Self-Assembly

“On the Dot”—The Timing of Self-Assembled Growth to the Quantum Scale

Sanjiv Sonkaria,[a] Sung-Hoon Ahn,[a, b] Caroline S. Lee,[c] and Varsha Khare*[a]

© 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim
Abstract: Understanding the complex world of material growth and tunability has mystified the minds of material scientists and has been met with increasing efforts to close the gap between controllability and applicability. The reality of this journey is frustratingly tortuous but is being eased through better conceptual appreciation of metal crystalline frameworks that originate from shape and size dependent solvent responsive growth patterns. The quantum confinement of TiO$_2$ in the range of 0.8–2 nm has been synthetically challenging to achieve but lessons from biomineralization processes have enabled alternative routes to be explored via self-induced pre-nucleation events. In driving this concept, we have incorporated many of these key features integrating aspects of low temperature annealing at the interface of complex heterogeneous nucleation between hard and soft materials to arrest the biomimetic amorphous phase of TiO$_2$ to a tunable crystalline quantized state. The stabilization of metastable states of quantum sized TiO$_2$ driven by kinetic and thermodynamic processes show hallmarks of biomineralization controlled events that suggest the inter-play between new pathways and interfacial energies that preferentially favor low dimensionality at the quantum scale. This provides the potential to re-direct synthetic assemblies under tightly controlled parameters to generate a host of new materials with size, shape and anisotropic properties as smart stimuli responsive materials. These new stabilities leading to the growth arrest of TiO$_2$ are discussed in terms of molecular interactions and structural frameworks that were previously inaccessible via conventional routes. There exists an undiscovered parallel between synthetic and biomineralized routes enabling unprecedented access to the availability and tunability of novel quantum confined materials. The parametrics of complex material design at the crossroads of synthetically and biologically driven processes is only now surfacing.

Introduction

Amidst an era marked by an endless plethora of nanostructured transformations from their bulk counterparts emerging effortlessly through a hidden sequence of chemical instructions unknown to the experimentalist, hybridized patterns of size,$^{[1]}$ shape and dimensionality have soared in recent years. The underlying importance of surface chemistry,$^{[2]}$ and chemical bond relaxation and its ability to participate in short- or long-range ordering bordering at the metal-organic interface through assisted or self-organized twists and turns in complex architectures has dwindled in comparison to the spectacular display and enormity in the range of reported nano-engineered metal organic frameworks.$^{[3]}$ Experimental science has rather surrendered to theoretical physicists who have impressively embraced the challenge of predicting accessibility to novel atomic configurations and attempting to decode the elemental basis of existing structures using powerful computational approaches.$^{[4]}$ Arguably, a mechanistic and structured approach to resolving problems in surface chemistry that better define the chemical events at the nano and quantum scale promises to directly impact our current knowledge in driving selective pathways to achieve desired structures that can be tuned by increasing our controllability over shape and size. From this view point, re-thinking conceptually by intrusively examining the nature of chemical bond flexibility$^{[5]}$ to advance and acquire new materials or attain quantum confinement of existing ones must be provoked with renewed passion. Although, significant progress continues to incite experimentalists to view material desirability as a combinatorial problem of composition, there lies a delicate balance between order and disorder coupled to physically and chemically driven parameters particularly in self-assembly processes$^{[6]}$ at the metal–polymer interface.$^{[7]}$ With considerable interest in superlattices of nanostructured TiO$_2$ fuelled by its unmatched semiconducting characteristics, we aim to discuss unprecedented or sufficiently unexplored directions in materials engineering exemplified by the surface properties of TiO$_2$ in advancing a potential wealth of new materials at the quantum scale.

A focus of developing interest inspired by natural processes has offered alternative routes to explore and imitate biosynthetic pathways to control material assemblies at the nanoscale. Deciphering the elemental routes to engineer biomimetic strategies has not been short of challenging and the realization of mimicking functionalities within self-assembled cages would have profound implications for the quantum dimension range$^{[8]}$ as a viable alternative to a purely synthetic approach. The biomineralized inspired synthesis of TiO$_2$/RGO (reduced graphene oxide) composites however reported particles between 10–12 nm diameter$^{[9]}$ at best far from quantum confined states of ≤2 nm. In hindsight, biomineralization routes often form crystallized structures mediated through an amorphous-disordered phase. The material advantage in engineering the nanobiomi-
micry of TiO2 to an amorphous phase is the potential of increasing access to new electronic states altering the band gap properties. Conceptually, an amorphous induced biomimetic approach in engineering TiO2 can deliver new physical and chemical characteristics by:

1) enabling synthetic parameters favoring pathways that trigger biomineralization-like processes at the hard-soft material interface;
2) ensuring strong interfacial interaction between thermally induced cationic defect vacancy sites on reduced titanium oxide with reactive nitrogen anionic templates;
3) driving surface-amorphized TiO2 by low temperature annealing favoring an amorphous phase under a thermally controlled environment conditioning pathways to a disordered phase;
4) regulating size control of crystal growth through controlled addition of organic/ inorganic additives;
5) allowing unprohibited stoichiometric access to the potential wealth of nucleating sites in the alkylated phosphonium ionic liquid medium favouring an amorphous metastable geometry ensuring structural flexibility, low packing density and high hydration;
6) inducing crystallinity from an amorphous state by a solvent responsive anisotropic process and tuning dimensional size and band gap by changing solvent strength.

The proposed route to applying a biomimetic approach to acquire the above characteristics for surface-amorphized TiO2 is summarized in Figure 1. Here, the ligand chemistry of an ionic liquid environment dominated by nitrogen cationic/ anionic complex chemistry plays a key role in passivating surface defects of TiO2 that drive chemical modification at the metal oxide surface.

**Shifting dimensionality to the quantum scale**

The quantum era and its technological impact

The desire to drive the dimensionality of materials to quantum levels (Figure 2) is being met by uncovering the novelty of new surface chemistries, new bond associations at contrasting interfaces, confinement effects, broader electronic energy transitions and an enrichment of hybrid properties offering task specific functionalities. Currently, titanium dioxide is the most promising hybrid material for energy harvesting in dye sensitized solar cells as a patentable technology for environmental applications, display monitors, drug delivery, imaging and energy harvesting (Figure 3). However, at the quantum scale due its size, property-structure convergence could provide unprecedented access to material controllability through improved structure manipulation. This also has important implications in driving “point-of-care” technologies in the future (Figure 3). The organization of matter at the quantum scale gives rise to significantly altered behavioral characteristics in which selectivity becomes increasingly dominant. Selectivity broadens the scope to drive photo-luminescence properties of biocompatible titanium dioxide cores surrounded by polymer interfaces.
coats, for example, towards therapeutic or diagnostic applications. The utility of quantum sized materials is directly correlated to their predictability and advances in meeting this criterion in the next generation of functional materials must converge upon acquiring “smarter materials” in which their anisotropic behavior and properties can be controlled by external stimuli such as temperature, electric fields and shape inducing materials. If quantum materials assembled as unique or fragmented characteristics of conventional materials arise as a function of new symmetries from shape and size effects are considered sufficiently different topologically, the possibility to tune material properties on a very fine scale can generate a new order of functional materials. There is deep interest in driving discovery programs to uncover new morphologies and exploring inter-relationships between quantum confinement and unexplored interfacial surface properties that may introduce new physical parametric constraints limiting growth properties to generate low dimensional materials. The fabrication of metamaterials are the key to pioneering innovative technologies as a spin off from quantum material engineering to deliver exotic states of matter by trapping electron-electron interactions and spin dynamics for future applications.

Experimental hurdles to attaining spatial confinement in TiO₂ are extremely challenging limiting access of carriers to reputedly discrete forbidden quantum band regimes. This is distinguished from higher band-gap regions that serve as energy barriers effectively separating the behavioral characteristics of nanoscale from quantum scale materials. Improving the availability and efficiency of stimuli responsive materials requires the removal of such barriers permitting the mobility of carriers to migrate along a broader spectrum of energy distributions across the semiconductor surface through the confinement of lower band-gap accessibility.

The current perspective on quantum scale synthesis of TiO₂

A range of methods applied for the preparation of semi-conductor quantum dots have proved demonstrably successful through processes involving the integration of metal ions with heat treated metal oxide preparations expelling the excess as quantum dots into the precipitate and exerting both nucleation and inhibitory growth processes. Routes to implementing quantum dots into the precipitate and exerting both nucleation and inhibitory growth processes have proved demonstrably successful. Heat treated metal oxide preparations expelling the excess as quantum dots into the precipitate and exerting both nucleation and inhibitory growth processes have proved demonstrably successful.

<table>
<thead>
<tr>
<th>Titanium bulk precursor</th>
<th>Template/Solvent</th>
<th>Temperature/Washing</th>
<th>Structural features and size</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiCl₄</td>
<td>([C₄mim]⁺ [BF₄]⁻)</td>
<td>RTIL self-assembly</td>
<td>TiCl₄ water hydrolysis 80 °C (2 h) removal of RTIL 50 °C (8 h) mesoporous crystalline 70–100 nm composed of 2–3 nm spheres</td>
</tr>
<tr>
<td>TiOBu₄</td>
<td>hydrofluoric acid (HF)</td>
<td>TiO₂ nanosheets 180 °C (24 h) water/ethanol Crystalline 6 nm width 40 nm length</td>
<td></td>
</tr>
<tr>
<td>TiOCH₃Bu₄</td>
<td>hydrofluoric acid (HF)</td>
<td>TiO₂ nanosheets 180 °C (24 h) water/ethanol TiO₂, crystalline nanosheets 40–50 nm length 6 nm width</td>
<td></td>
</tr>
<tr>
<td>TiOBu₄</td>
<td>isobutyl alcohol</td>
<td>TiO₂, anatase 10–30 nm TiO₂, anatase 10–30 nm 1.2 μm length</td>
<td></td>
</tr>
<tr>
<td>TiOCH₃Bu₄</td>
<td>hydrofluoric acid (HF)/H₂O</td>
<td>TiO₂, anatase 50 nm length 10 nm thickness</td>
<td></td>
</tr>
</tbody>
</table>

Experimental hurdles to attaining spatial confinement in TiO₂ are extremely challenging limiting access of carriers to reputedly discrete forbidden quantum band regimes. This is distinguished from higher band-gap regions that serve as energy barriers effectively separating the behavioral characteristics of nanoscale from quantum scale materials. Improving the availability and efficiency of stimuli responsive materials requires the removal of such barriers permitting the mobility of carriers to migrate along a broader spectrum of energy distributions across the semiconductor surface through the confinement of lower band-gap accessibility.

The current perspective on quantum scale synthesis of TiO₂

A range of methods applied for the preparation of semi-conductor quantum dots have proved demonstrably successful through processes involving the integration of metal ions with heat treated metal oxide preparations expelling the excess as quantum dots into the precipitate and exerting both nucleation and inhibitory growth processes. Routes to implementing self-assembly methodologies have bordered between wet-chemical and vapor-phase methods that rely stringently on control of parameters in one-pot reaction mixtures exposed to thermal and time-dependent cooling procedures drastically affecting interfacial growth patterns of a defined composition of reactants. Despite the enormity of shape and size evolution and directional growth patterns sensitive to interfacial energies at crystallographic edges, environmental composition, chemically driven enthalpies of elemental and complex group functionalities, unassisted growth arrest of TiO₂ to the quantum phase is reputedly regarded as non-trivial among aqueous based semiconductor nanocrystals. However, confusion has arisen by reports claiming unassisted synthesis of TiO₂ quantum dots in the sub-nanometer range or in some cases assisted but not in the correct quantum confined range of ≤3 nm. In contrast, Pan et al. applied a hydrothermal procedure over a duration of 72–168 h and successfully reported nanosheets of anatase TiO₂ quantum dots in the size range of 1.5–3 nm. This method involving hydrofluoric acid treatment of the TiO₂ bulk precursor at 180 °C initiating the crystalline phase considerably enhanced the possibility of obtaining sheet embedded quantum confined TiO₂ particles. The loss of the aqueous fluoride TiO₂ precursor in [18] from the use of the ionic liquid 1-butyl-3-methyl imidazoliumtetrafluoroborate ([C₄mim]⁺[BF₄]⁻) for the preparation of TiO₂ quantum dots during the reaction or the access from washing steps provided sufficient dispersability to the formation of self-assembled mesoporous aggregates composed of 2–3 nm spherical TiO₂ particles, respectively. The literature describes reported attempts to synthesize TiO₂ quantum dots and Table 1 provides a summary of synthetic methodologies to assemble crystalline structures of TiO₂ and their dimensional sizes to highlight synthesis-size correlations. To date, the attainment of ≤1 nm TiO₂ quantum dots to our knowledge has not been reported since this finding which is indicative of specific surface interactions at material interfaces favoring the anatase crystalline phase. The authors emphasize that a defect free surface is critical to achieving low dimensionality of the semiconductor oxide.

An important observation indicated by authors Zhao and Antonetti in their analysis is the lack of an amorphous phase observed for reaction conditions with a high water content that brings into question the role of water molecules and their binding modes in stabilizing a crystalline state under modest temperatures. Table 1 shows that variation in synthetic condi-
tions that dramatically alter the size of TiO_2 crystals re-empha-
sizing the influence of physical parameters on nucleation pro-
cesses and the inability of the reaction environment to suffi-
ciently initiate surface chemistries that might favor growth re-
striction at the quantum scale. This underlines the need to fur-
ther examine how water dynamics and amorphous precursor states for example could make way for alternative chemical pathways more accessible to quantized states of matter. Clues to broadening and redirecting surface group chemis-
tries at TiO_2 bulk precursor sites to generate novel organic–in-
organic interactions and phases begins with identifying key physical and chemical parametric information that stress the important inter-play among elemental doping and defect sites that are primarily driven by interfacial surface energies through kinetic or thermodynamic effects or indeed a combination of both. In view of the results of the investigations presented here, these parameters have been judged as significant to the (1) composition of aqueous or non-aqueous solvent environ-
ment of the reaction medium and bulk precursor structure (b) nature of defect states that are induced at specific surface sites at (c) temperatures over a given (d) time duration. This is evi-
dent from the conclusions from the above studies and some-
what vague but it is predicted to have important implications in reaching the quantum state of TiO_2. How these are interre-
lated and how they affect each other is a matter of much com-
plexity. However, with much more certainty, it can be claimed that solid surfaces at the nanometer scale are a mixing pot of heterogeneous catalytic reactions that operate at the intersec-
tion of adsorption–desorption and diffusion processes in which product selectivity can be accelerated, decelerated or indeed altered in a chemically programmable fashion. This direction of thought becomes more feasible and achievable when a change in size and shape of materials during the course of a reaction can alter the homogeneous nature of a catalyst to embody a heterogeneous role[29] re-routing the order and structure of catalyzed products. Hence, the transition from nano- to quantum scaling might be expected to transform processing of small catalytic products to generate new ligands at the metal surface via size[30] and shape[31] dependent selec-
tive processing.

Engineering the impact of surface defect chemistry

Surface defects that arise from cationic or anionic interaction effects or from time dependent thermal effects and their pat-
tern of distribution on surfaces necessarily have a strong impact on their interfacial properties. Externally disrupted sur-
faces and symmetries are an abundant source of specifically lo-
cated chemical anchoring sites for ligand assemblies distribut-
ed transversely across the metal oxide. A useful analogy to in-
trude at this stage relates to the dimensional control of crys-
talline nucleation exerted by organisms in biomineraliza-
tion introducing strain or compression randomly within crys-
talline lattices. A useful analogy to in-
trude at this stage relates to the dimensional control of crys-
talline nucleation exerted by organisms in biomineraliza-
tion introducing strain or compression randomly within crys-
talline lattices.

If such pathways can be successfully incorporated for non-bio-
logical surface manipulation leaving the crystal phase and size unaffected, biomimicry at the level of defects and their con-
trolled evolvement might be feasible. Tailoring of interfacial sur-
faces to meet these requirements is a complex area and under-
standing of property–structure correlations between heteroge-
neous reaction mediums and their ability to generate defect patterns at metal surfaces under defined conditions is a labori-
ous process of trial and error but one that is necessarily crucial. If synthetic systems can be re-ordered to generate similar sur-
face specificities to biomolecular assemblies, this could offer a cost-effective route to design more elaborate metal-organic structures with enhanced performance. This task may become easier between contrasting materials at the soft–hard interface.

Ab initio approaches have been particularly informative in correlating the bias introduced by surfaces, defect states and the effect of ligands on semiconductor properties. A significant insight of this approach has led to the importance of organic surfactants and their interaction with nano-metallic surfaces. This has important implications in the permeability of multi-
component and multifunctional soft materials at hard material interfaces and their localization in sub-surface regions main-
taining pore–wall cavities that accommodate chemical produ-
cts of heterogeneous nucleation. Intrinsic disorder of metallic surfaces initiated from bulk to nano and quantum phase transi-
tions is inherently coordinated to defect site evolution and al-
tered geometrical configurations from atom removal or substi-
tution introducing strain or compression randomly within crys-
tal lattices.

Driving quantum confinement of the metal oxide through elemental doping

It is well known that site selective binding introduced through bond associations from the cationic or anionic reaction envi-
ronment can re-direct growth kinetics and thermodynamic pathways from surface interactions altering interfacial energies and size comparably to protein constituents in biominaliza-
tion.[32] Newly introduced paramagnetized centers and structur-
al relaxation of intrinsic defect sites in titanium complexes such as those associated with oxygen vacancy sites (Ti^{4+}) can be directed through heteroatoms of non-transition metals. The underlying motivation for driving heteroatomic molecular chemistry has been pursued to gain accessibility to energy configurations coupled to the generation of new surface chemistries that are sensitive to structural alterations at the metal oxide exterior arising from unexpected interfacial phe-
nomena. The incorporation of new regions of stability through unusual bond associations should selectively aid re-tuning of catalytically derived chemical units as structural building blocks for larger assemblies. This will necessarily occur through the deliverance of alternative pathways balanced co-jointly by enthalpic and chemical driven arrangements. The precise nature and effects of dopant materials[33] are not coherently understood and this aspect has been perplexed by the broad use of variable synthetic protocols and the dependency on synthetic positioning, location and bonding associations of...
modified impurities within the target lattice. Given the doping efficiency is largely governed by adsorption properties related to surface morphology, nanocrystal shape and surfactant composition,

doping chemistry is predictably a difficult task among various complexed elements.

Previously it has been noted that Pan et al.

applied a non-heteroaromatic hydrothermal method to yield 1.5–3 nm TiO₂ quantum dot nanosheets reactive to HF (40%) in a time-dependent process. Under slow rates of hydrolysis with NaOH, the expulsion of F⁻ ions generated degrees of enthalpically stabilized phases via pre and post-treatments with ethanol and water to obtain a defect free surface interface with alteration in size of sheets but not their surface chemistry. In view of the lack of detailed analysis from F1s XPS binding energy profiles in conjunction with Raman molecular spectroscopy, it has been difficult to determine the role of HF in the fluorolysis of the metal oxide at Ti-OR sites where R represents a reactive functional group type. In other words, the removal F⁻ ions suggest its interaction with the metal surface is interstitial by nature and not substitutional. Further, the identity of the binding energy peak close to 464 eV has not been discussed in terms of its structural significance and surface chemistry of functional building blocks that might contribute to the quantum confinement of TiO₂. The binding associations at 464 eV has previously been seen to be accompanied with lower binding energies at 458.5 eV as a doublet peak in TiO₂@MOF-5 within the porous coordination polymer [Zn₄O(bdc)₃] (bdc = 1,4-benzenedicarboxylate, MOF-5), a characteristic that has been demonstrated by Pan et al. but the accompanying signal in the latter study is signified by a lower binding energy of 457.7 eV equating to a difference of 0.8 eV. The observed XPS peaks lie in close proximity in the range of 458.6–458.9 and 457.3–457.7 eV, respectively and form sub-peaks of Ti 2p³/₂ representative of oxides of titanium. The latter range of binding energies are commonly ascribed to Ti₂O₃ equivalent to the availability of Ti¹⁺ oxygen vacancy sites assigned to the 2p³/₂ elemental spectral line which is strongly suggestive of electron distribution densities around shared or overlapping orbitals. Binding energies of this order involving nitrogen substitution have not been demonstrated explicitly to indicate quantum confinement. Current efforts have rather focused on critically examining the consequences of nitrogen substitutions at defect sites relative to interactions of an interstitial nature within the TiO₂ lattice and a discussion of some the ambiguities in N1s peak assignments. This has led to a shift in the importance of selecting precursors and reaction conditions to physical parameters such as temperature.

The atomic configurations and shape geometry of Ti2p often show heterogeneous orbital characteristics that manifest as Ti 2p₁/₂ and Ti 2p₃/₂ transitions that greatly exceed binding energies around 398 eV and 500 eV with respect to titanium nitrides Ti-N, and titanium oxide Ti-O bond associations. Interpretations of mixed valance states of oxynitrides Ti-Oₙ-N and Ti-Nₙ-O require more special attention and such binding patterns have not thus far been considered below the nanoscale. In contrast, the interpretation that considers the relative electronegativity of oxygen atoms in O-Ti-N and O-Ti-O-N-C in reducing the electron density around N around BEs 401 eV, the lower binding energy at 398 eV are more consistent with the formation of Ti–N₂ bond types. New surface chemistries indicated through substitutional nitrogen events at the titanium oxide surface have been reported to be associated with the formation of metastable assemblies under a reduced band gap.

Acquiring new material assemblies as a function of size—A conceptual thought

Synthetic processes are beginning to surface that allow the assembly of complex supramolecular structures exhibiting architectural periodicities with nanocage like geometries that were considered unimaginable less than a decade ago. Recent examples include interlocking nanocages, metal-organic frameworks composed of nano-sized voids, polymer-linked and surfactant-driven polypyrrole nanocages, coordination driven spherical nanocages and others comprising of more simpler noble-metal nanocaged structures. Nanocage like structures that bear the hallmarks of hierarchical porous morphologies have tremendous scope for exerting size confinement effects via chemically constructed cavities initiated at the level of growth nucleation around the metal oxide surface. An important facet to advancing such materials necessarily involves the design of useful precursor complexes from the controlled interaction of bulk metal oxide materials in chemical environments that can be parametrically driven to select for structural features at the level of nucleation. Tuning selectivity in catalysis to the quantum scale requires major adjustment to current synthetic protocols that deploy conventional routes to nucleation. These further dominate growth and assembly processes favoring size evolution of crystals in the nanometer range. In this context, exploring divergent pathways directed towards metastable assemblies that exhibit lower surface energies in which thermodynamic and kinetic control is analogous to biomimORIZATION, the introduction of new enthalpic factors may help steer new directions.

Synthetic biomimicry as a driving mechanism to enable tight control over titanium oxide precursor complexation is a conceptual challenge. A key structural feature of biomimORIZATION as an important component in biomimetics is the process of compartmentalization of nucleating products which is an effective route to organize and orientate chemical building blocks during scaffold assembly of surface catalysed products. This is also an important determinant to size and shape architecture and homogeneity of crystalline morphologies. The ability to successfully mimic nucleating events that faithfully encompass these key stages is not trivial. Steering selectivity at the organic–inorganic interface to meet these criteria is an underlying issue. Predicting the behavioral properties of charged species in the reaction environment may show considerable deviation from the exquisite specificities of polyanionic/polycationic proteins involved in biomimORIZATION events. Reduced temperature and reaction times could potentially play an important role in off-setting these constraints. In the interests of utilizing abundantly green elemental materials comprising carbon, hydrogen, nitrogen, oxygen, and phosphorus inspired
by nature and biomineralization machineries in organisms, starting materials were sought to encompass the spectrum of these elements in a reaction template comprising the bulk titanium precursor and reaction medium at the liquid-solid interface. In this context, this hypothesis favored the use of a multi-elemental stable soft cationic-anionic heterogeneous reaction medium exhibiting features of a semi organic-inorganic composition of bond donating and accepting nitrogen rich complexes, heteroaromatic hydrocarbon rings and alkyl chains anchored to a phosphonium center. This rationale was used to explore possible advantages in forging new covalent and non-covalent interactions, hydrogen binding networks, weaker associations (dipole-dipole, electrostatic and van der Waals forces) at the material interface between newly formed defect sites of TiO$_2$ and the reaction environment. The morphological enrichment in catalysis, reaction selectivity and accessibility towards dominant nucleating crystallographic faces of the bulk titanium precursor hosting surface specific reaction products was envisioned to substantially initiate simultaneous pathways allowing surface ligands, linkers, bridges and polymers to self-assemble under low temperature conditions.

Biomineralization and Biomimicry

Interface engineering of TiO$_2$ quantum materials

Dimensionality can dramatically alter the intrinsic nature of materials and probably the most unique and significant challenge in nano and quantum chemistry at the present time is recognizing the limitations of synthetic protocols and underlying processes that prohibit access to quantum scale shape and size transitions. Shape and size adaptation of contrasting materials with dissimilar interfacial properties show an unusual level of complexity that correlates to their interaction behavior at adsorbed surfaces during nucleation and post-nucleation growth phases. An emerging area of such systems that utilize a combination of weak and strong chemical bond associations formed at a flexible interface that offer a potential route to generate pathways to novel geometrical transitions are those that occur between hard and soft materials. Conditioning porosity at the hard-soft interface at surface and sub-surface levels of the metal oxide caters for pore spaced geometries that hold the potential to introduce internal and external structural anomalies at the intersection of heterogeneous nucleation.

Exploiting semiconductor nucleation and growth characteristics that unfold at the interface of hard and soft matter is decidedly an important consideration in determining desirable material compositions. Surface directed effects paralleled by a chemically templated environment can introduce structurally and enthalpically driven pathways on altered time scales that have a profound geometrical impact on length, dimension and order. Directing such interfacial molecular assemblies through specific elemental doping of chemically susceptible sites affecting the motility and interaction of newly emerging structures from the basic inter-play of small molecular blocks to confined spaces is a worthy pursuit.

The idea that a chemical matrix might assemble into pre-nucleation clusters of an architectural type synonymous with some biomineralization processes via metal–organic bond associations imply nucleating mineral species are able to adopt an energy landscape consistent with an amorphous state. The key parameters driving this phase and confinement properties are summarised in Figure 4. Such determinants that quantitatively minimize the energy demands of a crystallized state in more conventional processes where energy barriers are lower (as for high temperature reactions) might be re-directed to form disordered phases stabilized by weaker interactions that may necessarily make use of the solvation properties of the underlying matrix. Competing pathways at the boundary of kinetic and thermodynamic processes coupled to their specific and non-specific interactions characteristic of their respective binding patterns are events that have been sparsely investigated. A remarkable facet of biomineralization involving downsizing of reaction droplets on the scale of picolitre volumes have reportedly demonstrated delayed nucleation growth relative to the bulk exhibiting an amorphous phase in which spatial confinement effectually generates thermodynamic pitfalls to stabilize reaction intermediaries. This suggests that slowing or perturbing the onset of crystallization is energetically feasible under amorphous conditions and can provide opportunities for spatial confinement of the metal oxide directly at the quantum scale and might be achievable under thermodynamically controlled growth conditions. However, spontaneous entropic intervention of the amorphous trapped state can effect lower activation energies triggering more stable phase transitions shifting the thermodynamic equilibrium via water-solvent ordering to lower energy structural arrangements of increased stability. Allowing biomimetic strategies that take advantage of dynamical flexibility, orientation and mobility of functional groups in non-biological systems broadening bond selectivities at transient or intermediary stages of pre-crystallization via an amorphous precursor pathway is critical to shape and size control. The most exquisite examples of biomimetic control over shape and size that might be usefully applied to

Figure 4. Key elements of the dynamics of nanobiomimicry driving an amorphous phase that effect the characteristics of crystallization, ring confinement of TiO$_2$ and band gap properties.
deliver quantum sized materials are processes involving ligand directed compartmentalization of metal complexes that permit their insertion in organic structural cavities locked into a tetrahedral symmetry. In hindsight, if we consider both biomineralization and synthetic chemistry processes to share key characteristic routes to mineralized growth through a precursor phase, biomimicry as a parametric guide to drive chemically synthetic assemblies can be usefully applied to generate a host of new materials. An appreciation of this conceptual argument at the nano and quantum scale between soft organic and hard inorganic materials can be extrapolated to key reported observations focused on surface directed biominalization systems related to 1) particle size affects\cite{48} 2) pre-nucleation clustering,\cite{49} non-equilibrium morphologies and confinement\cite{50} 3) pre-crystallization transient molecular events specific to the amorphous phase\cite{51} and 4) heterogeneous to homogeneous crystallization.

With the view of applying the concept of hard-soft matter interfaces as potentially "structure-directing" and/or "process-directing" materials and their relative influence on the shape and size of metal oxide assemblies, we have investigated nitrogen-rich liquid-based cationic/ anionic phosphine centered polymer coated templates as soft material counter-parts to the harder bulk TiO$_2$ precursor and the extent of their participation as sacrificial structures and as nanoreactors. The ability to synthetically program confinement of nucleating TiO$_2$ assembled from surface catalyzed products under unusually low temperature conditions was investigated.

Exploring heterogeneous to homogeneous size dependent selectivity favoring spatial confinement of TiO$_2$

Implications of nitrogen doping on quantum scaling of TiO$_2$

Nitrogen doping of titania has recently been suggested to exert growth suppression and shape deformation effects evidenced by a change in lattice parameters at the crystal surface.\cite{52} The fabrication of ultrathin TiO$_2$ nanowires in the anatase phase are reportedly attributed to the presence of nitrogen\cite{53} supporting its role in the confinement of morphologies to an unprecedented low order on the dimensional scale. This interesting phenomena specific to nanowires is remarkably independent of bulk TiO$_2$ precursor chemistry.\cite{54} The influence over these parameters were notably more pronounced with the increase in nitrogen content in crystal lattices but exhibited a structural dependency with the nitrogen precursor at optimum doping concentrations. These conclusions support the view that the involvement of molecular factors that are extrinsic to the host material can significantly impact nucleation events dramatically. This notion based on recent findings in our group extends beyond the participation of nitrogen reactant complexes as modulators of reaction pathways but points to their chemically driven association with catalyzed products and by-products formed at the titanium oxide surface bulk phase leading to extended nitrogen complexes originating from interstitial or substitutional nitrogen–oxygen interactions at oxygen vacancy sites. However, complex materials subject to low annealing temperatures might exhibit structure sensitive characteristics of flexible materials intrinsic to both amorphous and crystalline states.

Structure based selectivity transitions at the TiO$_2$ surface as a function of size sensitivity: Mimicking and stabilization of amorphous metastable states

Amorphous precursor pathways are well recognized and accepted routes to biominalization that defy more conventional processes to crystallinity. A lowering of the surface energy of the hydrated state of TiO$_2$\cite{55} contributes to increased thermodynamic and kinetic stability which is substantially enhanced with decreased particle size of an amorphous state. The hallmark characteristics of such materials often exhibit inconsistencies in lattice structuring and misaligned matrix patterns. Weakly observed but localized Bragg peaks of the amorphous state under high electron beams are associated with lattice restructuring signifying a pre-crystalline or in some cases an amorphous precursor arrangement depending on the extent of the non-equilibrium state. In the metallic glass transition phase which occurs under the influence of a high energy barrier (low reaction temperature), nitrogen doping at the TiO$_2$ surface progresses to a distribution of uniformly spaced centers of nucleation that lack periodicity judged by a non-crystalline diffraction pattern. The conglomerate of densely packed amorphous spheres are characteristic of short range order suggesting that the lack of periodicity in the amorphous state is not necessarily representative of lattice disorder but an interruption to long range order. This may be unusual for a multi-constituent complex and an unidentifiable diffraction pattern or indeed weak Bragg peaks formed at local regions under a high electron energy beam may indeed be indicative of lattice mismatch in bonding geometries preventing long range order. This provides a compelling argument for a high degree of distortion at bond coordination sites associated with polymer trapping of porphyrin confined quantum-sized TiO$_2$ increasing the probability of misaligned configurations during growth. This defining feature involving the accumulation of an infinite body of tiny spheres that might be reasoned to represent a dispersed but suppressed population of heterogeneous reaction centers limited by low temperature effects highlights the use of applying reduced thermal processing to induce a random pattern of disordered metal organic frameworks (MOFs) in which thermodynamically trapped states can be morphologically manipulated responsively.

Heterogeneous nucleation described here occurs by metal center activation of surface anchored substrates that are catalytically processed to synergistically release multiple reaction products via olefinic chemistry, aromatization and dearomatization\cite{56} events which has recently been demonstrated. Here, the reactive TiO$_2$ isopropoxide precursor [Ti(OCH(CH$_3$)$_2$)$_4$] in the presence of a sacrificial cationic-anionic trihexyltetradecyl phosphonium dicyanamide [P$_6$6,6,14][N(CN)$_2$] reaction medium generates lateral interactions dominated by two mutually independent reactions driving the formation of 1) tetraphenylporphyrin...
phyrin-TiO₂ complexes 2) metal-phosphonic ligand assembly and 3) cationic polymerization of styrene monomers to a stable cross-linked polystyrene (PS) matrix by a metal-ligand cooperative process. The interactive chemistry of these processes provide unique opportunities for the growth arrest of TiO₂ to the quantum phase.

With relevance to biomimetics applied at a synthetic level, an array of discontinuous polymers surrounding the TiO₂ or ganometallic core was indicative of amorphous materials composed of sub-nanometer quantum-sized spheres reminiscent to that of biominalizing organisms. Insufficient energy of a low annealing temperature and finite reaction time drives the intermittent phase to a multi-thermodynamic state of equilibrium defined by existing barriers inherently coupled to dopant impurities and their surface occupied positions. The structural pattern of control of the metastable phase and surface chemistries dictate the nature of thermodynamic pits and their influence on crystallographic folds. Particle size effects at the quantum scale arise possibly from polymer growth restriction and ligand structure entrapment of TiO₂. The influence of polymer chemistry is clearly evidenced by the effect of solvent at the amorphous phase and its evolution to the crystalline phase. These events are illustrated in Figure 5 showing the effects of solvent and temperature on polymer tactivity from the amorphous to a semi-crystalline phase that progresses to the crystalline state.

Quantum confinement of TiO₂ via metal insertion in porphyrin ring complexation

The growth arrest of TiO₂ to the quantum scale requires bond coordination with porphyrin to impart an inhibitory nucleating phase (Figure 5) and evidence of a dominant N-Ti-O type configuration associated with BEs residing midway between assigned interstitial and chemisorbed states composed of nitrogen or more commonly nitrogen organic complexes suggests ambiguity in structural assignments which remains an on-going challenge. However, the positioning of nitrogen dopants in the crystal lattice relative to their ligand associations as shown here with porphyrin-metal complexes might be better assisted by structurally driven methods using a templated approach demonstrated here or by group-specific nitrogen doping that directly impacts nucleation and growth events with a degree of tunability. For example, ring deformity adapting to variability in QD size affecting surface interaction binding affinities with varying degrees of complexion demonstrates a broader range of size-based selectivity with altered characteristics.

These are not the final page numbers!
This is seen to occur after TiO₂–TTP bond conjugation evidenced by the complete suppression of the unbound porphyrin to the metal occupied state at 600 nm. Strong interaction between the porphyrin nitrogen bonds with the TiO₂ metal center in contrary to weaker metal–porphyrin interactions are distinguished by an increase in the Q-band peaks (Figure 7) which otherwise remain undisturbed or slightly shifted. This characteristic in irregularity is dominated by alterations in the binding symmetry between the metal surface and cavity bonds in the metalloporphyrin. Infrared frequency range (798–806 cm⁻¹) coincide agreeably with trivalent and tetravalent metal occupancy in tetraphenylporphyrins (TTPs) that exhibit an invariable C–H stretch as a result of metal insertion that forms the metalloporphyrin. The absence of vibrational frequencies in the range of 3039–3600 cm⁻¹ associated with in C–H and N–H stretches, hydrogen and non-hydrogen bonded interactions with aromatic groups demonstrate that such functionalities result from solvation effects which are enhanced by temperature changes but not inducible by temperature alone. We observed that the UV behavioral pattern of the TiO₂ porphyrin polymer complex exhibits electronic absorption behavior that can be correlated to excited states that characteristically occur along the Soret or Q band transitions representing π–π* mobility along HOMO–LUMO orbital arrangements aligned to the conjugated structures. The UV generated oscillator type spectral pattern observed for porphyrin bound TiO₂ (Figure 7) typifies a metalloporphyrin assembly consistent with a symmetric Ti–N bond ligand character of the centrally bound titanium oxide with energy states of higher and lower magnitudes specific to the Soret (B-band) and Q-band UV reflectance resulting from merged molecular orbitals. The consensus here shows that self-assembly processes are equally effective in selecting for pathways that generate porphyrin MOFs composed of a titanium oxide core to more commonly reported Fe driven cyclopentadienyl structures directed by alternative ionic liquid synthetic based methods. The degree of distortion on the metal centered co-planar ring geometry is affected by external bridging of the outer phenyl ring moieties of porphyrin and is related to the alkyl chain length. A red shift of the Soret band maxima from 422.1 to 446.1 nm reported by the authors representing the same order of deformity of the MOF we observed here emphasizes the magnitude of strain generated at the ring orbitals induced by successive bridging of MOF layers at the site of the porphyrin structure but also the flexibility of central C–N bonds surrounding the TiO₂ core and the energy distribution around π orbitals relative to the d-orbitals of metal surface, bridging linker and anchoring groups. This leads to the assumption that the geometric size confinement of TiO₂ may be attributed to the deformation and contraction properties of the inner metal binding cavity of the porphyrin C–N bonds resulting in a number of out-of-plane distortions tolerated by metal directed assemblies and the conformational properties of the porphyrin binding pocket as a flexible metal ligand. This arrangement might place an unfavorable energy burden as a direct consequence of the geometric rigidity at the PS interface of the outer ring that may be offset by lowering of orbital energies of a stable chelation effect in which the bond contribution of the central nitrogen atoms are more favorably harmonized by d-orbital splitting accompanied by binding of metals of higher oxidation state thereby lowering spin state configurations and better balance of charges in terms of orbital occupancy and magnitude of interacting bond energies. This peculiarity in metal–porphyrin complexation is further evidenced by broader Q-band assignments detected for band energies of 2.07 and 1.68 eV corresponding to 600 and 737 nm, respectively. Energy transitions beyond the Q-band range to lower energy regions are explicitly observed at 912.5 and 1070 nm residing in the near infrared region (NIR) (Figure 6) and the corresponding photoluminescence intensities spectrum provides an estimated quantum yield (photons emitted/ photons absorbed) of 5.70 and 39%, respectively, with peak photon absorption recorded at 1070 nm. The extremity in the red shift intensity towards longer wavelengths could be attributed to a solvent induced behavioral pattern representing a structurally altered state of the adsorption geometry or reorientation of the ligands around TiO₂.

The size and shape changing properties of porphyrin around metal complexes are attributes that can affect the electronic characteristics of the ring stabilized QDs. Here, we infer that the ligand binding cavity of self-assembled porphyrins are intrinsically adapted to bind TiO₂ assisted by the host-guest chemistry of the PS polymer network and this configuration might be expected to show distinguishable optical and behavioral features to the freely mobile ethyl group modified porphyrins that may show a pronounced, diminished or loss of interaction with QDs. The PS outer shell itself based on guiding parameters that border on mass driven networks of long range order supporting an architectural arrangement that exerts shape and size metal growth restriction often demonstrated by vinyl functional polymers is a hallmark of block co-polymer type composition and behaviour of tunable porosity giving rise to an established anisotropic characteristic of morphologi-
cally altered nanostructures in ethanol as solvent. The amorphous nature of PS and its contribution to a template induced spatial environment is advantageous for the self-assembly of chemically bulky groups in which solvation of ethanol can establish a new order of chemical periodicity in a solvent dependent manner. Thermo-induced changes in the crosslinking density of a PS co-polymer blend at the metal oxide interface showing thermo-response behavior and correlation with a phase volume transition\textsuperscript{[66]} demonstrate the flexibility of spatial reorganization around self-assembled vinyl aromatic polymers. The identity of the compartmentalized metal center and the order of the size confinement imposed by the porphyrin-PS-phosphorane scaffold along the metal surface influencing its characteristic properties can drastically alter the energy landscape and excitation threshold of electron transitions. The dominance of a PS polymer framework in the immobilization of porphyrin is substantiated by the unusual appearance of the PS UV spectral peak shift of 4 to 286 nm relative to the reported value of 290 nm\textsuperscript{[67]} adjacent to the Soret band of the porphyrin ring. The alignment of porphyrin supported between alternating aromatic rings supplied by synergistically positioned PS chains show a definitive network of a sterically organized rigid nanocrystalline framework as a host lattice for TiO\textsubscript{2} complexation. The use of PS as an extensively layered non-sacrificial polymer catalyst support is uniquely different to chloromethylated poly(styrene) which was shown to function as a reactive modified starting material to assist the catalytic role tetrakis(pentafluorophenyl)porphyrin (FeTFPP)\textsuperscript{[69]} The structural feasibility of quantum confined TiO\textsubscript{2} formed by the ring complexation of TPP bound by PS rings and the phosphorane oxide ligand with a linker molecule CH\textsubscript{3}-(C\textsubscript{5}H\textsubscript{3}N)-N=C\textsubscript{6}H\textsubscript{5}(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}(OH)(OH) is supported by MM2 force field calculations based on the parameters obtained from XPS and FTIR (unpublished work).

**Role of water molecules**

The increased presence of water molecules points to an altered hydrated state that establishes not only a re-orientation in the binding modes of water molecules but also leads to a possible re-ordering of neighboring groups affecting the equilibrium of surface states among other functional groups. This scenario becomes apparent if the phase transition ordering is interrupted above the glass transition temperature ($T_g$) of the polystyrene polymer and its re-direction to allow for interfacial restructuring through the inter-positioning of water molecules assisted by the solvent. This may be particularly applicable to templates that are completely or partially reactive to synthetic conditions and processes but sufficiently capable of generating a degree of periodicity intermediate to the glass and crystalline phase of the polymer.

Here, the dynamic role of water increases the intensity of the conjugated carbonyl band component now visible along the regional stretch 1670–1820 cm\textsuperscript{-1} at 120°C but again this frequency band is not exposed at RT suggesting its role in the stabilization of water molecules is less critical for the non-crystalline phase as evidenced by thermogravimetric analysis (TGA). It may be important to consider that the bond orientation and extent of hydrogen bonding and hence differences in the molecular motion of water between the two vibrational frequencies may be a determining factor in the level of hydration at the vicinity of the phosphine ligand and polymer interfacial regions during the crystalline phase transition. Evidence of the interaction of the hydrocarbon chain of P\textsubscript{66614} with carbonyl groups in the TiO\textsubscript{2} complex is supported by FTIR of the hydration of mono-oleylglycerol\textsuperscript{[69]} demonstrating structurally the important role of water in forming hydrogen bonded linkages within the PS matrix (Figure 7).

The behavioral assignment of water is favored by a masked weaker band at 2130 cm\textsuperscript{-1} characteristic of liquid state materials and a high energy vibrational band at 700 cm\textsuperscript{-1} consistent with the frequency of oscillating molecules of bulk water associated with a polymer matrix. Although these band assignments are somewhat tentative\textsuperscript{[70]} their use in supporting the molecular vibration of water can be reasonably applied here in combination with the peak intensity at 1652 cm\textsuperscript{-1}. Temperature induced changes at 120°C is deterministic of key morphological events between the TiO\textsubscript{2} precursor and [P\textsubscript{66614}]\textsubscript{2}[CN]=N\textsuperscript{[70]}\textsubscript{1} generating solvent specific interactions in the colloidal phase different to binding events at RT. One distinguishing feature relates to the bonding association of water molecules in the complex that may not be specific to trapping of molecules at the polymer-metal surface but instead may extend across the larger polymer surface. The vibration band at RT is characterized by a broader peak width in TGA and presents a substantially reduced frequency intensity band of the peak maximum at 3328 cm\textsuperscript{-1} coupled with the absence of the prominent water band at 1652 cm\textsuperscript{-1} signifying a depressed state of chemical reactivity between ethanol and the surface chemistry of TiO\textsubscript{2}.

![Figure 7. Optical properties of colloidal polystyrene-porphyrin-TiO\textsubscript{2} quantum dots showing B and Q band behaviour typical of porphyrin or porphyrin rich hybrid materials. The therapeutic window of tissue absorption (630–1350 nm) supports potential for biomedical applications of such newly acquired materials.](image-url)
Indeed, the energy burden in releasing chemisorbed water from polymer surfaces is significantly less than expelling polymer embedded water suggesting differences in the bonding order of water and the degree of hydration.\textsuperscript{71} The interacting water molecules may also exhibit significantly different binding modes such as bending conformations to its more conventional -OH stretching adaptation synonymous with hydrogen-bonding activities. Overall, the complete detachment of water from the complex at 450 °C supports the idea that water is more loosely bound compared to bulk water or surface adsorbed associations. This provides hints that water based interactions might be directed towards “thermosetting” events at higher temperatures offset by products of reactions from catalytic process at the metal-polymer interface. This is contrary to the role of water at RT showing incomplete dissociation of water from the complex with 4.6% of water molecules being retained by the surface. We envisage that loosely bound water molecules internalized in the polymer matrix provide essential spatial ordering of TiO$_2$.

**Concluding Comments**

The worked discussed here addresses the emerging question central to the structural tunability of functional materials and a cornerstone to change the broader perspective on achieving growth confinement in nanocrystallinity. The extent to which surface modification predominately through bond re-ordering growth confinement in nanocrystallinity. The extent to which a cornerstone to change the broader perspective on achieving central to the structural tunability of functional materials and the utilization of interfacial energy processes, here we have discussed the convergence of simultaneous polymer pathways leading to the growth arrest of TiO$_2$ to the quantum scale from kinetically and thermodynamically driven geometric constraints from the onset of nucleation.

We postulate that bonding differences in the chemical environment of the metal coordinated porphyrin ligand confined within an exterior polymer network during the self-assembly process show an unusual pore and narrow metal size selectivity that are co-related to the relative sensitivity of HOMO–LUMO electronic transitions. Certainly, the versatility in the surface chemistry of bulk TiO$_2$ can lead to the recognition and selection of chemical routes to divert the assembly of functional specific ligands to improve material performance and must be considered an important direction to advance the growth of the field.

The “cage within a cage” type geometry that accommodates TiO$_2$, the stabilizing forces and energies at interfacial regions that particularly involve contrasting material surfaces and chemical bond functionalities must be met with dimensional freedom to reorganize structures to an energy minimum or approaching a thermodynamically trapped conformation through distorted coordinated networks assisted by intermolecular bonding with solvents proceeding thermal annealing procedures. The importance of bond orientation and structural adjustment around phenyl-porphyrin adsorption sites that aims to improve steric adaptability and increase the π-orbital contribution of molecular constituents in the conjugated structure\textsuperscript{72} become critically more important in ridged structures. The lack of structural sensitivity to solvation by ethanol in the PS-porphyrin caged pockets functions as a credible indicator of deformation and rigidity not only at the polymer-polymer interface but also at the metal oxide-polymer boundary. This leads to the assumption that the geometric size confinement of TiO$_2$ may be attributed to the deformation and contraction properties of the inner metal binding cavity of the porphyrin C–N bonds resulting in a number of out-of-plane distortions\textsuperscript{80} tolerated by metal directed assemblies and the conformational properties of the porphyrin binding pocket as a flexible metal ligand. This arrangement might place an unfavorable energy burden as a direct consequence of the geometric rigidity at the PS interface of the outer ring that may be offset by lowering of orbital energies of a stable chelation effect in which the bond contribution of the central nitrogen atoms are more favorably harmonized by d-orbital splitting. This is accompanied by binding of metals of higher oxidation state thereby lowering spin state configurations and better balance of charges in terms of orbital occupancy and magnitude of interacting bond energies.

In such systems, we might conclude that an equilibrium between PS and non-PS caged porphyrin in the self-assembly system described here is modulated by the free energy of complexion that shows a degree of dependency on the size of the host–guest porphyrin–metal core assembly, nature of the bond and orientation of interactions and the re-ordering of water/solvent interactions. This work supports the assertion that size complementarity associations and bond specific inter-
actions occur autonomously for both caged and uncaged events concurrently established by independently driven enthalpic processes that are stable over both temperatures (RT and 120°C) forming a colloidal slurry in ethanol. In conclusion, nanobiomimicry is an important and feasible alternative to more conventional routes to acquire hard-to-achieve quantum trapped materials with tunable shape driven properties. Future directions towards understanding and controlling surface energies of the amorphous state to better steer shape and size geometries in desired ways to novel crystalline states akin to biomimicry should predictably yield more interesting crystal structures enhancing the applicability of commonly known materials. This inevitably falls upon how we can use surface chemistry to address energy landscapes particularly at the intersection of thermodynamic and kinetic processes.

Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the government of Korea (MEST) (No. NRF-2015R1A2A1A10027910, NRF-20121A1A2080196, NRF 2012R1A2A2A01047189). VK gratefully acknowledges financial support from BK21 program of the government of Korea.

Keywords: anisotropy · biomimetics · polystyrene · tetraphenylporphyrin · TiO2; quantum dots


Manuscript received: October 26, 2016
Accepted Article published: December 23, 2016
Final Article published: 0000

These are not the final page numbers!
Case in question: Accessibility to new synthetic materials to sub-nanometer levels to quantum scales is not trivial, in this case it is TiO₂. The evolution of some biominerals with equilibrium morphologies stabilized by ligand compartmentalization enabling control over shape and size reveals mechanistic clues to engineer biomimetic approaches. This establishes a new route to material tunability and accessibility to quantum sub-bands that show a profound interdependence on anisotropic growth patterns.

Accessibility to new synthetic materials to sub-nanometer levels to quantum scales is not trivial—TiO₂ is a case in question. The evolution of some biominerals with equilibrium morphologies stabilized by ligand compartmentalization enabling control over shape and size reveals mechanistic clues to engineer biomimetic approaches. Using the principles of biomimicry it is shown that the quantum confinement of TiO₂ to 0.8–2 nm can be achieved through the manipulation of a synthetic amorphous precursor using low temperature annealing and an alkyl rich multi-elemental reaction environment. This establishes a new route to material tunability and accessibility to quantum sub-bands that show a profound interdependence on anisotropic growth patterns. For more details, see the Concept by V. Khare et al.