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# Labyrinth-Induced Faceted Electrochemical Growth

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Theseus' heroic escape from the lethal fate awaiting him in the windings of the inextricable Cretan maze marks the start of a 5000 year old fascination with labyrinths and motion within them.<sup>[1,2]</sup> A path-length bias of nucleated electrochemical growth in a 3D periodic nanomaze is equally intriguing, leading to facet formation of an intrinsically isotropic material in a porous, self-assembled gyroid network. In electrochemical growth, the facets reflect long, convoluted pathways through the intricate network of interconnected nanochannels to the nucleation site. Facet edges arise from the shortest paths, as substantiated by computer simulations. This is the first report of faceted electrochemical growth that is not based on the crystallographic order of the constituent building blocks, but rather reflects the symmetry of the template in which the material is synthesized.

Faceted growth resulting in 3D polyhedral shapes with flat faces and defined edges is typically observed in (quasi) crystalline materials.<sup>[3,4]</sup> The driving force responsible for facet formation is the anisotropic crystal growth along different crystallographic directions which results in facet-normals parallel to the slow growth directions.<sup>[5,6]</sup> Amorphous or highly polycrystalline materials, in contrast, lack any underlying crystallographic long-range order and exhibit only isotropic spherical growth. Wang and co-workers recently reported rhombic dodecahedron formation by chemical reduction synthesis of platinum nanocrystals within a mesoporous gyroidal matrix,<sup>[7]</sup> but the single-crystallinity of the nanoparticles obscured the origin of the faceted growth mode.<sup>[8]</sup> Furthermore, the experimentally observed cluster shape and the predictions of a simulated ballstick gyroid model are not in agreement.

In this study we show that nucleated electrochemical growth of polycrystalline platinum clusters inside a 3D periodic mesoporous template possessing the double-gyroid (DG) morphology leads to a faceted cluster surface, even though the deposit itself is highly polycrystalline (**Figure 1a**).<sup>[9]</sup> This isotropic growth is demonstrated by the almost spherical Pt deposits that were electrosynthesized in the absence of a template, under otherwise identical experimental conditions (Figure 1b). The facet formation therefore is a consequence of the gyroidal maze surrounding the nucleation sites.

The double-gyroid morphology with cubic  $Ia\overline{3}d$  symmetry is a 3D continuous equilibrium structure arising from the selfassembly of strongly segregated diblock copolymers.<sup>[10,11]</sup> The

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structure comprises two interwoven single-gyroid (SG) surfaces with I4132 symmetry that are related by inversion and are separated by the so-called matrix phase. Each SG network consists of tubular segments interlinked by nodes with 3-fold connectivity that form two adjoining spirals of opposite chirality along both the  $\langle 100 \rangle$  and  $\langle 111 \rangle$  directions (Figure S1).<sup>[12]</sup> The experimental realization of a double-gyroid nanomaze is schematically shown in Figure S2. Poly(4-fluorostyrene)-b-poly(D,Llactide) (PFS-b-PLA) of molecular weight  $M_n = 24 \text{ kgmol}^{-1}$ containing 38% PLA and polydispersity 1.10 was synthesized as reported elsewhere.<sup>[13,14]</sup> 1-2 µm thick films were spincast onto fluorinated tin oxide substrates and annealed for 20 min at 173 °C to form a DG morphology. The PLA microphase was selectively degraded in an aqueous solution of pH  $\approx 13$  to form a network with  $\varphi \approx 38\%$  porosity. The resulting porous films clearly have a DG morphology but lack long-range order (Figure S3a). Highly polycrystalline platinum was deposited potentiostatically at room temperature from an aqueous solution containing 50 mM chloroplatinic acid (99.9%, Sigma Aldrich) using an Autolab PGSTAT302N potentiostat with a saturated calomel electrode (SCE) and a platinum counter electrode. The styrenic template was subsequently removed by dissolution in toluene. A low nucleation density and isolated platinum deposits were observed when a deposition potential of 0.0 V vs. SCE was applied for 500 s. Negative potentials cause higher nucleation densities and deposition rates, resulting in continuous platinum films (Figure S4).

Platinum clusters grown inside a DG matrix show clear facets (Figure 1a), in contrast to the spherical growth in the absence of a polymer template (Figure 1b). The faceted cluster of Figure S3b however lacks a well-defined symmetry, reflecting the randomly orientated multi-domain DG of Figure S3a. An improvement in matrix order utilizes the temperature dependence of the enthalpic interaction parameter, which controls the diblock copolymer morphology upon microphase separation. When annealed at an elevated temperature of 205 °C for 3 min, the copolymer adopts the cylinder morphology with a long-range order (Figure S3c). On subsequent cooling to 173 °C at a rate of 6 °C min<sup>-1</sup> and further annealing a this temperature for 10 min, a phase transition from the cylinder to the DG morphology is induced,<sup>[15]</sup> preserving the long-range order. The resulting microphase separated film has a DG-morphology that extends across the entire film thickness and has lateral dimensions of several micrometers (Figure S3d). The Pt clusters shown in Figure 1a were grown within such an ordered matrix.

**Figure 2** shows polyhedral Pt clusters grown within wellordered DG films, alongside simulations discussed below. Amazingly, deposits that have formed within only a few voided DG unit cells already show clear facets (Figure 2d). All Pt clusters grown within mono-domain matrices have distinct tetrahexahedral symmetry with 24 equal faces, but lack any underlying crystallographic long-range order (Figure 2). In contrast,

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**Figure 1.** Labyrinth-induced faceted electrochemical growth. SEM images (a) of faceted platinum particles grown within a DG template and (b) spherical deposits grown in the absence of a template, showing pronounced surface roughness.



**Figure 2.** Pt particles grown in DG mazes compared to simulations. SEM images of faceted platinum particles prepared by electrochemical growth in a DG similar to Figure S3d. They are shown next to tetrahexahedra simulated for a DG with  $\varphi = 2\%$  (Figure 3d). In (c) and (d) the particles are viewed along the [100] and [111] directions, for which gyroidal spirals lie on cubic and hexagonal lattices, respectively. The particle shown in (d) contains only twelve DG unit cells. All scale bars are 400 nm.

the tetrahexahedral shape of non-templated Pt nanocrystals prepared by Tian and co-workers reflects their single-crystalline nature. Furthermore, the formation of these nanocrystals requires precise control over the electrosynthesis conditions.<sup>[16]</sup>

The perfect shape alignment of particles that grew in close proximity within the same ordered DG domain provides further evidence that the facet formation is induced by the template (Figure S5a,b) and so does the formation of deposits on a substrate which was only partially covered by a DG-patterned film, revealing the simultaneous formation of faceted and spherical clusters (Figure S6).

The polycrystalline nature of the platinum was verified by transmission electron microscopy (TEM). Pt clusters were directly grown on gold-covered TEM grids (Figure S7). Faceted clusters were realized by preparing a voided DG film surrounding a gold grid, which was used as working electrode during electroplating. The resulting DG-structured platinum deposits are shown in Figure 4a,S7. The high resolution TEM image and selected area diffraction pattern show a polycrystalline platinum deposit with crystallite dimensions comparable to the gyroidal strut length, excluding the possibility that the faceted growth of the deposited clusters arose from the atomic (face-centered cubic) symmetry of Pt (Figure 4a,S9).

Furthermore, the high magnification images of individual Pt-struts do not show any evidence of faceting, as would be expected for the formation of atomic crystals. Instead, the grainy appearance of the platinum struts indicate an electrodeposition growth mode which follows a typical 3D nucleation-coalescence mechanism also found in other high melting point metals, such as Co, Ni and Rh.<sup>[9,17]</sup> This growth mechanism is also evidenced by the grainy surface structure of the non-templated spherical deposits (Figure 1b,S6c).

In order to rationalize faceting of the Pt clusters grown within the nano-structured symmetric network, we have developed a numerical model. An approximation of the interwoven DG network morphology is given by a level surface function,

$$f(x, y, z) = \pm F_{(110)} - tF_{(220)} = c \tag{1}$$

with  $F_{(110)} = \cos 2\pi x \sin 2\pi y + \cos 2\pi y \sin 2\pi z + \cos 2\pi z \sin 2\pi x$ and  $F_{(220)} = \cos 4\pi x \cos 4\pi y + \cos 4\pi y \cos 4\pi z + \cos 4\pi z \cos 4\pi x$ , where the unit cell length is set to unity. The constants  $t \ge 0$ and c > 0 control the tubularity (a measure for the uniformity of the tubes that make up the maze) and the volume fraction occupied by the network phase  $\varphi$ , respectively.<sup>[18,19]</sup> f(x, y, z)mathematically describes two equivalent non-intersecting SG networks (Figure S1) that form the DG morphology. Hence, all obtained results apply to both DG and SG mazes.

Next, the shortest path connecting any two points within the triply periodic SG maze is determined by a modified version of Dijkstra's algorithm, a graph search algorithm that solves the single-source shortest path problem.<sup>[20]</sup> This algorithm was implemented for a cubic lattice with a resolution of  $N \times N \times N$  points per gyroid unit cell. It propagates in the following fashion:

1. Mark all points as unvisited and assign a provisional cost of occupation of infinity.



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**Figure 3.** Computer simulations based on the Dijkstra's algorithm. a) Spherical growth is predicted for free electrochemical growth (top row) and facets emerge for growth in a SG maze (bottom row). The simulated template comprised  $7 \times 7 \times 7$  unit cells ( $\varphi = 12\%$ ) with a lattice resolution of 74 million points (N = 60). The full 3D propagation map is obtained by mirroring across the coordinate planes. b) Growth speed along the different crystallographic directions as a function of volume fraction of the gyroidal network phase (t = 0.05), relative to isotropic free growth. c) Development of the SG and the shortest pathway through the maze for increasing network phase volume fractions  $\varphi$  ( $1 \times 1 \times 3$  unit cells) viewed along the [100] direction. The black areas mark the entrance into the maze and the white spot for  $\varphi = 38\%$  indicates a straight, unhindered path through the maze. The growth shapes derived from (b) form a tetrahexahedron (d) and a hexoctahedron (e) for volume fractions of  $\varphi = 2\%$  and  $\varphi = 38\%$ , respectively.

- 2. When using a gyroid template, identify all points that lie outside the SG maze by solving Equation (1) and tag them as visited.
- 3. Select a 'nucleation site' as starting point and set its occupation cost to zero.
- 4. Consider all unvisited neighbors and calculate their provisional cost which is given by the sum of the cost of the current point and the cost of propagation from the current point to the considered neighbor. If this cost is less than the previously recorded provisional cost, overwrite.
- 5. Mark the current point as visited.
- 6. If the set of unvisited points is not empty, determine the one with the lowest provisional cost, set it as the next current point and return to step 4.

In this algorithm, the cost of propagation is equal to the Euclidean distance and all points that lie within a range smaller or equal to  $\sqrt{22}/N$  from the current point are considered neighbors. The propagating growth front is visualized by plotting all points with an associated total cost of propagation smaller than a given value.

The algorithm was first tested in the absence of a template (Figure 3a). The obtained spherical growth front is similar to the electrodeposition in the absence of a DG network of Figure 1b, confirming that the algorithm correctly implements the locally isotropic growth and does not show artifacts induced by the cubic lattice used in the simulation. Increasing the number of considered neighbors will result in an even smoother spherical surface, but is computationally more expensive and might cause unwanted tunneling between different maze channels.

Figure 3a also shows a simulated cluster inside a SG tubular network, with facets that arise from fastest growth in the  $\langle 100 \rangle$  and  $\langle 111 \rangle$  directions. A consistent result was obtained for a gyroidal maze that was rotated by 45° around the [001] axis, confirming that the facet formation is not an artifact of the propagation algorithm.

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The algorithm was then applied to quantify the volume fraction dependent growth speeds along certain crystallographic directions (*hkl*), denoted by  $v_{hkl}(\varphi)$ . First, the shortest path connecting any pair of points A and B that lie within a maze of volume fraction  $\varphi$  fulfilling the relation  $B = A + h \cdot e_1 + k \cdot e_2 + l \cdot e_3$ was computed using multiple applications of Dijkstra's algorithm, with  $e_i$  being the three cartesian unit vectors. Because of the periodicity of the maze it is possible to limit the set of potential starting points A to one (hkl) plane within one network strut. Second, the minimal path length L was determined from the set of all calculated shortest paths. The growth speed  $v_{hkl}(\varphi)$  normalized with respect to growth in the absence of a template is then given by  $\sqrt{h^2 + k^2 + l^2} / L$ .

The volume fraction dependence of  $v_{hkl}(\varphi)$ 

was studied by repeating the numerical calculations with a resolution N = 100 for  $\varphi$  values between 2% and 99%. The growth speeds through a gyroidal maze with a tubularity t = 0.05 are plotted in Figure 3b. As expected, the growth speeds along all directions increase with widening maze channels for increasing  $\varphi$ . Growth along the  $\langle 100 \rangle$  and  $\langle 111 \rangle$ directions (containing the gyroidal spirals) proceeds significantly faster for all values of  $\varphi$  compared to all other directions and only for these two directions is the speed of non-templated growth reached. Note that  $v_{hkl}(\varphi)$  determines the cluster propagation measured from the nucleation point and not the rate of material addition within the channels, which is constant. The differences in the  $v_{hkl}(\varphi)$  values of Figure 3b arise instead from variations in the length of the convoluted channels that have to be traversed to reach a given end-point.

Figure 3c shows the inner spiral radius along the  $\langle 100 \rangle$  directions, which decrease with increasing network volume fraction  $\varphi$ , while the pitch remains unmodified. For  $\varphi < 32\%$  the shortest path huddles the maze wall and thus resembles the shape of the inner spiral. For  $\varphi \geq 32\%$  this spiral degenerates to a straight line, permitting a straight shortest path, leading to the same growth speed as in absence of a template.

Propagation along the  $\langle 111 \rangle$  directions follows a similar argument, but in all other directions the growth front follows longer, staggered pathways, crossing the spiral windings along the  $\langle 100 \rangle$  and  $\langle 111 \rangle$  directions. DG mazes constructed for *t* values of 0 and 0.1 yielded similar results and growth speeds normalized with respect to the  $\langle 111 \rangle$  directions are given in Figure S10.

The analysis of Figure 3b gives rise to different growth symmetries depending on the value of  $\varphi$ . For  $\varphi = 2\%$  (the smallest volume fraction for which a continuous network is formed), the

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**Figure 4.** Template-based growth of electroplated platinum. a) TEM images and selected area diffraction pattern of DG-structured platinum carried out on a FEI Philips Tecnai 20 TEM operating at 200 kV. Top: Low magnification image showing the faceted DG deposit; Bottom: High magnification image and diffraction pattern revealing that the deposit consists of an agglomerate of small crystallites. b) Schematic illustration of a templated-based growth mode that closely follows the shortest path through the SG maze. For  $\varphi = 38\%$  this results in the hexotahedral shape shown in Figure 3e. c) If growth proceeds via the nucleation-coalescence of small crystallites, the average growth follows the center line of the template channel. In a gyroidal nanomaze with  $\varphi = 38\%$  this results in a growth mode that is similar to a maze with  $\varphi = 2\%$  (right, blue network), yielding the tetrahexahedral shape of Figure 3d.

symmetry of the Pt deposit is determined by the fast growth in the  $\langle 111 \rangle$  and  $\langle 100 \rangle$  directions, which form the vertices of a tetrahexahedron with 24 equal faces, shown in Figure 3d. As long as the growth velocity in the  $\langle 110 \rangle$  directions is sufficiently slow, the  $\langle 111 \rangle$  vertices are connected by straight edges. For faster  $\langle 110 \rangle$  growth, additional  $\langle 110 \rangle$  vertices form on the  $\langle 111 \rangle$  connection lines, turning the tetrahexahedron into a hexoctahedron with 48 equal faces. Geometrically (see Figure S11), this requires  $\nu_{110}(\varphi) = \sqrt{2/3}\nu_{111}(\varphi)$ , as is the case for  $\varphi = 2\%$ . Since  $\nu_{110}(\varphi)$  increases with respect to  $\nu_{110}(\varphi) = \sqrt{2/3}\nu_{111}(\varphi)$  (i.e. above  $\varphi > \%$ ). This hexoctahedron shown in Figure 3e was calculated for  $\varphi = 38\%$ , reflecting the parameters of the experimental DG matrix.

Figure 2 and S12 show the computed polyhedral shapes alongside the grown Pt clusters. Interestingly, all experimentally produced structures were tetrahexahedra and no shapes



with 48 faces were found. This seemingly contradicts the model based on Dijkstra's algorithm which finds tetrahexahedra only in the low volume faction case.

The prediction of hexoctahedra relies on the assumption that Pt growth in the channels occurs atom-by-atom and follows the shortest curvilinear path, as indicated in Figure 4b. Such a growth mode should result in crystalline Pt within the channels, exhibiting growth fronts with crystal facets on the nanometer scale as schematically shown in Figure 4b. Figure 4a however reveals the granular nature of Pt arising from a nucleation-coalescence mechanism.<sup>[9,17]</sup> This leads to a growth front that proceeds along the center of the channels rather than the minimal path along their wall (Figure 4c). While this reduces the effective growth speeds in all directions, it has a relatively large impact on the more convoluted growth paths. In particular, it retards growth in the (110) directions and therefore causes tetrahexahedral growth for large experimental values of  $\varphi$ .

In conclusion, we have demonstrated that path length variations in a periodic 3D maze induce facet formation during electrode synthesis. This generalizes the concept of faceted electrochemical growth, which traditionally was believed to be strictly based on an underlying crystallographic order of the electrodeposited material itself.

### **Supporting Information**

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

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- [1] P. R. Doob, The idea of the labyrinth from classical antiquity through the Middle Ages, Cornell University Press, **1990**.
- [2] H. Kern, Through the Labyrinth: Designs and Meanings Over 5,000 Years, Prestel, 2000.
- [3] D. Shechtman, I. Blech, D. Gratias, J. W. Cahn, Phys. Rev. Lett. 1984, 53, 1951–1953.
- [4] A. S. Finnemore, M. R. J. Scherer, R. Langford, S. Mahajan, S. Ludwigs, F. C. Meldrum, U. Steiner, *Adv. Mater.* 2009, *21*, 3928–3932.
- [5] J. Villain, Nature 1991, 350, 273-274.
- [6] E. D. Williams, N. C. Bartelt, Ultramicroscopy 1989, 31, 36-48.



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- [7] H. Wang, H. Y. Jeong, M. Imura, L. Wang, L. Radhakrishnan, N. Fujita, T. Castle, O. Terasaki, Y. Yamauchi, J. Am. Chem. Soc. 2011, 133, 14526–14529.
- [8] A. Tonscheidt, P. Ryder, N. Jaeger, G. Schulz-Ekloff, Surf. Sci. 1993, 281, 51–61.
- [9] M. Tian, J. Wang, J. Kurtz, T. E. Mallouk, M. H. W. Chan, Nano Lett. 2003, 3, 919–923.
- [10] A. J. Meuler, M. A. Hillmyer, F. S. Bates, *Macromolecules* 2009, 42, 7221–7250.
- [11] H.-Y. Hsueh, H.-Y. Chen, M.-S. She, C.-K. Chen, R.-M. Ho, S. Gwo, H. Hasegawa, E. L. Thomas, *Nano Lett.* 2010, *10*, 4994–5000.
- [12] S. Vignolini, N. A. Yufa, P. S. Cunha, S. Guldin, I. Rushkin, M. Stefik, K. Hur, U. Wiesner, J. J. Baumberg, U. Steiner, *Adv. Mater.* 2012, *24*, 23–27.

- [13] M. R. J. Scherer, L. Li, P. M. S. Cunha, O. A. Scherman, U. Steiner, *Adv. Mater.* **2012**, *24*, 1217–1221.
- [14] M. R. J. Scherer, U. Steiner, *Nano Lett.* **2013**, *13*, 3005–3010.
- [15] M. W. Matsen, Phys. Rev. Lett. 1998, 80, 4470– 4473.
- [16] N. Tian, Z.-Y. Zhou, S.-G. Sun, Y. Ding, Z. L. Wang, Science 2007, 316, 732–735.
- [17] M. Paunovic, M. Schlesinger, Fundamentals of Electrochemical Deposition, John Wiley & Sons, 2006.
- [18] K. Michielsen, J. S. Kole, Phys. Rev. B 2003, 68, 115107.
- [19] M. Wohlgemuth, N. Yufa, J. Hoffman, E. L. Thomas, *Macromolecules* 2001, 34, 6083–6089.
- [20] E. W. Dijkstra, Numer. Math. 1959, 1, 267–271.