

# Preface

Inspired by the work of Edward Crossland et al. on using a thin porous polymer film with double-gyroid morphology for the template-assisted precision patterning of inorganic materials on the 10 nm length scale, [1–5] and due to the fact that all of this polymeric material which was custom synthesized in small quantities by Prof. Dr. Marc Hillmyer had been used up, I established a recipe for preparing thin gyroid films using commercially available polymers during my graduate studies [6, 7]. However, the latter system had some shortcomings as will be discussed below, thus the supply of double-gyroid templates for the patterning of functional materials remained a challenge.

Neat diblock copolymers form the desired double-gyroid morphology during microphase separation only for a very narrow range of block volume ratios. Nevertheless, Prof. Hillmyer succeeded in synthesizing a pure diblock copolymer, poly(4-fluorostyrene)-*b*-poly(D,L-lactide) (PFS-*b*-PLA), which adopted the gyroid morphology in thin films during temperature annealing [1–5]. In contrast, the system I investigated was a binary blend of a lamellae forming diblock copolymer, poly(styrene)-*b*-poly(isoprene) (PS-*b*-PI), and a homopolymer, poly(styrene) (hPS), which forms a gyroidal film during slow solvent-casting from toluene [6, 7]. The solvent evaporation and thereby the film formation is controlled by sandwiching the polymer solution between a teflon foil and the substrate.

The main advantage of the PS-*b*-PI/hPS system is that commercially available copolymers of a wide block composition range can be used since the final blend composition, which determines the microphase separated morphology, can be altered by addition of hPS homopolymer. However, compared to the neat PFS-*b*-PLA the PS-*b*-PI/hPS blend has some major drawbacks. The preparation of templates using PS-*b*-PI/hPS is very time-consuming and involves a drying process that typically takes several days, while the PFS-*b*-PLA films only require brief temperature annealing for less than an hour. Further, film areas of homogeneous thickness are limited to a square centimeter, while PFS-*b*-PLA templates of arbitrary dimensions can be easily fabricated by spin or blade-coating methods. But most importantly, in contrast to PFS-*b*-PLA, the blend system formed non-porous wetting layers at the air/polymer and polymer/substrate interfaces. Especially, the latter layer prevents the usage of the films as templates for the

electrodeposition of functional materials, which requires the voided network to be continuous all the way down to the conducting substrate.

The objective of this work, concerning the template-assisted patterning of functional materials on the nanoscale to enhance specific material properties, is fivefold. First, to develop a highly reproducible synthesis pathway for large quantities of double-gyroid-forming diblock copolymers. Second, to replace the previously used fluorinated monomers with an inexpensive and environmentally sustainable alternative making large-scale applications feasible. Third, to establish a reliable and fast fabrication technique for fully porous gyroidal templates. Fourth, to replicate these templates with inorganic as well as organic functional materials using electrochemical and atomic layer deposition. Finally, to apply and characterize these novel double-gyroid structured materials in devices such as photovoltaic devices, electrochromic displays, and supercapacitors.

The first part of this thesis introduces the different techniques of modern nanotechnology employed in three-dimensional nanopatterning of functional materials and seeks to highlight the possibilities and advantages of using self-assembled, mesoporous polymeric templates for this purpose. [Chapter 2](#) explores the fascinating gyroidal intermaterial dividing surfaces formed by self-assembling systems, such as microphase separating diblock copolymers. [Chapter 3](#) focuses on the synthesis of double-gyroid-forming diblock copolymers consisting of poly(4-X-styrene) and poly(lactic acid) via atom transfer radical and organocatalytic ring-opening polymerization using a bifunctional initiator. The preparation of mesoporous templates with double-gyroid morphology based on a rapid thermal annealing protocol is described in [Chap. 4](#). Importantly, it is shown that copolymers prepared from inexpensive, non-substituted styrene can yield fully porous thin films.

[Chapter 5](#) reports the template-assisted electrodeposition of metal oxides, such as  $V_2O_5$ , using the previously prepared voided styrenic templates. Further, the performance of these materials as electrodes in electrochromic displays and supercapacitors is tested. [Chapter 6](#) describes an alternative approach to obtain double-gyroid-structured metal ceramics via the post-nanostructuring thermal oxidation of electroplated metals. Nickel is chosen to demonstrate this highly versatile fabrication route and to study the nanoscale Kirkendall effect of three-dimensional structures. Further, the electrochromic performance of NiO is investigated. [Chapter 7](#) deals with yet another electrodeposition technique, namely the electropolymerization of conjugated polymers. Identification of suitable solvents for the templated electrosynthesis and the subsequent template dissolution enable the three-dimensional nanopatterning of PPy, PEDOT, and PT. The refilling of the organic template via atomic layer deposition, including the necessary chemical modification of the styrenic scaffold for an improved thermal resistance and surface functionality, is discussed in [Chap. 8](#).

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