Perspective

Inverse Methods for Material Design

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Introduction

Discovery and design of new materials can be conceptualized via the hierarchy shown in Figure 1, in which engineering performance derives from dominant structural characteristics exhibited at various length scales. Structural features in a material can emerge spontaneously via self- or directed-assembly of primary building blocks (molecules, nanoparticles, colloids, etc.), and they can also be imposed using top-down fabrication techniques. This hierarchical perspective has been enriched by the widespread use of powerful experimental characterization techniques, which provide microscopic to mesoscopic information about the morphologies of materials with known macroscopic behaviors. Meanwhile, advances in both simulation methods and computing resources enable the modeling of materials from quantum to continuum scales, offering new opportunities to understand not only how specific structures can form in materials but also how those structures relate to other properties of interest.

Both new materials and new material design rules have been discovered by traversing the hierarchy of Figure 1 from bottom to top via "forward" strategies, in which (i) samples with diverse structures are examined to understand how morphology impacts a macroscopic property, or (ii) precursors and synthesis parameters are explored combinatorially to explore the structures that are accessible to a system. That materials with certain periodic structures, such as diamond, can exhibit desirable photonic properties[1,2] or that nanoscale lamellar motifs on the feet of geckos might be mimicked to create dry adhesive materials[3] represent types of findings that have resulted from the first approach. An example of the second forward strategy is the structural characterization of materials with self-assembling units, such as colloids,[4] quantum dots,[5–7] or metallic nanoparticles,[8,9] in which the particle composition and other system parameters are varied to tune the kinetics of assembly and the symmetry of the resulting superlattices.[10–12]

From a design perspective, however, it is perhaps most natural to begin with a set of macroscopic properties specified by an application and then proceed down the hierarchy of Figure 1 (from top to bottom) using "inverse" strategies to discover which structures, material precursors, and fabrication methods can produce materials consistent with those specifications. At the coarsest level, such inverse approaches simply ask whether there is a class of morphologies that would be optimal (within known material property constraints) for realizing the specified macroscopic properties. Once optimal morphologies are identified, the focus redirects toward how best to design fabrication or assembly routes with appropriate material precursors for realizing the required structures.

In this Perspective, we highlight several recent studies that illustrate how inverse strategies using appropriate physical models and computational methods can address the following complex materials design questions within the hierarchical framework of Figure 1.

- Which microstructures reflect—or, alternatively, suppress transmission of—target wavelengths of light for design of structural color or photonic band gap (PBG) materials, respectively?

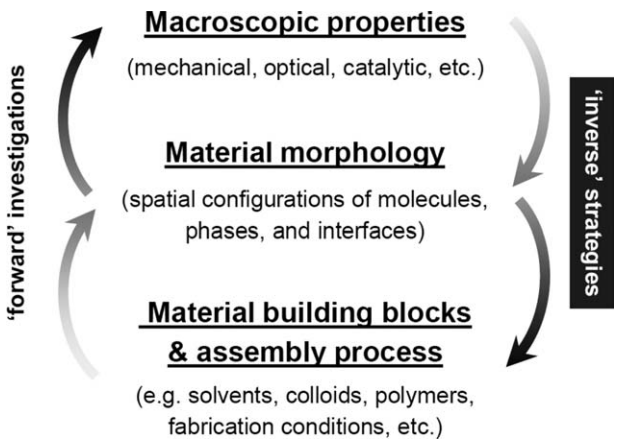

Figure 1. A hierarchical view of material discovery and design.

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- Which "sparse" template structures direct the assembly of block copolymers into target morphologies for graphoepitaxial nanopatterning applications?
- Which isotropic interactions between colloidal particles promote their self assembly into targeted, open superlattice structures?

We also briefly consider future applications where inverse design methods might return rapid dividends, highlight current limitations of inverse strategies, and speculate on how some of the challenges of this field might be addressed.

Designing Structures for Target Properties

Dielectric thin-film morphologies for structural color applications

Numerical methods, led by finite-element based topology optimization (TO), have been used since the late 1980s to determine material microstructures that meet design specifications.[13] Initially, these methods were used to design heterogeneous or multiphase materials with targeted thermal expansivity[14,15] as well as elastic[16] and piezoelectric[17] properties. During the past decade, however, the TO algorithm has been extended to discover new microstructures consistent with desired acoustic,[18] nanophotonic,[19] and photovoltaic[20] behaviors as well. Nonlinear constrained optimizations have also been used to design surface textures of thin film solar cells for enhanced photon absorption[21] and to discover novel amorphous photonic structures.[22]

Inspired by the vibrantly hued yet nonpigmented scales of *Morpho* butterflies[23,24] and other insects,[25] in which the apparent colors arise from the interaction of light with the wings' nanoscopic cuticle-air features, researchers recently used TO to control perceived color solely by manipulating material architecture.[19] Specifically, the authors optimized thin-film dielectric morphologies to produce specific and high-intensity structural color responses; that is, without the use of individual pigments. In Figure 2, the left-hand panels illustrate silica (SiO_2) and titania (TiO_2) dielectric films with nanostructural features optimized for a green response upon exposure to daylight at a specular angle of 0°. Two design optimizations were explored. Figure 2a shows the result when the dielectric material was required to be alternately layered (i.e., one-dimensional gratings), and Figure 2b shows the more complex structure of the unconstrained optimum. The right-hand panels provide the red-green-blue (RGB) response curves over a wider angular spectrum with the background displaying the perceived color. While both the layered and disordered morphologies meet the set objective, the intensity is clearly optimized by the disorganized microstructure.

More broadly, it was demonstrated that the qualitative structural features of the optimal films depend sensitively on the desired color response in a way that could not be guessed *a priori* without theoretical guidance. Designs for a wide range of colors were presented, and for some wavelengths even the unconstrained optimizations surprisingly found layered morphologies that were optimal.[19] For angle-dependent (iridescent) color responses, entirely different microstructures are required with the details depending on the manufacturing constraints. In short, this theoretical strategy, rooted in deeply established physics principles,[26–28] provides an example of how inverse methods can make very specific and nontrivial theoretical predictions about the classes of microstructures that should be tested and possibly pursued in the next stage of experimental design.

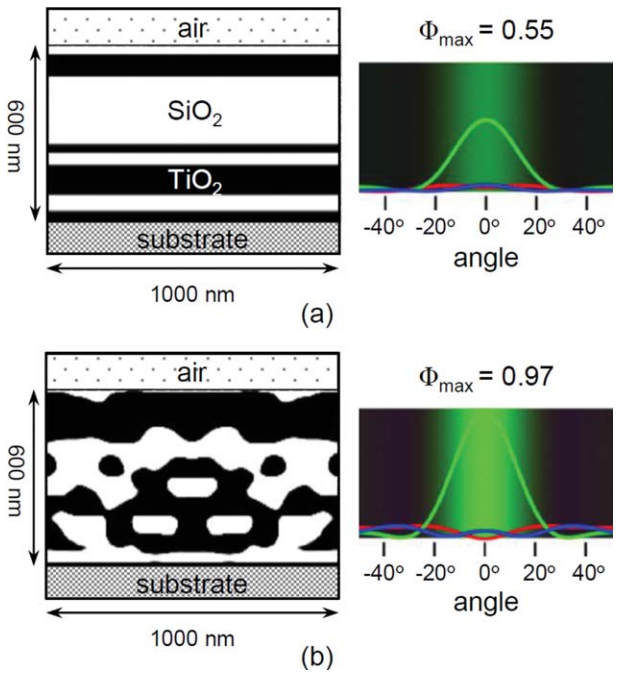

Figure 2. Left panels illustrate silica (SiO_2) and titania (TiO_2) thin-film morphologies optimized to maximize intensity of a prescribed color (green) in a prescribed direction (o°). Right panels show simulated RGB response curves for the designs under exposure to full-spectrum daylight at various incident angles, where Φ_{max} is the maximum intensity. In (a), the optimization was constrained to test only alternately layered phases; in (b), this constraint was relaxed.

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Disordered materials with complete PBGs

A PBG is a frequency range over which transmission of incident electromagnetic waves is blocked. By combining at least two material components with disparate dielectric constants in specific ratios and configurations, the transmission of light frequencies can be blocked for some or all incident directions and polarizations, the latter corresponding to a "complete" PBG.

Both forward and inverse studies of photonic materials have discovered periodic microstructural configurations that exhibit PBGs,[29] including diamond[1] and woodpile structures,[2] and cylindrical packings in hexagonal[30] and honeycomb[31] patterns. Beyond periodic structures, a developing research area considers how light interacts with disordered and nonperiodic structures.[32] Examples include photonic glasses,[33] display of structural colors in animals,[24] and packing of avian photoreceptors.[34] Despite the interest in disordered photonic materials, broad principles for designing disordered PGB microstructures have been slow to emerge.

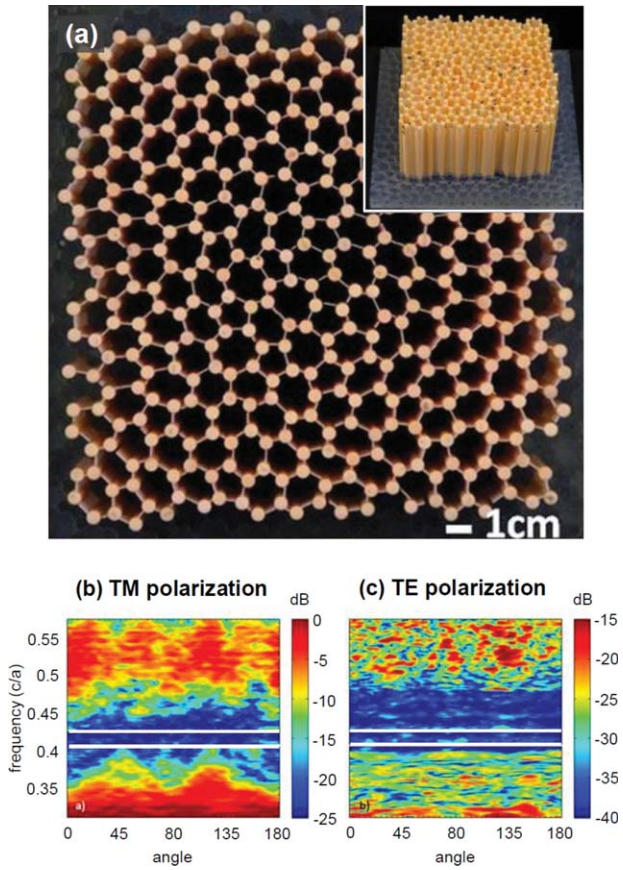

Figure 3. (a) A fabricated amorphous 2-D pattern comprising alumina cylinders and connective sheets, designed to display a complete PBG (inset shows a side view of the structure); the lower panels show measured transmission strength (in dB) for various light frequencies and incident angles; the PBGs in response to (b) transverse magnetic (TM) and (c) transverse electric (TE) polarizations are bounded by white lines.

Adapted with permission from Ref. 22.

A recent inverse design study[22] focused on discovering novel microstructures consisting of irregular two-dimensional (2-D) point patterns that exhibit complete PBGs. To make the optimization tractable, the authors constrained their design space to "hyperuniform" structures only,[35,36] which exhibit suppressed density fluctuations (all crystals, quasicrystals, and a subset of disordered patterns—e.g., those corresponding to maximally random jammed particle packings[37]–are hyperuniform). Using pregenerated hyperuniform point patterns to position alumina cylinders, the authors numerically optimized the common cylinder radius to maximize the PBG frequency range. Figure 3 illustrates a fabricated version of the optimal 2-D pattern and the measured PBGs, which matched the theoretical predictions. Most importantly, the authors were able to quantify common structural characteristics of optimal hyperuniform 2-D structures for PBG materials, including their enhanced short-ranged geometric order (as characterized by the strength of cylinder–cylinder spatial correlations) and the uniformity of their local topology (as measured by the cylinder coordination number). The combination of these characteristics—suppressed density fluctuations, short-range correlations, and uniform topology—provides a new structural "design rule" discovered by inverse methods that has more recently been used to generate, using Direct Laser Writing techniques,[38–40] synthetic disordered three-dimensional (3-D) photonic structures yielding complete PBGs.[41]

Designing Directed- and Self-Assembly Processes for Target Structures

Once desirable target structures are identified, there remains the challenge of determining the best approaches to synthesize the required morphologies. Broadly speaking, there are two types of approaches: (1) top-down fabrication and (2) bottom-up assembly. Top-down approaches typically use pattern transfer, etching, or deposition technologies to impose the desired structural features on the materials of interest.[42–47] Assembly, conversely, relies upon spontaneous formation of target morphologies, which can be driven by "self" interactions between the primary units or building blocks of the material or additionally "directed" by carefully chosen external fields or boundaries in the system.[48–50] In many applications, both top-down and bottom-up strategies play a role. For example, directed assembly often relies upon top-down fabrication methods like lithography to create an initial template (e.g., a chemically or topographically prepatterned substrate) that helps to steer the assembly of smaller primary units (e.g., block copolymers) into a desired structure.[51–54]

From a fundamental perspective, directed- and self-assembly methods pose challenging questions about how best to choose system parameters and material components in order to promote organization of a condensed matter system into a target structure instead of a competing morphology. As we describe below, inverse methods for assembly can take advantage of multidimensional optimization methods and statistical mechanical theories of complex fluids, and thus they are natural tools to help address these questions.

Templates for directed assembly of block-copolymer morphologies

As a first step, templates for directed assembly are typically designed by intuition, i.e., imprinting physical or chemical patches along regions where complementary phases are to be located. A key challenge is to use inverse design theory to develop templates with minimum feature density and complexity while still inducing assembly of structures consistent with device-pattern specifications.[55,56] A recent series of studies[57–59] used Monte-Carlo (MC)-based optimizations to design substrates with maximally sparse patterns that promote target block-copolymer (BCP) phase-separated patterns, including technologically relevant features like bends, junctions, and terminations. The templates consisted of posts selectively attracted to one of the BCP phases situated on a phase-neutral substrate. Figure 4 presents the authors' inverse workflow, in which they (a) specified the target BCP morphology and (b) optimized the post

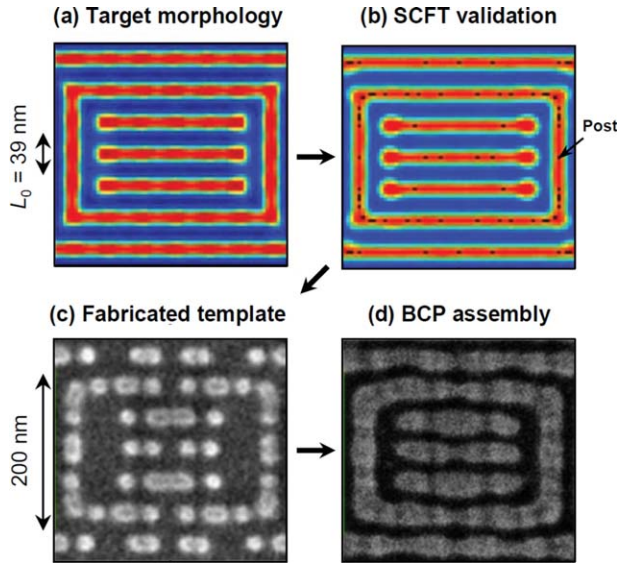

Figure 4. (a) Target PS-b-PDMS BCP morphology (minority PDMS regions are red, majority PS regions are blue). (b) Simulation results confirming the target structure is displayed using the inversely optimized template of posts (shown as black dots). (c) The optimal template, fabricated via electron beam lithography. (d) SEM scan of the resulting BCP morphology.

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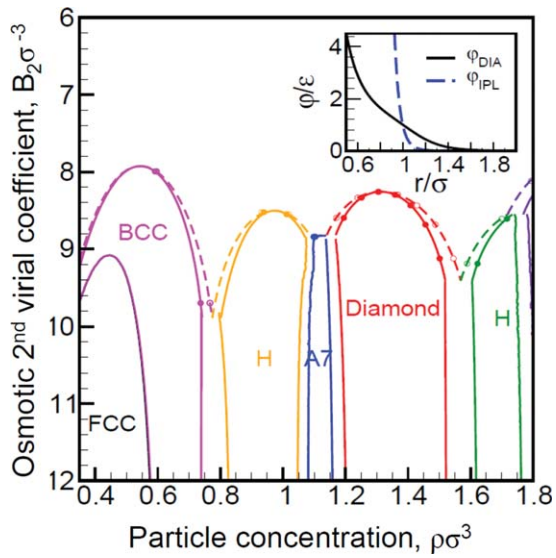

Figure 5. Superlattice-fluid phase diagram of particles with an isotropic interparticle potential optimized to exhibit a diamond crystal ground-state over the widest possible density range. The inset shows the diamond-forming potential (φ_{DIA}) compared against an inverse power law ($n = 12$) potential (φ_{IPL}), which highlights the main feature of the optimized potential: its softer repulsion. Coexistence lines were obtained via free-energy MC simulation methods from Ref. 91–93.

configuration (shown as dots) based on predictions from self-consistent field theory. They then (c) fabricated the template using electron beam lithography and (d) demonstrated that the target polystyrene-b-polydimethylsiloxane (PS-b-PDMS) BCP morphology was indeed assembled in the optimized post configuration. As an alternative to the MC-based inverse strategy, other researchers[60] designed similar BCP templates using an evolutionary algorithm based on Cahn-Hillard equations for nonequilibrium phase separation. While their optimal templates have yet to be validated experimentally, the authors emphasized that using analytical theories should make increasingly complex design problems computationally tractable.

Designing interactions for targeted superlattice self-assembly

An important focus of the modern self-assembly literature has been on understanding which equilibrium superlattice phases are formed by various nanoscale or microscale colloids[61] based on their shape,[62–67] size,[12,68,69] surface texture,[70] surface coating,[71–73] particle–solvent interactions,[10] and so forth. A particularly fruitful topic has been the examination of assembly driven by particle-surface functionalizations which provide orientation-specific interparticle interactions[74–76] that mimic atomic covalent bonding via, e.g., DNA sticky ends[77–80] or similar interactions promoted by complementary inorganic ligands.[71,81,82]

However, outstanding challenges remain in characterizing the effective interactions between suspended nano- (colloidal-) particles as well as in elucidating their stable equilibrium phases. A key challenge is to identify the basic limitations that interaction isotropy between particles places on the types of achievable periodic structures. This is important because there are practical advantages in terms of the synthesis and assembly kinetics of nano- (colloidal-) particles with approximately isotropic (versus orientation-dependent or "patchy") interactions.[83]

Statistical-mechanics based computational studies[84–88] have demonstrated that isotropic interactions can drive assembly of exotic, low-coordinated 2-D (e.g., Kagome, honeycomb, snub-square) and 3-D (e.g., diamond, simple cubic) lattices, which represents a break from the conventional understanding that directional interactions are necessary to self-assemble such open lattice structures. Recently,[85] authors have used inverse statistical-mechanical optimization methods to design pairwise interaction potentials that maximized the phase diagram footprints (i.e., density ranges) over which specific 3-D lattice (e.g., diamond) ground states were favored. In this study, the potentials were constrained to be short-range and convex-repulsive, features qualitatively similar to measured interactions between particles uniformly grafted with ligands interacting in a solvent medium.[89,90] Using free-energy based MC methods,[91] the associated superlattice phase diagrams were calculated (see Figure 5) and target phases based on the designed potentials were found to be robust to variations in the osmotic second-virial coefficient of the interparticle interaction (i.e., solvent quality, analogous to temperature in these systems).

While these inverse strategies can provide precise mathematical interactions that drive assembly to target structures, realizing these effective potentials in real systems remains an open challenge.[82,94,95] Certainly, experts in colloidal particle synthesis can attempt to creatively intuit the precursor materials and fabrication conditions that result in approximations of optimal effective potentials, although at present this represents a rather open-ended enterprise. A more insightful line of inquiry might be to optimize interaction models composed explicitly of experimentally controllable parameters (e.g., colloidal core material, particle size, grafted ligand lengths, graft densities, etc.). In one such investigation,[96] researchers used genetic algorithms to design the density and length of complementary sticky ssDNA strands to be grafted on spherical colloids to form target binary crystal structures. They based their optimization on a previously established numerical model[97] and, thus, were able to replicate experimental observations of crystalline assembly for similar DNA-grafted colloidal systems.[97] Unfortunately, few existing models capture the overarching physics of colloidal interactions over accessible design spaces while remaining tractable for optimization search routines.[98–100] Overcoming this knowledge gap necessitates a return to theoretical work in complex fluids, focused on establishing accurate analytical and numerically feasible models that reflect nanoscale and microscale colloidal physics.

Outlook and Challenges

Beyond the highlighted studies above, there are several emerging technologies in which computational inverse strategies are already being used, and others where they might return quick dividends. A variety of studies have focused on optimizing solar cell domain distributions for increased photovoltaic efficiency[21]; mesoscale architectures composed of nanocrystals for enhanced energy flow[101]; dopant concentrations in polymer and inorganic matrices for target functionalities[102]; structure and composition of surface alloys for target catalytic activity[103]; multiphase interfaces for thermoelectric transport[104]; external fields[105] and interparticle interactions[106] for enhanced single-particle mobility; and faceted colloids that form target periodic structures and tesselations.[64,107] Inverse strategies should also prove useful in optimizing new fabrication approaches, for example, identifying ideal blade microfeatures for controlling thin-film organic-semiconductor crystals at industrial manufacturing scales,[108,109] and also offer the opportunity to revisit long-standing physical questions, including the evolution of granular shapes that possess target macroscopic stress responses.[110]

We note that the hierarchy of Figure 1 is a coarse simplification, meant to encompass the broadest possible collection of contemporary material design problems. It may not always be reasonable or advantageous to pose inverse design problems that separately address either Property → Structure or Structure → Assembly connections in isolation. Especially when macroscopic properties can be related to the chemical make-up of the material precursors, it may be possible to tune the precursors directly for the desired property, without explicitly specifying structural connections. Additionally, in some design problems, one can traverse the hierarchy of Figure 1 from top-to-bottom by designing microscopic components for a target property by explicitly defining the structural constraints, which may be known *a priori* due to fabrication-related limitations or otherwise. For example, the remarkable successes in using density functional theory (DFT)-based calculations for surface processes has enabled the computational design of solid electrocatalysts with increased catalytic function.[103] In a recent study,[111] a new superior catalyst consisting of bismuth and platinum was designed for a hydrogen evolution reaction by a high-throughput combinatorial screening method which used a database of DFT solutions for binary transition metal alloys combined with on-the-fly calculations—limited to close-packed geometries only—to determine the stability and catalytic activity.

Information databases of material properties can also be incorporated into inverse strategies to evaluate objective functions more efficiently than calculating the relevant property at every iteration of the design process. For example, in design problems drawing upon quantum-mechanical approximations such as DFT, databases like the AFLOWLIB.org consortium,[112] Materials Project,[113] and Open Quantum Materials Database,[114] are being currently used along with powerful data-mining techniques to discover new materials for a variety of applications,[115] including solar materials,[116,117] solid catalysts,[111] battery materials,[118] and so forth.

It cannot be overemphasized that along with advances in computing capabilities and numerical tools,[119–123] the utility of inverse strategies relies on the physical accuracy of the underlying hierarchical connections between properties, structure, and assembly. Especially, as device properties are increasingly understood to emerge from material attributes at the nanoscale and smaller, continuum and classical descriptions of materials may reach their fundamental thresholds of applicability. Going forward, their validity needs to be established across multiple lengthscales, and, if necessary, new integrated multiscale connections must be developed. Such challenges are already apparent in terms of holistically understanding the physics of assembly, as exemplified in our discussion of the inverse design of self-assembling colloids. And while significant knowledge gains are being made through extensive forward-strategy investigations, their successful integration into inverse methods depends on distilling and validating computationally tractable physical theories.

The physical models and problem constraints, that is, "user inputs," that must be chosen while formulating the inverse strategies are ultimately validated when the outcomes of experimental synthesis and characterization match promising solutions. When outcomes do not match the theoretical predictions, there are still gains to be made. Forward investigations, including both experiments and simulations, can be used to clarify system responses within regions of the design space where predictions failed, and the underlying theoretical connections can be revised in light of new experimental findings. This feedback loop between theory and experiments can iteratively provide novel and nonintuitive physical insights that bridge different levels of the material design hierarchy. Subsequently, these new connections can streamline the development of an expanding portfolio of technologically relevant materials, from desired device properties down to the choice of modular and inexpensive material precursors.

Acknowledgments

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