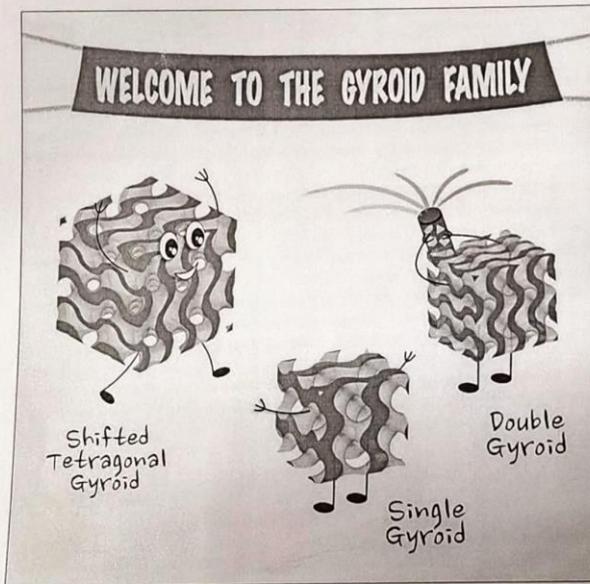


11.3

Article

Tetragonal gyroid structure from symmetry manipulation: A brand-new member of the gyroid surface family



A new gyroid family member, the tetragonal gyroid surface (shifted tG), was designed on the basis of a binary self-assembly system containing diblock copolymer PS-*b*-PAA as the main building block and the small surfactant cetrimonium bromide (CTAB) as the structure manipulator. Featuring shifted double-gyroidal networks, shifted tG belongs to a tetragonal symmetry with the low-symmetry space group $I4_1/a$ and shows a widened photonic band gap along with shifting degrees, initiating a new gyroid symmetric system.

Shuqi Wang, Hao Chen, Tianyu Zhong, ..., Yuan Yuan Cao, Yongsheng Li, Lu Han

yuan yuan cao@ecust.edu.cn (Y.C.)
ysli@ecust.edu.cn (Y.L.)
luhan@tongji.edu.cn (L.H.)

Highlights

Symmetry manipulation of gyroid surfaces is realized through binary assembly system

The shifted double-gyroidal networks possess a brand-new tetragonal structure

The structure features periodic wall thickness due to local concave free energy

The tetragonal gyroid exhibits intriguing optical properties due to symmetry breaking



Wang et al., Chem 10, 1406–1424
May 9, 2024 © 2023 Elsevier Inc.
<https://doi.org/10.1016/j.chempr.2023.12.017>



Article

Tetragonal gyroid structure from symmetry manipulation: A brand-new member of the gyroid surface family

Shuqi Wang,^{1,5} Hao Chen,^{2,5} Tianyu Zhong,¹ Quanzheng Deng,³ Shaobo Yang,¹ Yuanyuan Cao,^{1,*} Yongsheng Li,^{1,4,*} and Lu Han^{3,6,*}

SUMMARY

Gyroid (G) surfaces, the most famous naturally occurring triply periodic hyperbolic surfaces, are well known for their amazing properties closely associated with their intriguing symmetries. Although mathematicians and physicists are devoted to exploring new G surface family members, it remains a mystery whether any novel symmetrical G substructure can be experimentally validated beyond its well-known cubic-symmetrical systems. Herein, we report a tetragonal G substructure (shifted tG) obtained from a cooperative binary self-assembly system consisting of polystyrene-*b*-poly(acrylic acid) and cetyltrimethylammonium bromide. Shifted tG features periodic distributions of uneven matrix thicknesses with local concave free energies, exhibits an extraordinarily shifted double-gyroidal network with a low-symmetry space group of $I4_1/a$ (no. 88), and possesses shifting-degree-dependent photonic band gaps that are never present in its unshifted cubic-symmetrical counterparts. The emergence of new G structures demonstrates a new frontier in the minimal surface subject, crucial for its exploration and innovation.

INTRODUCTION

Gyroid (G) surfaces, first discovered by Alan Schoen in 1970,¹ are the most complex and functionally valuable three-dimensional (3D) geometries yet discovered in that they possess infinite, non-self-intersecting triply periodic minimal surfaces (TPMSs), or constant mean curvature surface structures.^{2–4} Since the discovery of G, the beauty of its peculiar symmetrical and geometrical features has ensured that G structured materials sparkle in interdisciplinary areas, such as mechanical (e.g., exceptionally high strength networks),⁵ catalytic (e.g., electrocatalysts and photocatalysis),^{6,7} electronic (e.g., superconductive materials and hybrid solar cell),^{8–10} and optical (e.g., antireflection, 3D photonic crystals, and chiral metamaterials)^{11–15} materials. Therefore, theoretical and experimental investigations of Gs are a long-lasting topic in interdisciplinary science. The naturally occurring G surfaces have been discovered in numerous biological systems^{4,12,16} and are regarded as paragon inspirations to learn from nature's complex design principles particularly in cell membranes and *Lepidoptera* wing scales.^{17–19} Attempts to artificially fabricate G surface structures include top-down approaches, such as angled etching, 3D printing, interference lithography, and two-photon polymerization,^{20–22} yet these methods are challenging in controlling submicron details. Another approach is bottom-up synthesis, such as thermotropic^{23–25} and lyotropic liquid crystals,^{26–28} block copolymer assemblies,^{13,14,29–32} and their inorganic replicas,^{33–35} whose length scales can

THE BIGGER PICTURE

Triply periodic minimal surfaces (TPMSs), the unique three-dimensional geometry characterized by infinite and non-self-intersecting periodic networks with complex symmetries, are diamonds shining in mathematics, physics, and soft matter science. Gyroid surfaces, the most appealing and complicated TPMSs, possess extraordinary properties highly associated with their symmetrical features and have inspired various terrific man-made artifacts. Manipulating the symmetry of gyroid surfaces is crucial to exploring the beauty of their geometry, but all of their known stable structures are restricted to cubic space groups. In this study, by manipulating symmetry in a designed binary self-assembly system to break the principles of thermodynamic restriction of the polymer phase separation, we obtained a brand-new tetragonal gyroid with intriguing optical properties, which opens up new avenues for generating novel materials with exceptional structures and understanding the minimal surface families.