrochemical etching at lower potentials.<sup>[40]</sup> Here, the initial etching was fast, and the NP size reduced rapidly, and only few pores formed in the NP (Figure 3B:  $t - t_0 \le 6$  s). At  $t - t_0 \ge 6$ s, the pores expand due to continuous etching of the remaining Ag on the NP. Note that the intermediate structure of the NP at  $t - t_0 = 10$  s (Figure 3B) and the way the NP evolves within the first 10 s is similar to that of chemical etching described in Figure 2A. However, afterward, the ligaments supporting the outer shell degraded, and the shell collapsed onto the core (Figure 3B:  $t \ge 10$  s).

A clear difference between the electrochemical etching at low (+0.5 V) (Figure 3D) and high (+0.8 V) (Figure 3C) voltages, as highlighted in the schematic of the etching pathway shown in Figure 3E, is the dependence of the pore sizes on the potential. There are fewer but larger pores for the low voltage etching than for the higher voltage etching (≈5 nm at +0.5 V vs  $\approx$ 3 nm at +0.8 V) (Figure S12 and Section S5 in the Supporting Information). It is worth noting that the ability to tune the pore sizes through applied potential highlights the advantage of electrochemical etching over chemical etching by providing a very simple approach to control the NP architecture. The noted difference in pore sizes can be understood by noting that the dealloying process is a competition of Ag dissolution and Au diffusion, in which Ag dissolution creates small pores, while Au diffusion drives the coalescence of the pores.<sup>[1]</sup> Hence, the pore sizes can be tuned by controlling the dissolution rate of Ag and the diffusion rate of Au during dealloying.<sup>[1]</sup>

The dissolution and diffusion rates can be expressed as<sup>[1]</sup>

$$k_{\rm n}^{\rm diss} = v_{\rm E} \exp\left[-(nE_{\rm b} - \varphi)/k_{\rm B}T\right]$$
<sup>(5)</sup>

$$k_{\rm n}^{\rm diff} = v_{\rm D} \exp\left(-nE_{\rm b}/k_{\rm B}T\right) \tag{6}$$

Here,  $v_{\rm E} \approx 10^4 \text{ s}^{-1}$  and  $v_{\rm D} \approx 10^{13} \text{ s}^{-1}$  are the attempt frequencies for dissolution and diffusion, respectively,  $E_{\rm b} \approx 0.15$  eV is the bond energy for Au–Ag, Ag–Ag, and Au–Au bonding,  $\varphi$  is the external electrochemical potential,  $k_{\rm B} = 1.38 \times 10^{-23}$  J K<sup>-1</sup> is

the Boltzmann constant, *T* is the absolute temperature, and *n* is the number of the nearest neighboring atoms.<sup>[1]</sup> For an atom to diffuse or dissolve, it needs to overcome the net binding energy of  $nE_{\rm b}$ . With the applied potential  $\varphi$ , the energy barrier for dissolution reduces to  $nE_{\rm b}-\varphi$ , significantly increasing the dissolution rate. Meanwhile, the external electrochemical potential has no impact on atomic diffusion rate. Therefore, at high electrochemical potential (e.g., +0.8 V), the surface Ag dissolves more rapidly than that at a low electrochemical potential (e.g., +0.5 V), while the diffusion of surface Au atoms is similar in both cases. As a result, more but smaller pores form during the electrochemical etching at a high potential than at a low potential (Figure 3E).

As a final remark, we emphasize that two key features of dealloying during the selective chemical and electrochemical etching of core-shell Au-AuAg NPs—Au-rich passivation layer and pores—are not specific to the core-shell NPs, and form in a similar way for uniform alloy AuAg NPs as well (Sections S7 and S8, Supporting Information). This indicates that the observed dealloying pathway is likely to be general to a wide-range of multimetallic alloy NPs.

Our in situ observations show that porous NPs with different architectures can be obtained by selectively removing Ag from the Au-AuAg NPs via chemical and electrochemical etching processes. In the electrochemical etching, pore sizes can be readily tuned by altering the applied potential, in contrast to porous NPs derived by the chemical etching, where the pore sizes within the NP vary greatly. In both cases, Aurich passivation layer forms on the NP surface during the initial stages of etching, which helps the NPs to retain their shell-like structure, as the Ag in the underneath AuAg region is selectively etched away, transforming the alloy shell into a porous shell. Our results identifying the structural evolution and elemental redistribution in the alloy NPs during selective etching provide insights that can be used to tailor the properties of multimetallic NPs for a broad range of industrial and scientific applications.

### **Supporting Information**

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

# Acknowledgements

This work was supported by the Singapore National Research Foundation's Competitive Research Program funding (NRF-CRP16-2015-05).

# **Conflict of Interest**

The authors declare no conflict of interest.

# Data Availability Statement

Data available on request from the authors.

ADVANCED SCIENCE NEWS \_\_\_\_\_

#### **Keywords**

chemical etching, dealloying, electrochemical etching, liquid phase TEM, porous nanoparticles

Received: November 5, 2020

Revised: January 13, 2021

Published online: March 14, 2021

- [1] J. Erlebacher, J. Electrochem. Soc. 2004, 151, C614.
- [2] T. Fujita, P. Guan, K. McKenna, X. Lang, A. Hirata, L. Zhang, T. Tokunaga, S. Arai, Y. Yamamoto, N. Tanaka, *Nat. Mater.* 2012, *11*, 775.
- [3] J. Snyder, T. Fujita, M. Chen, J. Erlebacher, Nat. Mater. 2010, 9, 904.
- [4] C. Xu, Y. Li, F. Tian, Y. Ding, ChemPhysChem 2010, 11, 3320.
- [5] L. Sun, C.-L. Chien, P. C. Searson, Chem. Mater. 2004, 16, 3125.
- [6] J. Hayes, A. Hodge, J. Biener, A. Hamza, K. Sieradzki, J. Mater. Res. 2006, 21, 2611.
- [7] Q. Chen, K. Sieradzki, Nat. Mater. 2013, 12, 1102.
- [8] C. Xu, J. Su, X. Xu, P. Liu, H. Zhao, F. Tian, Y. Ding, J. Am. Chem. Soc. 2007, 129, 42.
- [9] K. Hu, D. Lan, X. Li, S. Zhang, Anal. Chem. 2008, 80, 9124.
- [10] J. Biener, A. Wittstock, L. Zepeda-Ruiz, M. Biener, V. Zielasek, D. Kramer, R. Viswanath, J. Weissmüller, M. Bäumer, A. Hamza, *Nat. Mater.* **2009**, *8*, 47.
- [11] A. Forty, P. Durkin, Philos. Mag. A 1980, 42, 295.
- [12] H. W. Pickering, Corros. Sci. 1983, 23, 1107.
- [13] K. Sieradzki, N. Dimitrov, D. Movrin, C. McCall, N. Vasiljevic, J. Erlebacher, J. Electrochem. Soc. 2002, 149, B370.
- [14] I. McCue, E. Benn, B. Gaskey, J. Erlebacher, Annu. Rev. Mater. Res. 2016, 46, 263.
- [15] J. Erlebacher, K. Sieradzki, Scr. Mater. 2003, 49, 991.
- [16] F. Renner, A. Stierle, H. Dosch, D. Kolb, T.-L. Lee, J. Zegenhagen, *Nature* 2006, 439, 707.
- [17] R. Yang, P. Strasser, M. F. Toney, J. Phys. Chem. C 2011, 115, 9074.
- [18] I. C. Oppenheim, D. J. Trevor, C. E. Chidsey, P. L. Trevor, K. Sieradzki, *Science* **1991**, *254*, 687.

[19] J. Erlebacher, M. J. Aziz, A. Karma, N. Dimitrov, K. Sieradzki, *Nature* 2001, 410, 450.

NANO . MICRO

www.small-journal.com

- [20] F. M. Ross, *Science* **2015**, *350*, aaa9886.
- [21] H.-G. Liao, H. Zheng, Annu. Rev. Phys. Chem. 2016, 67, 719.
- [22] M. H. Nielsen, S. Aloni, J. J. De Yoreo, Science 2014, 345, 1158.
- [23] Z. Aabdin, X. M. Xu, S. Sen, U. Anand, P. Král, F. Holsteyns, U. Mirsaidov, Nano Lett. 2017, 17, 2953.
- [24] X. Ye, M. R. Jones, L. B. Frechette, Q. Chen, A. S. Powers, P. Ercius, G. Dunn, G. M. Rotskoff, S. C. Nguyen, V. P. Adiga, *Science* 2016, 354, 874.
- [25] Y. Jiang, G. Zhu, G. Dong, F. Lin, H. Zhang, J. Yuan, Z. Zhang, C. Jin, *Micron* **2017**, *97*, 22.
- [26] M. Sun, X. Li, Z. Tang, X. Wei, Q. Chen, Nanoscale 2018, 10, 19733.
- [27] Z. Baraissov, A. Pacco, S. Koneti, G. Bisht, F. Panciera, F. Holsteyns, U. Mirsaidov, ACS Appl. Mater. Interfaces 2019, 11, 36839.
- [28] S. F. Tan, S. W. Chee, Z. Baraissov, H. Jin, T. L. Tan, U. Mirsaidov, J. Phys. Chem. Lett. 2019, 10, 6090.
- [29] H. Shan, W. Gao, Y. Xiong, F. Shi, Y. Yan, Y. Ma, W. Shang, P. Tao, C. Song, T. Deng, H. Zhang, D. Yang, X. Pan, J. Wu, *Nat. Commun.* 2018, *9*, 1011.
- [30] S. Liu, G. Chen, P. N. Prasad, M. T. Swihart, Chem. Mater. 2011, 23, 4098.
- [31] G. Chen, I. Roy, C. Yang, P. N. Prasad, Chem. Rev. 2016, 116, 2826.
- [32] C. J. Kirubaharan, D. Kalpana, Y. S. Lee, A. R. Kim, D. J. Yoo, K. S. Nahm, G. G. Kumar, *Ind. Eng. Chem. Res.* 2012, *51*, 7441.
- [33] W.-J. Kim, S. Kim, A. R. Kim, D. J. Yoo, Ind. Eng. Chem. Res. 2013, 52, 7282.
- [34] P. Liu, Q. Chen, Y. Ito, J. Han, S. Chu, X. Wang, K. M. Reddy, S. Song, A. Hirata, M. Chen, *Nano Lett.* **2020**, *20*, 1944.
- [35] D. Rioux, M. Meunier, J. Phys. Chem. C 2015, 119, 13160.
- [36] L. Wang, C. Darviot, J. Zapata-Farfan, S. Patskovsky, D. Trudel, M. Meunier, J. Biophotonics 2019, 12, 201900166.
- [37] S. Link, Z. L. Wang, M. El-Sayed, J. Phys. Chem. B 1999, 103, 3529.
- [38] D. R. Lide, CRC Handbook of Chemistry and Physics, Vol. 85, CRC Press, Boca Raton, FL 2004.
- [39] X. Li, Q. Chen, I. McCue, J. Snyder, P. Crozier, J. Erlebacher, K. Sieradzki, Nano Lett. 2014, 14, 2569.
- [40] S. Chen, S. Thota, G. Singh, T. J. Aímola, C. Koenigsmann, J. Zhao, RSC Adv. 2017, 7, 46916.